Opportunities and Challenges in Research With Transplutonium Elements: Report of a Workshop

DETAILS

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PREFACE

I am grateful to my colleagues from the United States and abroad, identified in Appendix B, whose intense, dedicated efforts during the workshop produced the panel reports that follow. These reports, together with the individually authored resource papers attached as appendixes, were prepared in response to the U.S. Department of Energy's (DOE) request for an assessment of future directions and prospects for transplutonium element research.

The workshop clearly showed that the products of the High Flux Isotope Reactor and Transuranium Processing Facility (HFIR/TRU) are essential for tackling many important, even exciting, research problems in nuclear physics and chemistry, in inorganic and metal-organic chemistry, in spectroscopy, and in solid-state sciences. In many instances such research will throw light on questions that go far beyond the narrow confines of the transplutonium elements themselves. These points are, I believe, amply demonstrated in the reports of the workshop panels. I also know from conversations during the workshop that a number of participants who had little prior familiarity with transplutonium work came away with greatly stimulated interest in and appreciation for the field.

Thus there seems to be little question that, in the general context of chemistry and physics, there is considerable interest in further work with transplutonium elements, and the workshop report sets forth the most promising directions for such work as well as the requirements for specific elements and isotopes and the quantities needed.

The report does not contain a detailed comparative evaluation of transplutonium research versus other areas of chemistry and physics supported by DOE, because the participants were both unwilling and unable to undertake one. Such an evaluation would require developing priorities for all the chemistry and physics supported by DOE--including research involving transplutonium elements--and information on the quantity, quality, and significance of both existing projects and new research proposals in each area. In allocating research resources, one would hardly ever completely eliminate research areas perceived as being of lower priority; one would, instead, support fewer projects in such areas. Clearly, such an undertaking could not have been accomplished by the Steering Committee within the existing time constraints. Furthermore, such responsibilities belong to the program officers of the Office of Basic Energy Sciences. Their skill and foresight is the key to making proper judgments, in terms of DOE's long-range mission and the nation's needs, in the selection of research proposals to support. I am confident that the workshop, by identifying exciting research areas, will provide useful guidance to program officers in making such choices.

Nevertheless, I sympathize with the difficulty faced by the DOE staff. The operation of the HFIR/TRU is so expensive that it represents a sizable fraction of the total Division of Chemical Science's budget, and its support is perceived by some as cutting into the support of other areas. In this context two remarks seem germane: (1) The uniqueness of the fact that its support is essentially an all-or-nothing matter (it cannot be cut by 20 percent) should weigh heavily in comparison with other areas. In other words, one must consider whether an entire field should be irrevocably wiped out in favor of increased support for many other small-science programs, worthy as they may be. (2) It is obviously not fair to consider the cost of the HFIR/TRU only in the context of the Division of Chemical Sciences, even though the program is funded through and administered by that office. The benefits are shared by nuclear science, solid-state science, and chemistry, and one should therefore look at the HFIR/TRU budget in relation to the overall Basic Energy Sciences' budget to put it in perspective.

My sincere thanks go to William Spindel and his staff (Peggy Posey, Robert Simon, Wendy Baker, and Frances E. Holland) for invaluable support in organizing and operating the workshop and in preparing this report.

Gerhart Friedlander
Chairman

OVERVIEW AND RECOMMENDATIONS

ORGANIZATION AND OPERATION OF THE WORKSHOP

Since their construction in the mid-1960s, the High Flux Isotope Reactor (HFIR) and the associated Transuranium Processing Facility (TRU) at Oak Ridge National Laboratory have provided the western world's supply of elements beyond curium (atomic number 96), either directly or by furnishing starting materials for further nuclear-synthesis reactions. Both facilities have a remarkable record of reliability and minimal downtime.

Despite the uniqueness of the HFIR/TRU complex, "the transplutonium element area has increasingly received special attention because of its high costs relative to those of other areas," as stated in a letter (see Appendix A) from Dr. Elliot S. Pierce, Director of the Division of Chemical Sciences of the U. S. Department of Energy's (DOE) Office of Basic Energy Sciences (OBES), which provides most of the funding for these facilities. As a result of this special concern, OBES asked the National Research Council (NRC) to convene a Workshop on Future Directions in Transplutonium Element Research. The specific charge for the workshop, as stated in the invitation to participants, was "to provide DOE with an assessment of the importance and future directions of research with these elements, viewed in the broader context of chemistry and physics."

The workshop was organized under the auspices of the NRC's Board on Chemical Sciences and Technology and its Committee on Nuclear and Radiochemistry, which jointly selected a steering committee composed about equally of active actinide researchers and other chemists and physicists. Attendance at the workshop was by invitation, and participants were carefully selected to represent practitioners in the various areas of research with transplutonium elements as well as experts in related fields not themselves working with these materials. The participants are listed in Appendix B.

To provide background material for the workshop, a number of experts prepared resource papers that were distributed to the workshop participants and that also served as the basis of oral presentations to the opening plenary session of the workshop. These papers are appended to this report as Appendixes C through J.

Following the initial plenary session, the participants formed five panels concerned with the following aspects of transplutonium element research: (1) nuclear reactions and the synthesis of new transuranium species, (2) nuclear structure and fission phenomena, (3) chemical properties, (4) spectroscopy, and (5) solid-state physics and chemistry. The panels prepared preliminary reports that were discussed in plenary sessions and then further refined by the panels. These panel reports, as written during the workshop and subsequently revised by panel members and by the steering committee, form the body of this report (Chapters 1-5).

Although this workshop was convened to provide an assessment of the significance of research with transplutonium elements or, more specifically, with nuclides of $Z > 96$ uniquely produced by HFIR and TRU, it should be kept in mind that the value of the HFIR/TRU goes well beyond transplutonium element production. HFIR has one of the highest fast-neutron fluxes available. With its high-flux neutron trap, its four neutron beam holes, and its "rabbit" for short irradiations, it is one of the very few operational facilities in the United States for neutron-diffraction and neutron-scattering experiments and is nearly unique for providing several high-specific-activity radioisotopes, including ^{192}Ir, ^{60}Co, and some isotopes for medical uses. TRU is essential for activities other than heavy-element separations, including defense-related work and development of reprocessing of spent reactor fuels. None of these activities is addressed in this report, but they must be considered in any overall evaluation of these facilities.

Another aspect of the HFIR/TRU program that must be borne in mind is its international character. As already mentioned, these facilities represent the only source of weighable amounts of transcurium elements in the western world, and very significant amounts of research in western Europe depend on the availability of these products as starting materials (for example, targets for further nucleosynthesis). Research expenditures by European countries in the use of these products are of about the same magnitude as those in the United States. Furthermore, this is a field that has been characterized by exceptionally fruitful international collaborations, with unique facilities and expertise freely shared to mutual advantage.

SUMMARY

Each of the five panels concluded that there are important and challenging scientific problems in its area of interest that can be solved only if products of the HFIR/TRU remain available. In the individual panel reports these problems are discussed in some detail. Some of the general reasons for the interest in transplutonium elements are summarized below and a few examples are given.

The uniqueness of the HFIR/TRU facilities was a central issue in all the workshop discussions. If these facilities were to cease operation, most of the rich body of investigations discussed in the following chapters would simply come to a halt. A particular point implicit in all the panels' considerations is the fact that some of the important HFIR/TRU products (e.g., ^{249}Bk, ^{252}Cf, ^{253}Es, ^{254}Es, ^{255}Es, ^{257}Fm) are short-lived and cannot therefore be stockpiled and thus require continued production.

In the area of nuclear research the exploration of the limits of nuclear stability is a prime motivation for studying nuclear species with the highest atomic numbers accessible. Improved understanding of nuclear-reaction mechanisms recently achieved gives great promise for reaching uncharted regions of nuclei at the upper end of and beyond the actinides, including presumably longer-lived isotopes of known elements than were previously available and possibly the long-sought superheavy elements of $Z \approx 114$ with neutron numbers near 184.

For the exploration of fundamental concepts of nuclear structure the transplutonium region offers unique advantages because of the large numbers of valence nucleons present and because there is a greater variety of angular momenta, shapes, and coupling of nucleon orbitals than in any other region. Since nuclear fission occurs only in high-Z elements and, with increasing atomic number, becomes a more dominant mechanism for limiting nuclear stability, detailed investigations of this important process, which is not yet fully understood, depend on the availability of a wide variety of high-Z nuclides. More specifically, the unexpected and dramatic changes in fission properties observed across a series of fermium isotopes make it imperative to investigate other, still heavier systems in order to understand the factors responsible for these changes.

Another interesting area of research that requires the highest-Z materials obtainable is the search for spontaneous positron emission predicted to occur as an extreme relativistic effect in the very strong Coulomb field near a nucleus of very high Z (> 137); such nuclei may have a transitory existence in the scattering of high-Z projectiles from high-Z targets; the possible observation of this phenomenon in recent experiments with ^{238}U ions scattered from ^{248}Cm calls for further systematic studies with other systems.

From the chemist's point of view the periodic table of elements is the most basic road map and to extend it to its farthest reaches is an obvious goal. More specifically, there is special interest in extending chemical, spectroscopic, and solid-state studies to the highest atomic numbers because of the increasing prominence of relativistic effects. Through such studies at high Z, where the effects are large, a better understanding can be gained of the role of relativistic effects throughout the periodic table. The differences between the actinide (5f) and lanthanide (4f) elements are highly instructive, and, since the 5f orbitals have properties that are in many ways intermediate between those of 4f and 3d orbitals, knowledge gained from actinide studies (e.g., spectra) can illuminate the behavior of lanthanides and transition metals as well. The quantum mechanics of the 5f electrons is in fact the central issue in the physics and chemistry of actinide elements.

The special importance of further studies of the higher members of the series arises from the fact that the spatial extension and bonding properties of the 5f electrons change quite markedly near plutonium, as evidenced, for example, by the disappearance of readily accessible higher valence states and the onset of lower valences; the anomalous contraction of atomic size in the actinide elements through plutonium and americium; and anomalous changes in other properties, such as melting points, compressibilities, and allotropic phases. A full understanding of the change in the character of the 5f electrons from extended bonding behavior in the early members of the series to 4f-like localized character in the higher actinides has important implications for the physics and chemistry of elements throughout the periodic table.

Beyond the actinides lie elements whose chemistry is even more difficult to predict but that is critical to defining the architecture of the periodic table. Only the most rudimentary properties of elements 104 and 105 have been determined, largely because such studies are made extraordinarily difficult by the elements' very short half-lives and because only minute amounts of material are available. The new synthetic routes mentioned in the discussion of nuclear reactions give promise of both larger numbers of atoms and isotopes of much longer half-lives, which would greatly facilitate chemical and spectroscopic investigations. Conversely, knowledge of the chemistry of the transactinide elements will be important in extrapolating to the chemical properties of the superheavy elements, which may be a crucial prerequisite to their discovery.

An interesting and promising application of a transplutonium species not covered in any of the panel reports is the use of ^{252}Cf in cancer therapy, which is discussed in Dr. Maruyama's resource paper (Appendix J). Californium-252 therapy appears to offer unique advantages over other forms of radiation treatment for certain types of malignancies. Further exploration of this technique certainly seems desirable, and, if it lives up to its early promise, the future availability of ^{252}Cf for medical use will have to be ensured.

RECOMMENDATIONS

In view of the broad interest in a number of areas of research that depend critically on transplutonium elements and isotopes uniquely produced by the HFIR/TRU it is recommended that the operation of these facilities be continued for at least several years and that their status be reviewed again three to five years from the date of this report. Such a follow-up review should take into account, in addition to the scientific merits of transplutonium research, a broader range of issues than could be addressed in this workshop, including, e.g., the importance of the facilities for training, for research on fuel reprocessing, for neutron scattering, and for medical and defense applications.

In the meantime, the highest priority in research with transplutonium material should be given to the support of those experimental programs identified in the panel reports as particularly interesting, promising, and crucially dependent on products of the HFIR/TRU.

1

NUCLEAR REACTIONS AND THE SYNTHESIS OF NEW SPECIES

EXECUTIVE SUMMARY

Targets of relatively short-lived, neutron-rich transplutonium isotopes, such as ^{254}Es, which are produced by the HFIR/TRU, when combined with the capabilities of modern heavy-ion accelerators, offer a unique possibility to expand our knowledge of chemical elements and atomic nuclei toward the limits of nuclear stability. This knowledge should enable us to delineate the forces that eventually terminate the periodic table at its upper end. Specifically, the panel concludes that significant research opportunities exist in several areas, which are highlighted below:

o Nucleon-transfer reactions between light heavy-ion projectiles (such as ^{18}O, ^{22}Ne, or ^{48}Ca) and ^{254}Es targets will give access to a completely uncharted region of neutron-rich isotopes. The elements from fermium (100) to lawrencium (103) can be produced in relatively large quantities, including nuclides with half-lives predicted to be long enough (perhaps minutes to hours) for detailed studies of their chemical behavior and decay properties.

o Cold-fusion reactions of ^{48}Ca projectiles with ^{254,255}Es targets should yield superheavy nuclei with neutron numbers very close to the predicted closed neutron shell at $N = 184$. Because of the low-excitation energy deposited in the compound nucleus in cold-fusion reactions, the survival probability for superheavy nuclei should be increased dramatically. If target quantities of tens of micrograms were available, a very sensitive search could be made for production rates of a few atoms per day.

- Mechanistic studies of nuclear reactions with heavy targets (such as nucleon-transfer and cold-fusion reactions) are important in their own right and need to be investigated in more detail. This information will be useful in understanding reaction on lighter nuclei.
- Sensitive and fast techniques for the detection and identification of new and very heavy nuclei must be developed.

INTRODUCTION

Throughout time our need to understand nature, the elements that comprise it, and the physical laws that govern it has led to the fundamental concepts of the chemical element, the atom, and its nucleus. Our desire to understand the elements in a unified way led to the establishment of the periodic table.

A half-century ago, based on the emerging art of nuclear transmutation, initial attempts were made to break through the confines of the upper limits of the periodic table as defined by the naturally occurring elements. The intervening years have been crowned with success as the natural effort to explore and to expand this frontier has continued. Today, as we look back on the synthesis and identification of 16 transuranium elements and nearly 200 isotopes in this region, we can feel that this exploration has indeed been profitable. We are still, however, a long way from the upper boundary of either the periodic table or of the knowledge of nuclear and chemical structure that continued expansion promises. The knowledge already gained in pushing these boundaries to the extreme limits of nuclear stability has been fundamental to our current understanding of the chemistry and physics of nature, but there is potentially much more to come.

Three of the new elements ($Z = 104, 105, 106$) and a large portion of the transfermium ($Z > 100$) nuclides discovered during the last 15 years were made from actinide isotopes produced in the HFIR/TRU facilities. In producing these new species we have learned a great deal about nuclear fission and the mechanisms involved in nucleus-nucleus collisions. To synthesize new elements, possibly longer-lived isotopes of the transfermium elements, or even superheavy elements, it is clear that target isotopes of the highest possible Z and A, such as ^{252}Cf (2.6 y), ^{253}Es (20 d), ^{254}Es (276 d), ^{255}Es (40 d), and possibly ^{257}Fm (100 d), must be used. These isotopes can be produced in the necessary quantities only by the HFIR/TRU.

For both physics and chemistry the potential benefits of continued research in this region are numerous. In nuclear science we are faced with the exciting challenge of understanding the properties of the nucleus in greater detail: its collective motions, its nucleonic motions and interactions, and the underlying strong nuclear forces. The delicate balance between Coulombic repulsion and cohesive nuclear attraction is exemplified by the phenomenon of spontaneous fission that is unique to the actinide and transactinide elements. Spontaneous fission lifetimes impose limits on the stability of these very heavy elements, and, in order to improve predictions of their half-lives and decay properties, we must increase our understanding of the fission process. Fission also imposes limits on the reaction paths that can be used to synthesize these high-Z nuclides. To maximize the number of nuclei that survive prompt fission, we must continue to search for nuclear reactions that minimize the excitation energy and angular momentum deposited in the heavy products.

At the present time the light heavy-ion reaction mechanisms that are potentially of most value for the synthesis of high-Z nuclides are compound nucleus reactions and transfer reactions. In contrast to compound nucleus reactions, where complete fusion of the projectile and target occurs, transfer reactions lead to products in which only a part of the projectile mass and energy is transferred to the target nucleus. An alternative reaction path, via heavier projectiles, is the deep inelastic transfer reaction. This reaction leads to the exchange of considerable mass and energy between the projectile and the target. The knowledge gained in studies of nuclear-reaction mechanisms involving the heaviest targets should ultimately allow the synthesis of very heavy elements, even superheavy elements, with half-lives that are sufficiently long and in quantities that are sufficiently large for both nuclear and chemical studies.

From a chemical viewpoint the study of the transactinide elements affords a real and unique possibility for observing relativistic effects in atoms. From the magnitude of these effects in heavy elements the importance of relativistic effects in lighter elements can be determined. Furthermore, some of the predicted consequences of relativistic effects can, in turn, be tested, and our basic understanding of the atom can be refined.

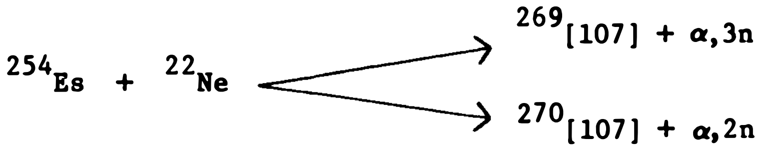
This chapter first describes some possible synthetic routes for the production of new neutron-rich transfermium isotopes. Previous attempts to synthesize superheavy elements are reviewed, and new approaches for reaching the "island of stability" are discussed. The third section addresses nuclear-reaction mechanisms that may be used for the production and study of very heavy elements and their contribution to the understanding of reactions involving lighter nuclei. The last section describes techniques that have been developed, and new ones that will be required, for the detection and identification of new isotopes in future studies of this region.

NEUTRON-RICH ISOTOPES OF HEAVY ELEMENTS

It is of utmost importance to study the uncharted region of the neutron-rich transplutonium isotopes if we are to understand the phenomenon of spontaneous fission, a process that ultimately limits nuclear stability at the upper end of the periodic table. Knowledge of the variation in spontaneous-fission properties (such as half-life, mass division, neutron emission, and total-fragment kinetic energy), as we move toward increasingly heavier nuclei, is crucial to our basic understanding of fission. Given this information, better theoretical models can be developed, tested, and further refined, permitting more reliable extrapolations to the even heavier, superheavy element region. Since the half-lives of some of these neutron-rich isotopes are expected to be sufficiently long for chemical experimentation, there are prospects for studying not only their nuclear properties but also their chemical properties.

One of the most exciting recent developments in the study of nuclear fission is the observation of the dramatic change to symmetric mass division accompanied by very high total kinetic energy of fragments for fermium isotopes with $N > 158$. A change of only a few nucleons appears to be important, since the $N = 158$ isotope of californium does not show these properties. Current indications are that these phenomena are unique to the heavy fermium isotopes and that they can be explained on the basis of fragment shell effects. Only a few isotopes beyond fermium have been investigated, and, although recent studies show that symmetric division persists in ^{259}Md and ^{260}[104], the total kinetic energy is no longer anomalously high. In the case of ^{259}Md, the rather dramatic change in properties occurs with the addition of a single proton! The abrupt change between Md and Fm appears to be related more to the disappearance of the second fission barrier than to the influence of shell effects in the nascent fragments. However, to gain a better understanding of the fission process and to assess the importance of various structural effects, the region of the neutron-rich transfermium isotopes must be explored further. Without the experimental access provided the HFIR/TRU target isotopes, our ability to make these investigations and to develop predictive fission models will be seriously impaired.

It also appears that transfer reactions involving relatively light, neutron-rich projectiles (such as ^{18}O, ^{22}Ne, and ^{48}Ca) and the highest available Z and A targets will produce isotopes in the desired neutron-rich, heavy-element region. For example, an ^{254}Es target with a ^{22}Ne beam might be used to produce heavy isotopes of element 107, as shown below.



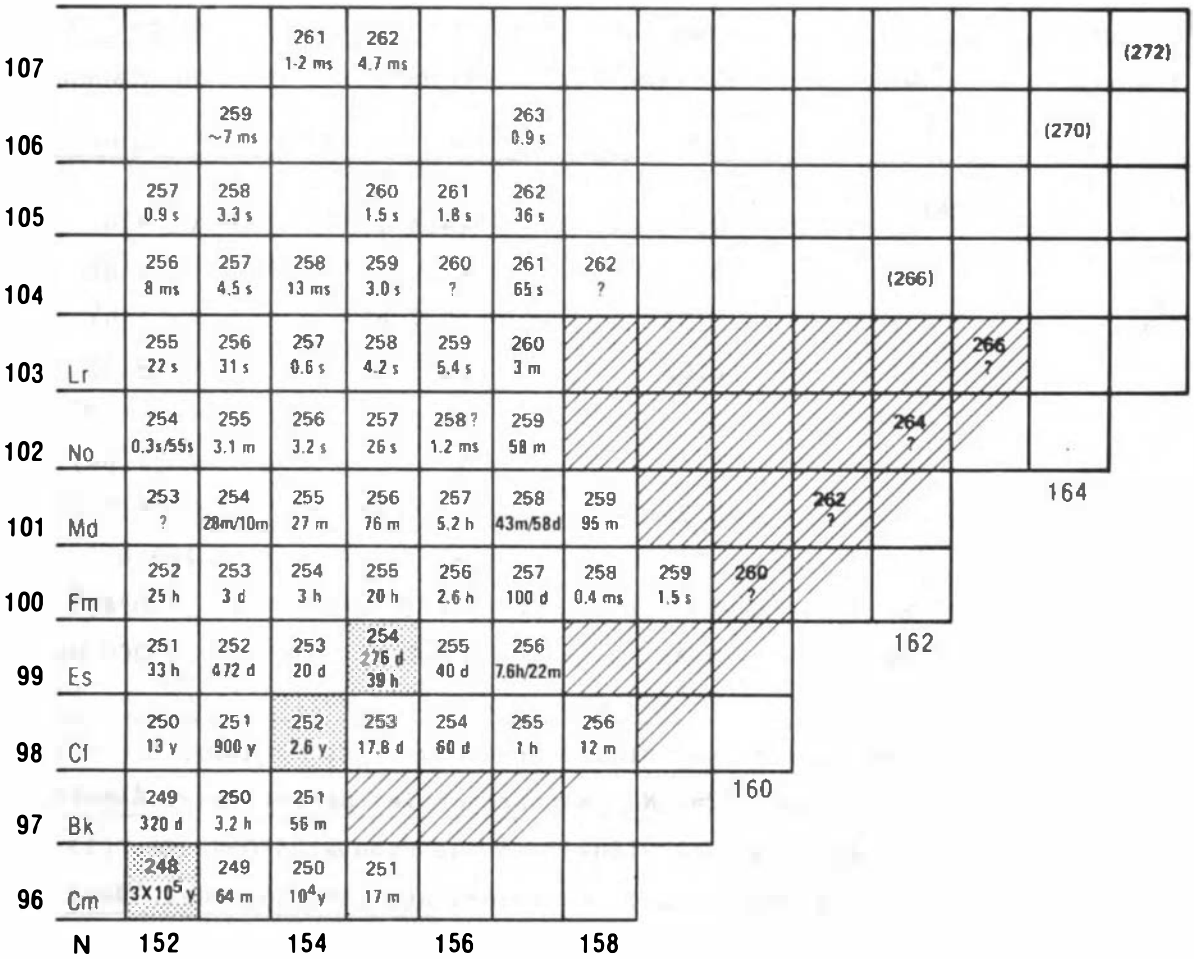
Currently, the heaviest known isotope of element 107 has a mass number of 262 and a half-life of only 5 ms. The heavier isotopes should be longer-lived and thus more tractable for detailed study.

Via such transfer reactions, isotopes of essentially all the elements between the atomic number of the target and the sum of the atomic numbers of the target and projectile can be made, although the production cross sections drops sharply with an increasing number of particles transferred. In many cases the ground-state Q-values are sufficiently negative that the products can be formed with very little excitation energy. Consequently, an enhanced survival probability can be expected for these "cold" nuclei. Figure 1 shows the region of new neutron-rich isotopes that is accessible using relatively light heavy-ion projectiles and ^{248}Cm, ^{252}Cf, and ^{254}Es targets.

A comparison of the measured yields of actinides produced in the reactions of ^{18}O and ^{22}Ne ions with ^{248}Cm and ^{254}Es, of ^{18}O ion with ^{249}Cf, and of ^{48}Ca ions with ^{248} Cm has shown that the yields for these systems are similar for transfers of the same number of protons and neutrons. Maximum yields are observed for the effective transfer of ^{2}H, followed in order by ^{3}He, ^{5}Li, and ^{6,7}Be transfers. Corresponding peak-yield cross sections are about 2000, 1000, 30, and 3 μb, respectively. Transfers of more neutron-rich fragments also occur but with lower yields.

From these data we estimate that ^{262}Lr and ^{263}Lr can be produced by ^{8}Be and ^{9}Be transfers to ^{254}Es with cross sections of about 300 and 50 nb, respectively. Estimated production cross sections and half-lives for other new neutron-rich isotopes from transfer reactions to an ^{254}Es target are given in Table 1.

At saturation, and assuming a 3 μg (30 μg/cm^{2}) target of ^{254}Es, these cross sections would allow the production of between 100 and 3000 atoms, depending on the isotope. If more ^{254}Es were available, the number of atoms would, of course, be correspondingly increased. Alternatively, we could use the larger quantities of ^{253}Es (~100 μg) currently available from the HFIR/TRU to increase the number of atoms produced, but the analogous reaction on ^{253}Es would lead to isotopes with one less neutron than in the case of ^{254}Es. The use of ^{253}Es would, however, have its own special problems: the 20-day half-life would severely limit the time "window" in which the target would be usable and could also affect the stability of the target because of



N	152		154		156		158		160		162		164	
107			261 1.2 ms	262 4.7 ms										(272)
106		259 ~7 ms				263 0.9 s							(270)	
105	257 0.9 s	258 3.3 s		260 1.5 s	261 1.8 s	262 36 s								
104	256 8 ms	257 4.5 s	258 13 ms	259 3.0 s	260 ?	261 65 s	262 ?				(266)			
103 Lr	255 22 s	256 31 s	257 0.6 s	258 4.2 s	259 5.4 s	260 3 m	▨	▨	▨	▨	▨	▨ 266 ?		
102 No	254 0.3s/55s	255 3.1 m	256 3.2 s	257 26 s	258? 1.2 ms	259 58 m	▨	▨	▨	▨	▨ 264 ?	▨		
101 Md	253 ?	254 28m/10m	255 27 m	256 76 m	257 5.2 h	258 43m/58d	259 95 m	▨	▨	▨ 262 ?	▨			
100 Fm	252 25 h	253 3 d	254 3 h	255 20 h	256 2.6 h	257 100 d	258 0.4 ms	259 1.5 s	▨ 260 ?	▨				
99 Es	251 33 h	252 472 d	253 20 d	░ 254 276 d 39 h	255 40 d	256 7.6h/22m	▨	▨	▨					
98 Cf	250 13 y	251 900 y	░ 252 2.6 y	253 17.8 d	254 60 d	255 1 h	256 12 m	▨						
97 Bk	249 320 d	250 3.2 h	251 56 m	▨	▨	▨								
96 Cm	░ 248 3×10^5 y	249 64 m	250 10^4 y	251 17 m										

FIGURE 1. The cross-hatched areas show new isotopes that can be produced in yields of more than 100 atoms per day by transfer reactions between relatively light, heavy ions and ^{248}Cm, ^{252}Cf, and ^{254}Es targets. (The yields were calculated assuming a cross section of 1 nb, a target of 100 μg/cm^2, and 20 A-hours of beam.) Target nuclei are shaded and the compound nuclei for reactions with ^{18}O are shown in parentheses.

TABLE 1. Estimated Cross Sections and Half-Lives for Selected Neutron-Rich Transfermium Isotopes Produced from the Reaction of ^{18}O, ^{22}Ne, or ^{48}Ca Ions with a 3 μg ^{254}Es Target.

Effective Transfer	Product	Cross Section (μb)	Half-Life Alpha[a] (unhindered)	Half-Life Spontaneous Fission[b]
^{7}Be	^{261}Lr	0.7	(4.6 m)	($\leq$ 4 h)
^{8}Be	^{262}Lr	0.3	(14 m)	($\leq$ 4 h)
^{9}Be	^{263}Lr	0.05	(0.7 h)	($<$ 5 h)
^{10}Be	^{264}Lr	0.02	(2.3 h)	($<$ 9 h)
^{5}Li	^{259}No[c]	6	60 m	--
^{6}Li	^{260}No	5	--	($<$1 ps)
^{7}Li	^{261}No	0.2	(1.1 h)	($<$6.5 d)
^{5}He	^{259}Md[c]	20	--	103 m
^{6}He	^{260}Md	2	(1-10 h β or EC)[d]	(200 d)[d]
^{7}He	^{261}Md	0.2	(0.7 y)	(2-200 μs)[d]

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[a] Estimated by using the semiempirical formalism of E. K. Hyde, I. Perlman, and G. T. Seaborg, The Nuclear Properties of the Heavy Elements, Vol. 1, Prentice-Hall, New York, 1964, and the tabulated Q-values (1) from V. E. Viola, Jr., J. A. Swant, and J. Graber, At. Data and Nucl. Data Tables 13 (1974) 35.

[b] Values are estimated both from extrapolated experimental data of C. M. Lederer and V. S. Shirley, eds., Table of Isotopes, John Wiley & Sons, New York, 1978, and from predictions of V. A. Druin, B. Bochev, Y. V. Lobanov, R. N. Sagaidak, Y. P. Karitonov, S. P. Tret'yakova, G. G. Gul'bekyan, G. V. Buklanov, E. A. Erin, V. N. Kosyakov, and A. G. Rykov, "Spontaneous Fission of the Heavy Isotopes of Nielsbohrium (Z = 105) and Element 106," Sov. J. Nucl. Phys. 29 (1980) 591.

[c] Known isotopes, cross sections, and half-lives.

[d] D. C. Hoffman, "Nuclear Properties of Mendelevium," In G. T. Seaborg, ed., Symposium Commemorating the 25th Anniversary of the Discovery of Mendelevium, LBL Report LBL-11599 CONF-800362, March 28, 1980, p. 45.

radiation damage. These problems are considerably reduced if the 276-day ^{254}Es isotope is used.

An exotic approach to the synthesis of neutron-rich transplutonium elements is the possible use of "secondary" heavy-ion projectiles (e.g., ^{16}C, ^{20}O, ^{30}Na) that contain a greater abundance of neutrons than do the most abundant stable isotopes, ^{12}C, ^{16}O, ^{23}Na. These species would have to be produced in an initial, relatively high-energy nuclear reaction. The resulting secondary beam of neutron-rich particles, when combined with the heaviest available targets, offers intriguing prospects for further heavy-element synthesis.

SUPERHEAVY ELEMENTS

Perhaps the most exciting frontier in nuclear and atomic physics is the potential discovery of an island of relatively stable nuclei well beyond our presently known limits. The stability bequeathed to a small group of elements and nuclei by the closed nuclear shells at $Z = 114$ and $N = 184$ should eventually allow their synthesis and study. Although attempts to produce these superheavy elements over the past decade have not been successful, the reasons for failure seem to be largely understood and the obstacles appear surmountable. At first it was not known that complete fusion did not occur with a high probability for many of the target-projectile combinations used, and thus the formation cross sections were much smaller than expected. As a result the detection technique used in the earlier work did not have the required sensitivity. In addition, none of the many target-projectile combinations tried thus far in fusion reactions has yielded a product near the center of the island of stability at $Z = 114$ and $N = 184$ (products were either close to $Z = 114$ and far below $N = 184$ or close to $N = 184$ and well above $Z = 114$).

It now appears that the effective stabilization, due to the closure of the neutron shell, is stronger than that of the proton shell; that is, the island of stability exhibits a ridge extending from the center downward along the $N = 184$ line. The effect of the $Z = 114$ shell is much less pronounced and appears to extend from the center of the island upward toward larger Z (see Figure 2). As a result, if we are to discover superheavy elements, it now appears vital that we approach more closely the peak of maximum stability at 184 neutrons. Only then can we ensure the production of relatively long-lived nuclides (with respect to spontaneous fission) with a low probability of destruction at birth by prompt fission. However, even in close approaches to the 184 neutron shell, the production cross sections may be so small and the half-lives so short that techniques need to be developed that are sensitive to picobarn (10^{-36} cm^2) production cross sections and nanosecond half-lives.

Some 10 years ago a new reaction mechanism, termed deep inelastic collisions, was observed for the interaction of heavy ions that offered yet another possible reaction pathway for synthesizing superheavy elements. It was suggested that through the massive transfer of nucleons between a target and projectile in a deep inelastic collision, one of the reaction partners may grow into a superheavy nucleus at the expense of the other partner. An example is shown in the following reaction.

$$^{248}_{96}Cm + ^{238}_{92}U \longrightarrow {}^{298}[114]_{184} + ^{188}_{74}W$$

Whether such a transfer could occur was investigated by identifying the projectile-like light fragments that are, of course, complementary to the target-like heavy fragments formed in the reaction. The fact that the charge (Z) and mass (A) distributions of the products observed in deep inelastic collision were quite broad was encouraging. However, the distribution of excitation energies and angular momenta of the products also was found to be quite broad. As a consequence, the probability of forming a superheavy element that survives fission in a deep inelastic collision depends not only on being formed in the "tails" of the charge and mass distributions (massive transfer of protons and neutrons) but also on being formed in the "tails" of the excitation energy and angular momentum distributions (low excitation and angular momenta). To date, this approach has been used in a search for long-lived superheavy elements in reactions between ^{238}U projectiles and ^{238}U and ^{248}Cm targets, but success has been elusive.

Current attempts to produce superheavy elements are focused again on fusion reactions and, in particular, on the fusion of ^{48}Ca and ^{248}Cm.

$$^{48}_{20}\mathrm{Ca} + {}^{248}_{96}\mathrm{Cm} \longrightarrow {}^{296-x}[116]_{180-x} + xn$$

Although previous attempts using this reaction were both elaborate and exhaustive, it is now believed that the incident energy of the projectile in these studies was too high. As a result, there was too much excitation energy (~44 MeV) in the compound system, which increased the probability of losses due to first, second, third, etc., chance fission.

$$\begin{tikzcd}
{}^{296}[116]^{*}_{180} \arrow[r, "-n"] \arrow[d] & {}^{295}[116]^{*}_{179} \arrow[r, "-n"] \arrow[d] & {}^{294}[116]^{*}_{178} \arrow[r, "-n"] \arrow[d] & \bullet\ \bullet\ \bullet \\
\text{fission} & \text{fission} & \text{fission} &
\end{tikzcd}$$

Scientists from the United States, West Germany, and the USSR are exploring the possibility of fusing ^{48}Ca and ^{248}Cm at beam energies near or below the interaction barrier (cold fusion) at the Berkeley, Darmstadt, and Dubna heavy-ion accelerators. Several detection techniques are being applied to span a half-life range from several years down to a few microseconds, with sensitivities of tens of picobarns ($\sim 10^{-35}$ cm^2) for the production cross section. The approach is encouraging, since the two heaviest known elements, $Z = 107$ and 109, were recently synthesized by cold-fusion reactions.

A much closer approach to the $N = 184$ is possible with targets of actinide isotopes heavier than ^{248}Cm and the extremely neutron-rich projectile, ^{48}Ca. Some examples are shown below.

$$^{255}_{99}\mathrm{Es} + {}^{48}_{20}\mathrm{Ca} \longrightarrow {}^{303-x}[119]_{184-x} + xn$$

$$^{254}_{99}\mathrm{Es} + {}^{48}_{20}\mathrm{Ca} \longrightarrow {}^{302-x}[119]_{183-x} + xn$$

$$^{252}_{98}\mathrm{Cf} + {}^{48}_{20}\mathrm{Ca} \longrightarrow {}^{300-x}[118]_{182-x} + xn$$

Figure 2 shows the location of the compound nuclei formed in the reaction of ^{48}Ca ions with ^{248}Cm, ^{252}Cf, and ^{255}Es targets in the landscape (atomic versus neutron number plane) of the island of superheavy nuclei. (Also shown on the figure are contour lines connecting nuclides with equal overall half-lives.)

The ^{48}Ca reaction on ^{255}Es appears to be most promising since this target offers the advantage of an additional neutron and thus a closer approach to the $N = 184$ shell than does an ^{254}Es target. In addition to problems associated with the fabrication and use of an ^{255}Es target (40-day half-life), there is the enormous difficulty of producing the necessary quantity of this isotope. If approximately 40 μg of ^{255}Es were available, a sensitivity of about 100 pb, or about 10^{-34} cm^2, could be achieved for the production cross sections of superheavy nuclei after only a few days of bombardment with ^{48}Ca ions. This amount is about 150 times the current HFIR/TRU production level, however. This same sensitivity would also be achieved for a 40 μg ^{254}Es target. For ^{254}Es, 40 μg represents only a tenfold increase in the current production level. With either isotope, an einsteinium target offers the advantage of producing, after the evaporation of a few neutrons, superheavy nuclei with odd numbers of both neutrons and protons. For these odd-odd nuclei the half-life would be considerably longer than those indicated for even-even nuclei in Figure 2.

Although, in principle, searches for superheavy elements using ^{48}Ca ions can now be performed with the available quantities of ^{252}Cf, the rather large spontaneous fission branch and thus the copious amounts of neutrons associated with the decay of ^{252}Cf impose serious experimental difficulties. First, due to the neutron shielding requirements, there would be the necessity of fabricating and handling the ^{252}Cf target remotely. Second, assuming these difficulties could be overcome, there would be the problem of separating a small quantity of spontaneously fissioning superheavy products from a vast surplus of spontaneously fissioning target atoms.

Because ^{254}Es and ^{255}Es have much longer spontaneous fission half-lives (smaller spontaneous fission branches), the use of these nuclides as target materials would considerably reduce many of these difficulties. Hence, the production of these nuclides in sufficient quantities in the HFIR is strongly recommended. Other target isotopes of interest in this context are ^{250}Cm and ^{251}Cf. From a long-range view, extremely neutron-rich projectiles such as ^{50}Ca, produced as secondary beams, may also become available and may make it possible to reach isotopes that are even more neutron-rich.

IMPROVED UNDERSTANDING OF REACTION MECHANISMS

A major impetus for nuclear-reaction studies involving heavy target nuclei has been the synthesis for new elements and isotopes. It is clear that such studies provide important insights into the reaction mechanisms and, conversely, that greater understanding of the mechanisms is essential to maximize the likelihood for success in the search for new nuclides. Three important questions are involved here: (1) What are the probabilities for nuclear fusion? (2) What are the probabilities for the various nonfusion reactions? (3) What are the probabilities for surviving prompt fission?

Recent studies of reactions between complex heavy nuclei reveal large cross sections for complete fusion at energies well below the Coulomb barrier. This subbarrier, or "cold" fusion, seems to be generally enhanced for all systems and also seems to exhibit particular structural preferences related to such properties as static deformation and low-lying surface vibrations of the target and projectile. On the other hand, recent theories of the dynamics of fusion reactions predict that in very heavy systems an "extra push" of energy, exceeding the Coulomb barrier, is needed to overcome the true saddle point for forming a compound nucleus. Recent studies on the formation of heavy nuclei by various projectile-target combinations give support to this conclusion but leave open the question of whether this dynamical hindrance plays a role in the asymmetric systems (such as ^{48}Ca with ^{254}Es) that have been considered for the synthesis of the heaviest nuclei. Even if this hindrance does occur, special structural properties may enhance the possibility for subbarrier fusion.

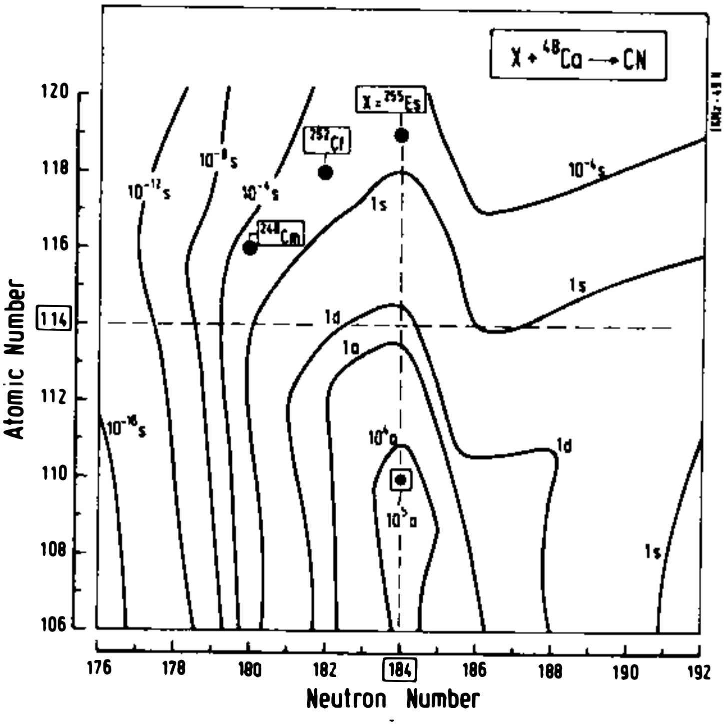

FIGURE 2. Landscape of the predicted island of superheavy elements. The contour lines connect nuclides with equal overall (alpha, beta, and fission) half-lives [J. Randrup et al., Physica Scripta 10A (1974) 60 and S. Aberg et al., unpublished calculations, 1979]. Points indicate the compound nuclei produced in reactions of ^{48}Ca with ^{248}Cm, ^{252}Cf, and ^{255}Es targets.

Heavy-ion transfer reactions that occur with the transuranium elements have two characteristics that are essentially unique: (1) nuclear fission is a deexcitation mode that competes effectively with neutron emission and (2) the emission of charged particles, relative to neutrons, is drastically hindered by the large Coulomb barriers. While causing very low production cross sections of transfermium nuclides, these two properties offer advantages for reaction mechanism studies by acting as "filters" to simplify the interpretation of the experimental observations. For example, in studying the formation of transfer products that have masses between those of the target and compound nucleus, we can be fairly confident that we are observing the products of a direct transfer, not the products of reactions that led to higher-Z elements with subsequently emitted charged particles. The parameters of interest are the variation of transfer probability with Z, A, and energy of the projectile, Z and A of the target nucleus, and especially Z and A of either the transferred fragment or the product nuclide.

It should also be stressed that, because of the "simplicity" of the results, radiochemical techniques in which the radioactive heavy reaction products are observed are a powerful complement to in-beam techniques that identify the multitude of light fragments from transfer reactions. Thus, such studies not only relate to searches for new nuclides in the region of $Z > 100$ but are also important additions to what can be learned about transfer reactions in lower-mass regions of the periodic table.

While recent emphasis in heavy-element complete fusion and transfer reactions has been on reactions in which fission deexcitation is minimized, it is clear that our understanding of the competition between particle emission and fission in elements with $Z > 90$ needs to be improved. Our knowledge is especially meager for nuclides with $Z > 100$ and $N > 155$, which just define the lower limits of the region that is of most interest in terms of new neutron-rich nuclei.

In recent years a variety of studies have indicated that neutron emission competes more favorably with fission than expected from phase-space considerations. The study of this competition is particularly important to an understanding of the dynamics of collective deformation toward fission and energy thermalization in evaporative decay. Heavy composite nuclei, with their special Coulomb fragility, are particularly interesting for exploring this competition.

NEW TECHNIQUES

We have noted in the preceding sections that because of fission competition the yields of heavy nuclides produced in nuclear reactions can be exceedingly small and may often be measured in terms of only a few surviving atoms. In addition, half-lives of these nuclei are likely to be exceedingly short because of the low fission barriers and enhanced rates for radioactive decay by alpha-particle emission. Both factors engender experimental difficulties rarely encountered in conventional nuclear experimentation. To overcome these serious difficulties for the detection and identification of new nuclides in the region of the heaviest elements, much imaginative instrumentation development has occurred in the past, but a "new generation" of techniques is now required.

It is important to recognize that the investment made in such instrumentation development has paid substantial dividends in the broad domain of experimental science in areas outside the study of transplutonium elements. We mention several examples: (1) ion exchange techniques for chemical separations of actinides and lanthanides, (2) remote-handling chemical techniques, (3) ultrafast chemical separation methods, (4) moving tape and gas-jet transport techniques, (5) electrostatic collection from gaseous media, (6) velocity filters, (7) semiconductor detectors for fission fragments and alpha particles, and (8) accelerator development for heavy-ion beams.

In the following two paragraphs a few "new generation" instruments are described. Over a period of years, mechanical transport devices served to move the product nuclei recoiling away from the target to detectors where alpha emission and other decay modes could be determined and the nuclides thus identified. Such instruments have been capable of detecting a few tens of atoms with half-lives down to a few tenths of a second. It seems quite possible to extend such mechanical techniques to the detection and measurement of nuclear decay properties for isotopes with half-lives as short as a few hundred microseconds. Indeed, this had already been demonstrated for millisecond spontaneous-fission decay. Because these methods provide only limited selectivity in isolating the desired product from other activities, it would be desirable to incorporate fast chemical separations into the recoil transport systems. Rapid gas-phase chemistry has shown the greatest promise for certain elemental separations and should be pursued further. Due to the kinetics of chemical reactions and the transport time between different phases, chemical techniques are, in general, applicable to isotopes with half-lives greater than a few tenths of a second.

One of the most needed instruments for the extension of research in the transplutonium element region is an on-line mass analyzer that is both fast (microseconds) and efficient (10-100 percent). Such a device is especially needed for nuclides spontaneously decaying by fission, since, unlike alpha decay, this decay mode cannot provide a genetic link with known decay products. Since many of the nuclides in the region of neutron-rich transplutonium isotopes and superheavy elements should decay preferentially by spontaneous fission, new on-line techniques for this purpose would greatly facilitate mass and atomic number identifications. A possible approach is the use of modern large-area gas-ionization detectors combined with time-of-flight techniques in order to record energy, velocity, emission angle, energy loss, and indeed the entire Bragg stopping curve of the fission fragments. From the determination of Z and A for each fission fragment, the Z and A of the parent nucleus could be reconstructed.

2

NUCLEAR PROPERTIES OF THE TRANSPLUTONIUM ELEMENTS

INTRODUCTION AND SUMMARY

The transplutonium elements offer unique tools for the exploration of concepts fundamental to nuclear structure. Among the advantages afforded by these heavy nuclides are large numbers of valence nucleons; the concomitant full development of collective modes of excitation; the unusually rich variety of single-particle angular momenta, shapes, and couplings of the active nuclear orbitals; and the onset of octupole (2^3) and of 2^6-pole deformations. Application of the full range of methods of modern nuclear spectroscopy to these interesting nuclei, therefore, holds special promise. To investigate these specific structural phenomena and at the same time to develop their essential systematic features, experimental efforts must cover as much of the transplutonium region as can be made available.

Challenging problems in the study of fission phenomena have also emerged from new discoveries, ideas, and technologies in this field. As a consequence of its strongly Z-dependent nature, the fission process displays its fullest richness only when the transplutonium elements are investigated. Extensive exploration of this region promises to yield critical clues to the ultimate limits of nuclear stability. Dramatic changes observed in the fission properties of the fermium isotopes test our ability to differentiate between mechanisms that rely critically on barrier properties and those that depend on fragment characteristics developed in the approach to the scission point. Recently developed fission fragment spectrometers, coupled to high-flux nuclear reactor facilities, are providing new high-quality data that reveal the intricacies of fine structure in the fission fragment yields; new aspects of the fission process such as the role of superfluid correlations in the fissioning matter are thereby probed. The full domain of available fissioning nuclei in the transplutonium region should be investigated with these new instruments. Prompt fission events induced by μ-mesic atom transitions permit us to test the influence of the delicate balance between nuclear and Coulomb forces. Because the negative charge of the μ-meson acts to raise the outer fission barrier, the elements heavier than curium--where the outer barrier is normally low--should most readily exhibit such effects. In addition, from observation of the site of the μ-meson after fission, an estimate can be made of the degree of adiabaticity with which the system adjusts between the saddle point and scission; this effect is best exploited with the heaviest elements, where the dynamic path toward fission is long.

Observation of spontaneous positron emission in ultra-strong Coulombic fields (as bound "atomic" levels are submerged in the Dirac sea) has long been sought. Such observations would be striking manifestations of extreme relativistic effects present in high-Z systems. Such studies can then only be conducted with systems of very high $Z_{\text{effective}}$ $(Z > 173)$; such a $Z_{\text{effective}}$ value can be created during the scattering and interaction of high-Z projectiles on high-Z targets. Recent experiments involving the scattering of uranium ions from curium targets have revealed an interesting, and perhaps definitively revealing, sharp structure in the positron spectrum. Clearly, this phenomenon requires investigation with a broader set of target-projectile combinations. Because of the extremely strong Z dependence of this effect, use of the heaviest possible target species is vital.

Developments of Interest to Related Fields

Studies of nuclear structure in the transplutonium elements enrich our understanding of numerous concepts fundamental not only to nuclear physics but also to physics more generally.

Collective aspects of nuclear behavior constitute one such area of widespread relevance, and, as mentioned above, the transplutonium region is especially rich in this respect. Analyses of the microscopic structure associated with these collective modes, as revealed by spectroscopic studies, emphasize the special quantal properties of this region of Z and N. In particular, the large variety of deformed single-particle states, originating from a number of different subshells, contribute to the development of the collective vibrations. Comparison of analyses and prediction of the structures of these collective states form stringent tests of many-body theories of nuclear structure. The large numbers of valence nucleons permit more complete studies of the evolution of these states as a function of proton and neutron number. Because of the presence of well-developed low-lying collective modes, it will be possible to study their interaction with one another.

A special opportunity to study the dynamic behavior of quantal Fermi fluids is afforded by the high fissionibility of the transplutonium elements. Because of the compact, nearly spherical fission saddle-point shapes, nuclear matter flows over large relative distances in the transition from saddle to scission. As a consequence, these processes manifest the basic features of the dissipation mechanisms, of general interest in many-body physics.

Measurement of the nuclear properties of the transplutonium nuclides--ranging from ground-state masses and lifetimes to detailed energy levels and deformations--will have an impact on many related areas of nuclear and other sciences. For example, the parameters of the liquid-drop mass formula depend directly on such measurements, and data for species of the highest Z and N are critical to guaranteeing the predictive powers of the mass formula for the heaviest elements. The mass formula serves as a basis for extrapolating the properties of the super-heavy elements as well as those of undiscovered nuclides far from the known valley of stability. It also plays an important role in defining the nuclear potential energy surface, essential to the study of heavy-ion reaction mechanisms. Furthermore, it is of central relevance to astrophysics in predicting the behavior of nuclides with large neutron excesses, which play a critical role in the path of r-process nucleosynthesis; this may be the only mechanism for producing the superheavy elements in nature. Of special interest for the understanding of the r-process would be experimental evidence for neutron-emitting or fissioning excited states of neutron-rich actinides, since such states have recently been postulated to account for some isotopic abundance features.

The uncertainties involved in the shell corrections that are important to predictions of the stability of superheavy elements can be reduced by specific spectroscopic investigations of the important $N = 8$, $k_{17/2}$ and $N = 7$, $j_{13/2}$ orbitals. These orbitals, part of the $N > 184$ shell, become experimentally accessible in the transplutonium region. The other important orbital, the $N = 7$, $h_{11/2}$, has already been studied in lighter actinide nuclei.

Extension of our knowledge of systematic nuclear behavior beyond the valley of stability in the vicinity of the very neutron-rich region around the doubly closed shell at $Z = 50$, $N = 82$ may be made possible by the use of heavy transplutonium nuclides as fissile targets.

As a by-product of the spectroscopic studies, long-lived isomers have been found (e.g., the 1/2-hour isomer in ^{256}Md). As spectroscopic studies in the heavy transplutonium nuclei are extended, it is hoped that such states will occur in the heavier transplutonium nuclides. Such long-lived isomers would be of obvious use in chemical investigations.

NUCLEAR STRUCTURE OF TRANSPLUTONIUM NUCLEI

In the transplutonium region, orbitals with unique characteristics ($N = 8$, $k_{17/2}$ neutron orbital and $N = 7$, $j_{15/2}$ proton orbital) first become accessible to valence nucleons. The appearance of numerous prolate, low-Ω, high-j neutron and proton orbitals that lie just above the Fermi surface provide the opportunity to attain ultrahigh angular momenta ($J \sim 30$ h) at extremely low angular frequencies. The large quadrupole and hexadecapole moments of these orbitals will take part in producing large changes in the gross nuclear shape at high angular momentum.

At low momenta, deformation modes unique to the actinides become active. The octupole deformation, first identified in the light actinides, should be seen much more clearly in the heavy transplutonium region where the $k_{17/2}$ and $h_{11/2}$ neutron orbitals, connected by large octupole matrix elements, approach the Fermi surface. This will be reinforced by the large octupole matrix elements connecting the $f_{7/2}$ and $i_{13/2}$ proton orbitals that lie just below the gap at Z = 114.

At both Z = 100 and N = 152, the orbitals at the Fermi level favor moderately large P_6 (2^6-pole) deformations. The inclusion of this deformation mode in theoretical calculations of ground-state masses in this region reduces the discrepancies between theory and measured masses significantly. Measurements of these P_6 deformations would provide an important test of theory.

The evolution of all collective modes as a function of neutron and proton number can be followed more completely in this region of Z and N due to the large numbers of available valence nucleons. The systematic changes from nucleus to nucleus, which occur over fractionally small intervals, can be studied as more nearly continuous functions. The very important possibility exists that simultaneous excitations of two or more collective modes can be isolated, so that their interaction characteristics can be analyzed.

The neutron orbitals that are significant for estimating the shell stabilization energy of superheavy elements are the $h_{11/2}$, $k_{17/2}$, and $j_{13/2}$ spherical states, which lie above the N = 184 gap in spherical nuclides. With deformation, however, the $\Omega = 1/2$ orbitals from all of these states drop sharply in energy. Their identification in the transplutonium nuclei is possible and can reduce the uncertainties in theoretical estimates of the shell corrections responsible for the possible stability of superheavy elements. The (1/2−)[761] orbital, which determines the position of the $h_{11/2}$ spherical state, has already been identified in several actinides. Transfer studies using N = 154 targets, e.g., ^{252}Cf or ^{250}Cm, can be used to locate the (1/2+)[880] and (1/2−)[750] orbitals, which will help fix the positions of the $k_{17/2}$ and $j_{13/2}$ orbitals, respectively. The (1/2−)[521] proton orbital that determines the shell effects at Z = 114 has already been determined; the effects of this orbital have been calculated to give rise to a shell stabilization energy of about 2.8 MeV.

To obtain experimental data that will elucidate the physical features of the transplutonium element nuclei described above, it is necessary to make complete measurements of individual nuclei, i.e., all levels are to be detected within specific ranges of angular momentum, parity, and excitation energy. Also, it is essential that various features of nuclear structure in these elements be sampled over a wide range of mass numbers so that systematics can be identified. Studies of this type are especially important in measuring the makeup of collective vibrational states, particle-collective-vibrational interactions, and particle-particle interactions. Since these residual interactions produce small changes in the measured parameters, careful, complex measurements are required. Among the experimental methods that will satisfy these criteria are spectroscopic measurements of the (n, γ) and $(n,\gamma$-conversion electron) reactions being performed at the research reactors of the Institut Laue-Langevin at Grenoble and Brookhaven National Laboratory. Nucleon transfer reactions are being done with accelerator-spectrometer facilities at laboratories at Argonne National Laboratory, Princeton, Los Alamos, and the Technical University in Munich.

The possibility of extending such spectrographic studies to high angular momentum states is very attractive. Indeed, the energy of high-j, low-Ω orbitals of interest in this mass region is lowered by the Coriolis-plus-centrifugal force when the nucleus is rotated. Therefore, it may be possible to study at high spins some of the most interesting orbitals that are not accessible at low spins. By the "blocking" of a particular configuration it is possible to dissect the pairing contributions between specific quasi-particle configurations. Thus, the study of high-spin states provides detailed information on residual interactions in specific multi-quasi-particle configurations. For such studies in the transplutonium region it is necessary to populate the nuclear species of interest with as little intrinsic excitation energy as possible to minimize fission competition. The use of Coulomb excitation, with or without heavy-ion-induced transfer reactions, promises to open such studies to a wider variety of nuclei in this region. The detection of the residual nucleus, as well as gating on a specific X-ray multiplicity and total cascade energy with a "crystal ball" spectrometer, should help reduce the background from the fission fragments.

The larger neutron excess of fissile nuclides in the transplutonium region also offers the possibility of spectroscopic studies on new neutron-rich fission products, e.g., near the interesting doubly "magic" ^{132}Sn nucleus.

A major question in nuclear structure studies concerns the stabilization of the 184-neutron shell. The energies of many of the orbitals that are important in determining the stability of this neutron shell decrease strongly with increasing deformation. At $\beta \sim +0.60$ these orbitals are the lowest-lying states of the mid-actinide region and might, with experimental advances, be observed quantitatively by spectroscopic studies of the excitation of fission shape isomers. The results would not only help define the position and stability of super heavy elements but would also yield information on the behavior of single-particle states at very high deformation--information not made available by other techniques.

A challenging and varied experimental program can be carried out with the transplutonium nuclides that are produced in the present operation of the HFIR/TRU facility. The pace of this program is limited by the manpower available to acquire, analyze, and interpret experimental data. Quantities of target material required for experiments range from tens of micrograms for transfer reaction studies to hundreds of micrograms for high-spin studies to milligrams or tens of milligrams for (n,γ) studies. Of course, the design of experimental programs is influenced by the availability of these transplutonium nuclides. A continuing supply of the heavier products of the HFIR/TRU complex (primarily ^{249}Bk, ^{249}Cf, ^{250}Cf, ^{253}Es, ^{254}Es, and ^{257}Fm) is required for experimental use. Of these, the most desired species are ^{249}Bk and ^{249}Cf in milligram amounts, ^{250}Cf in hundred microgram amounts, and ^{254}Es in tens of microgram quantities.

Most of the essential isotopes are already available in sufficient isotopic purity. However, there are a few species, currently unavailable to researchers and yet of value in a variety of experiments, that require isotopic enrichment. The availability of these rare nuclides, ^{242}Am, ^{243}Cm, ^{245}Cm, ^{247}Cm, and ^{251}Cf would considerably enhance the scope of this program. Although microgram quantities can be produced in laboratory-scale separators such as those operating at several national laboratories, the production of substantially larger amounts (milligrams of product) would require the operation of an ORNL Calutron with these highly alpha- and gamma-active materials. We recognize that enrichment at the Calutron scale would require a substantial financial investment. Nevertheless, we suggest that this possibility be considered and evaluated with respect to exploiting the unique aspects of HFIR/TRU transplutonium element production.

The potentially important nuclide ^{250}Cm has the greatest number of neutrons (154) of any long-lived nuclide and the greatest neutron excess ($N - Z = 58$) of any available actinide isotope and therefore is very desirable for many of the experiments discussed. While it is not produced as a standard product by the HFIR/TRU, special mention is made here to encourage study of methods of improved production.

FISSION

The static and dynamic properties of nuclear matter in extreme states of deformation can only be probed via studies of the nuclear-fission process. The equilibrium states that exist at the fission saddle point are characterized by shape deformations nearly twice as large as for the corresponding nucleus in its ground state. On a macroscopic scale these deformations reflect the delicate balance between nuclear attraction and electric charge repulsion. However, saddle-point properties are strongly modified by the influence of microscopic shell effects that bring into play several new shape degrees of freedom.

Even greater deformations are attained during the dynamic descent of a nucleus from the fission saddle point to eventual scission. This process involves large-scale motions of nuclear matter under low-temperature conditions where the effects of shell structure and superfluidity manifest themselves strongly in the final fragment distributions. As an example of the extreme sensitivity of the dynamics of fission to nucleonic composition in the heaviest elements, recent measurements have shown a striking variation in the mass and kinetic-energy distributions of fragments produced in the fission of different fermium isotopes (cf. Figure 3 in Appendix E). Furthermore, reactor studies of mass, charge, and kinetic energy measurements performed with unprecedented accuracy have given new insights into the role played by nuclear superfluidity in determining the relative mass yields of odd-A and even-A fragments.

In terms of experimental techniques, our ability to address challenging new aspects of the fission mechanism has undergone major advances during the past few years. Development of sophisticated magnetic spectrometers, electrostatic separators, and time-of-flight systems has led to spectacular advances in the precision with which fragment mass and kinetic-energy measurements can be performed. For the first time direct determination of fragment charges is now possible as the result of improved energy-loss spectrometers. Furthermore, the ability to observe rare and/or complex fission phenomena has been enhanced significantly by large solid-angle fission detectors, 4π-multiple gamma-ray detector systems, laser optical-pumping techniques, charge plungers, and electron-solenoid recoil shadow devices.

As a complement to these developments, the array of nuclear projectiles available for the production of exotic heavy nuclei in reactions with transplutonium elements has continued to expand. Transfer reactions using projectiles such as ^{18}O or ^{22}Ne provide a promising method for producing neutron-rich isotopes with $Z > 100$, whose fission properties have exhibited large anomalies. The prospect of using neutron-rich secondary beams (e.g., ^{16}C) or elementary probes such as muons, pions, K-mesons and antiprotons also provides intriguing new prospects for study of the fission process.

Since nuclear fission limits the synthesis of new elements both in the laboratory and in nature, a better understanding of fission phenomena in the very-heavy-element region is essential. As detailed below, it is clear that a thorough investigation of these phenomena will depend critically on the availability of nuclides produced in the HFIR/TRU facility.

Static Properties of the Fission Barrier

The interplay of classical mean-field properties and quantal single particle effects in nuclear matter is probably most dramatically demonstrated by the existence of fission isomerism in the actinide nuclei. This isomerism arises from the influence of shell effects that produce a secondary minimum in the potential energy surface of highly deformed heavy nuclei. Hence, three (quasi) equilibrium configurations that are amenable to experimental investigation exist at large deformations: the two maxima, corresponding to outer and inner barriers, and the secondary minimum.

The detailed properties of nuclei in the second well are best explored with targets of curium and lighter nuclides. Conversely, curium and heavier targets offer unique possibilities for investigation of the two maxima. This is especially relevant for the inner barrier, which becomes dominant for the heaviest elements. Theory predicts that the transcurium nuclei should have simple (nonresonant) fission excitation functions governed by the properties of the inner barrier. Hence, it is of great interest to define these properties, e.g., (1) the barrier energies, (2) the symmetry properties of the barrier shapes, (3) the quantum states (e.g., K^π) of the transition states, (4) the penetrability coefficient $\hbar\omega$, and (5) the coupling of barrier states to the fission continuum.

Three lines of investigation appear to be especially appealing. First, because of the decrease in the second barrier for the heaviest nuclei, fission induced by neutrons in the resonance region below 1 MeV allows unique spectroscopic characterization of the transition states at the first barrier. In this way the conservation of the spin-projection quantum number K during the descent from saddle to scission can be probed. Attractive targets for these studies include the curium isotopes, ^{249}Bk, $^{249-251}$Cf, and possibly ^{252}Cf and ^{253}Es. As a rule, these studies require target materials in milligram quantities of more than 90 percent isotopic purity.

Second, information about the barrier can be derived from fission following transfer reactions in the above-mentioned target materials using light-ion projectiles (d, t, ^{3}He, and possibly ^{7}Li). Here the barrier penetrability, with or without resonant features, can be sampled over a large range of excitation energies. Furthermore, the fission rate at energies above the barrier is sensitive to possible differences in symmetry types between the barrier shape and that of the compound nucleus. High-resolution experiments in the very-heavy-element region, e.g., using a Q3D magnetic spectrometer, may lead to the observation of unexpected features in the properties of these systems. For such measurements targets of about 100 μg are required.

A third avenue of investigation involves the fission of μ-mesic ^{248}Cm (cf. Figure 5 in Appendix E). There are few ways in which the energy and penetrability of the outer barrier can be determined if it is substantially lower than the inner barrier. However, when fission is induced by the absorption of a μ-meson via an inner-shell radiationless transition, the nuclear Coulomb field is reduced. As a result, the height of the inner barrier is reduced relative to the outer one, and it thus becomes possible to discern outer-barrier properties.

The Dynamics of Fission

The large-scale nuclear motion associated with nuclear fission and its inverse--heavy-ion reactions--provides our primary testing ground for theories of the dynamic behavior of nuclear matter. These theories range from microscopic approaches, as represented by time-dependent mean-field (Hartree-Fock) calculations, to macroscopic approximations based on the evolution of a few salient collective degrees of freedom. Central to our understanding of these processes is the question of nuclear dissipation and the mechanisms by which collective kinetic energy is converted into internal excitation energy.

Low-energy fission affords a distinctive advantage in the study of nuclear dynamics in that such processes are characterized by low temperatures, thereby enhancing the effects of nuclear shells and pairing. Of special relevance to the transplutonium elements is the fact that the dynamic path between the fission saddle point and the scission increases sharply with increasing fissionability ($\sim Z^2/A$) due to the relatively compact shapes at the fission barrier. These features, when studied experimentally, provide sensitive tests of current theoretical efforts in this field.

That rapid changes in fission properties can be expected in the transcurium region is demonstrated by the fermium isotopes, where it has been found that the addition or removal of a single nucleon or a few million electron volts of excitation energy can produce dramatic changes in the mass and kinetic-energy distributions of the fragments. Full exploration of this behavior, observed via spontaneous fission and neutron-induced fission studies, requires intensive further study as a function of both fissioning species and excitation energy. A particularly fruitful approach to this problem may be heavy-ion transfer reactions on the heaviest systems available, e.g., ^{248}Cm, ^{252}Cf, ^{254}Es and ^{257}Fm. Targets consisting of microgram quantities (except for ^{257}Fm) and 90 percent purity are required.

Similarly, the relative yields of fragments with even charge as compared with odd charge depend critically on the number of protons and neutrons as well as on the excitation energy of the fissioning nuclei. Using sophisticated fission-fragment mass spectrometers like Lohengrin (ILL) and Hiawatha (Illinois), fission events have been observed in which primary fragments are produced close to their ground states. Such events may provide crucial tests for dynamic-fission theories. They already show that neutrons and protons behave differently with respect to their pair-breaking probabilities during the fission process. To understand the nature and extract the consequences of these "large effects" of "small causes," improved systematic studies obtained by varying the fissioning systems and their excitation energies are needed. Targets of special relevance to these studies include ^{245,247}Cm, ^{249}Bk, ^{253}Es, and ^{249}Cf.

The dynamics of the fission process may be tested by two other more direct (but experimentally more difficult) approaches. One method involves studies of the angular distribution of light-charged particles emitted in ternary fission. This information can be used to deduce the pre-scission kinetic energies of the fragments, a quantity of vital importance to theories of nuclear dissipation. Both spontaneous fission the and particle-induced fission studies involving the same nucleus are required to explore this problem. Particularly interesting targets are pairs ^{249}Cf (n-induced)-^{250}Cf (s.f.) and ^{251}Cf (n-induced)-^{252}Cf (s.f.).

A second novel probe of the dynamics is to study the fission of μ-mesic atoms. At the point of scission the μ-meson must attach to one of the fragments. If the time scale of the fission process is slow, muon attachment should favor high-Z fragments; if it is fast, the probability for attachment should become independent of the fragment Z. Because of the long path from saddle point to scission, the heaviest elements are especially interesting for such tests of the dynamic flow of nuclear matter.

In summary, the fission reaction continues to serve as a rich source of information relevant to many-body theories of nuclear matter. The high sensitivity of fission observables found among the heaviest elements necessitates the existence of the HFIR/TRU facility to produce the basic nuclear materials for these studies.

SPONTANEOUS POSITRON EMISSION IN SUPERCRITICAL COULOMBIC FIELDS

A unique opportunity has arisen with the combined availability of very heavy projectiles and transplutonium targets to observe, for the first time, a fundamental property of quantum field theory that manifests itself under extreme conditions of ultrastrong Coulombic fields. The vehicle for such studies is the superheavy quasi-atom formed transiently in heavy-ion collisions near the Coulomb barrier. Extreme electric fields of about 10 kV/fm penetrate the space in the vicinity of the combined nuclear charges, simulating the environment found near a point charge with $\alpha Z > 1$. Under such supercritical-field conditions, the vacuum is unstable and it decays into a new lowest-energy state in which the nucleus is surrounded by electrons, with spontaneous emission of positrons. The search for this process is of interest as a zero-order process and has led to investigations of atomic systems in which relativistic effects are no longer a small perturbation but dominate wave functions and binding energies.

The defining features of spontaneous positron emission are (1) a threshold supercritical charge of $Z = 173$ (increased above the $\alpha Z = 1$ criterion because of finite-size and polarization effects) and (2) a striking Z^{70} dependence on the charge of the quasi-atom. This very sharp Z dependence, together with the fact that backgrounds from nuclear and other atomic processes show appreciably smoother Z dependences, emphasizes the need to explore with the highest-Z projectile-target combinations available.

Recently there has been the exciting observation of a narrow peak structure in the positron spectrum emitted in the collision of a uranium projectile with a curium target at a projectile energy near the Coulomb barrier. It is particularly significant that the line width corresponds to a lifetime for the emitting source greater than 5×10^{-20} s, which is relatively long compared with collision times. If subsequent experiments show that this time is not related to other mechanisms, such as nuclear-transition pair production, then this may well have been the sought-for observation of spontaneous positron emission in overcritical fields. There is also the important implication that superheavy nuclear complexes, with lifetimes an order of magnitude longer than the collision times, were formed in sub-Coulomb scattering.

It is, then, particularly important to expand the pool of systems studied to trace the Z dependence of the positron peak energy. Such a key study is not feasible without plutonium and transplutonium elements. Access to 1-mg quantities of ^{244}Pu, ^{248}Cm, and ^{249}Cf is essential to vary the electrodynamic and nuclear aspects of the physics. Since only the Z is important in these experiments, isotopic purity does not matter, except for handling problems.

Extensive investigations are being made of the properties of superheavy collision systems using characteristic X-rays, delta rays, and MO X-rays (X-rays characteristic of the nucleus resembling a molecule as opposed to a single nuclear mass center) as probes. The strong enhancement of those effects with even marginally increasing Z makes it most desirable to seek the highest-Z targets. The transplutonium targets are, therefore, indispensable to these experiments also. The above-noted targets would be used here; ^{254}Es at the microgram level is desirable as well.

These very interesting supercritical field studies depend entirely on the availability of the transplutonium targets for a successful, unambiguous outcome.

MATERIALS SUMMARY

As a result of our scientific evaluation of the research opportunities contingent on materials produced in the HFIR/TRU complex, the following list of nuclides of maximum interest is provided, along with amounts and purities. By stressing the importance of these materials for research, the panel is stating in specific terms the need for continued operation of the HFIR/TRU facility.

Nuclide	Quantity	Purity	Studies
^{244}Pu	~mg	--	Spontaneous positron emission
^{242}Am	~mg	--	Nuclear structure (n,γ)
^{243,5,7}Cm	~mg	Calutron separation	Nuclear structure (n,γ)
$^{244-8}$Cm	~mg	> 90 percent isotopic purity	Fission (n,f)
	~100 μg	--	Fission, transfer reactions, mass and energy distributions
^{248}Cm	~mg	--	Spontaneous positron emission
^{250}Cm	~μg	--	Nuclear structure, fission, superheavy elements

Nuclide	Quantity	Purity	Studies
^{249}Bk	~mg	--	Nuclear structure (n,γ)
	~mg	$>$90 percent isotopic purity	Fission (n,f)
	~100 μg	--	Fission, transfer reactions, mass and energy distributions
^{249}Cf	~mg	--	Nuclear structure (n,γ), spontaneous positron emission
	~100 μg	--	Fission, mass and energy distributions
$^{249-251}Cf$	~mg	$>$ 90 percent isotopic purity	Fission (n,f), ternary fission, nuclear structure (n,γ)
^{251}Cf	~mg	Calutron separation	Nuclear structure (n,γ)
^{252}Cf	~100 μg	$>$90 percent isotopic purity	Fission, transfer reactions
$^{253,4}Es$	~10 μg	--	Nuclear structure (n,γ), transfer reactions, fission, transfer reactions, mass and energy distributions, spontaneous positron emission, superheavy elements
^{257}Fm	~10^{10} atoms	--	Fission (n,f), transfer reactions

3

CHEMICAL PROPERTIES OF THE TRANSPLUTONIUM ELEMENTS

EXECUTIVE SUMMARY

The elements of the transplutonium region offer a unique chemical research opportunity because of two characteristics of their electronic configurations: (1) the presence of 5f orbitals and (2) the strong influence of relativistic effects. It is presumably the influence of these added factors that causes the large variations in chemical behavior of the elements composing the actinide series relative to those of the lanthanide series. At the lower end of the actinide series, for example, the III oxidation state that dominates the lanthanide series is readily exceeded and the IV, V, and VI states are common. At americium the III state is stabilized. By californium the II oxidation state begins to assume some stability, and in nobelium it becomes dominant. Theoretical interpretations are needed of the trends typified by this change in stability toward lower oxidation states with increasing atomic number (Z). It appears that such theoretical interpretations should be easier for the simpler chemistry observed in the heavier actinides. Understanding gained of the heavier part of the series should be useful for unravelling the more complicated chemistry of uranium, neptunium, and plutonium at the light end. It has long been clear, for example, that the understanding of uranium chemistry, even its placement in the periodic table, awaited the discovery of the elements beyond uranium.

Macroscopic quantities of the elements to einsteinium are available, but from fermium on, the chemistry must be carried out on the basis of quantities measured in atoms. Furthermore, from mendelevium on, the elements must be made with accelerators and have quite short half-lives. Nonetheless, experimental programs in the region of the heavy actinides and light transactinides are important in defining the architecture of the periodic table in this region, where a sharp discontinuity occurs from one series to the next. More than that, experimental knowledge of the chemistry of the transactinides gives an improved basis for extrapolation to the chemical properties of the superheavy elements. Accurate forecasting of these chemical properties may indeed prove crucial to the discovery of these elements.

To achieve the objectives outlined above, the major areas the Panel on Chemical Properties has identified for new or extended investigation are as follows:

- Exploit the long-lived isotopes of curium (^{248}Cm, $t_{1/2}$ = 3.397 x 10^5 yr) for the accurate determination of the chemical properties of this element and its compounds.
- Develop aqueous chemistry, especially in basic solutions (e.g., in carbonate media).
- Extend the range of accessible oxidation states, especially by making use of nonaqueous media, including molten salts.
- Determine the thermodynamics of complexation in solution with ligands, such as crown ethers and cryptates.
- Obtain hydration numbers of ions in solution.
- Measure thermodynamic properties of solids, such as binary (whether stoichiometric or intermediate) and complex oxides, with $Z > 96$.
- Extend organometallic chemistry and exploit bulky ligands to favor discrete molecular species.
- Study kinetics of complexation reactions and redox reactions.
- Use pulse-radiolysis techniques to explore rates of reaction of radiation-produced intermediates with metal ions and to explore the limits of oxidation and reduction.
- Develop new chemistry as a basis for separations chemistry in high-radiation fields, under highly acidic conditions, and for continuous processes.
- Focus on the most basic chemistry for the transeinsteinium elements, including determination of properties of the metallic atoms, range and stability of oxidation states, ionic radii and complexation behavior, and simple binary molecular species.

INTRODUCTION

In the transplutonium region of the periodic table, we are dealing with elements of the highest known atomic numbers, and scientific interest derives from the fact that the chemistry of these elements has not been widely explored. There is excitement in discovering previously unknown properties and in testing theories that have been developed for the elements of lower atomic number, relating electronic structure to chemical properties.

Of the transplutonium elements, only Am, Cm, Bk, Cf, and Es can be studied in milligram or greater amounts. Particularly useful isotopes of four of them, ^{248}Cm, ^{249}Bk, ^{249}Cf, and ^{253,254}Es, are derived solely from the HFIR/TRU facility. The heavier elements, which have such short half-lives and are available only on an extremely small scale, are produced from bombardments of targets best prepared from isotopes synthesized and isolated in the HFIR/TRU.

Because of the intermediate character of the actinides, comparison with the transition metals and with the lanthanides leads to greater understanding of both the actinides and the other transition metals. The properties of the heavier members of the series cannot be predicted from those of the lighter members with the same confidence that obtains when similar comparisons are made within the lanthanide series. With even less confidence can the properties of the actinides be predicted from those of the lanthanides. Thus, the need to extend the direct study of the chemistry of the actinides to those of higher atomic number is evident.

Bonding in the actinides exhibiting oxidation state III is somewhat more covalent than that in the lanthanides exhibiting the same oxidation state, and it is important to trace such effects to the end of the series where they are likely to be more prominent. In this connection the 4+ state is especially significant, and effects arising from ligand-to-metal charge transfer can be expected to be especially prominent for the actinides where the 4+ state becomes strongly oxidizing.

For the transactinides a major interest on the experimental side is that of meeting the challenge of establishing chemical properties for vanishingly small amounts of material; on the theoretical side, of tracing the relativistic effects of electron configuration and thus chemical properties. These elements, even more than the actinides, will challenge our capacity to understand chemical behavior in terms of electronic structure and will profoundly influence the way we think about the chemistry of the rest of the elements.

In terms of practical significance in actinide chemistry, there is the need to develop the chemistry that is important to the nuclear fuel cycle and among the transplutonium elements (especially Am and Cm) to develop the chemistry that is important to nuclear waste disposal and environmental concerns.

Research needs and opportunities are considered below under various headings, the choice of which we shall attempt to rationalize here.

The most common and important reaction medium is still water, and we begin with a discussion of chemistry in aqueous solution. Nonaqueous environments introduce some unusual opportunities and challenges that have been only partially exploited and met for any of the actinides. The chemistry of the actinides in such environments will offer our best opportunity to study covalency of 5f orbitals.

Although concerns with structure, stability, and lability pervade the sections on aqueous and nonaqueous environments, and although each of these issues is acknowledged as key basics in these sections, they have not been treated in parallel fashion. Because consideration of stability is crucial in searching for and exploring the chemistry of new elements, this issue is singled out in a separate section devoted to thermodynamic data. Separations methods are an essential and practical concern where many pressing problems remain to be solved, and these are considered in the next section.

The foregoing dealt mainly with chemistry as it can be studied or practiced using weighable quantities of matter. When the number of atoms is so small that studies in a condensed state are no longer possible, there are severe limitations on what can be done. Moreover, special approaches may be needed for the studies that are possible. For these reasons the later actinides and the elements following them are considered under a separate heading.

AQUEOUS SOLUTIONS

Extensive studies are necessary to provide an adequate description of the chemistry of the actinide ions in aqueous solution. Such studies should be directed to relating chemical properties to electronic structure and bonding. There are also important practical reasons for such research, since aqueous solutions are involved in separations and other chemical reactions involving these elements.

The characterization of the primary hydration spheres of these cations in aqueous, noncomplexing, acidic media is a fundamental problem that has not been satisfactorily resolved. The new techniques--such as EXAFS, neutron scattering, and fluorescence lifetime--provide promising approaches for the actinide elements through californium (and perhaps even einsteinium). For the heavier actinides, such physical measurements are not feasible. Correlation of the results from the physical and chemical studies of the actinides in the middle of the series could be used to understand more fully the chemical properties of the transcalifornium elements. Because of the predominantly ionic nature of actinide bonding, the work already done with those medium actinides provides a general guide to what can be expected for the heavier actinides. An important generalization is that the richest and most productive approach to complexation chemistry of the transplutonium metal ions will involve negative oxygen donor atoms and polar oxygen donor solvents and solutions.

The relative stabilities of the oxidation states of the actinide ions in solution are altered markedly by replacing water molecules in the primary coordination sphere with ligands that will have a more rigorously defined geometry. The approach would be to provide a data base by measurements of $\Delta G°$ and $\Delta H°$ for complexation with selected ligands using macroscopic-scale experiments for the lighter actinides through ^{248}Cm, ^{249}Bk, and ^{249}Cf. Such thermodynamic parameters would have to be obtained by tracer-level techniques on the transcalifornium elements.

Studies with oxygen donor complexes should be directed to provide the basic information needed for comparison with the properties of the lanthanides and early actinides, i.e., the formation of stable complexes of the most important oxidation states and the stabilization of the less common oxidation states to make them accessible for study both in solution and in the solid state. Information needed for these complexes includes thermodynamic stability; redox potentials; and kinetics of formation, dissociation, and exchange.

The stability of the oxidation states of actinides in solution (and in solids) is markedly perturbed by the interactions of the radioactive decay products with the substrates. Much more research is needed to describe these reactions fully. A satisfactory description of such radiolytic effects is important for modeling the behavior of actinides in waste repositories.

Oxidation States

The multiplicity of oxidation states and the increasing trend toward divalency across the actinide series suggest that much can be learned regarding the electronic structures of these elements by determining the relative stabilities of these oxidation states. Specifically, the following approaches are available for extending the range of oxidation states: use of powerful oxidants and reductants as well as electrolysis in aqueous media (e.g., radiopolarographic studies on nobelium have been done with 10^3 atoms per experiment) and stabilization of unusual oxidation states with specific ligands (an example would be the use of crown ethers to stabilize divalent species).

Beyond establishing the full range of oxidation states of these elements accessible in aqueous environments, redox potentials should be determined and efforts made to evaluate their systematic variation and to relate them to spectroscopic, magnetic, and other physical measurements. Oxidation-state studies may also provide insight into relativistic effects on the chemistry of the heavier actinides.

Some of the existing oxidation-state data on the transplutonium elements is of questionable reliability. Much of this work should be repeated using longer-lived isotopes (e.g., ^{248}Cm instead of ^{244}Cm).

Such longer-lived isotopes are available in the needed quantities only from the HFIR/TRU facility.

Kinetics

The rates of chemical transformations provide fundamental information on mechanisms and other kinetic factors and are of practical importance in designing experiments and separation procedures. The types of reaction to be considered are oxidation-reduction and ligand substitution. The redox reactions involving radiolysis products from water are of prime importance. Until these reactions are understood, many other changes that occur in actinide solutions will be difficult to interpret.

The reactions between actinide ions in various oxidation states and radicals, such as OH, a powerful oxidant, and the hydrated electron, a reducing agent, need to be studied more thoroughly by pulse-radiolysis techniques. These rate data are necessary for realistic modeling in aqueous neutral solutions.

The reduction potentials listed in Appendix F show three interesting couples that should be studied for comparison with existing results for the lighter actinides. Although the ionic forms in the Bk(IV)/Bk(III) couple are the same as in the analogous U, Np, and Pu couples, the potential is much larger. Studies of Bk redox reactions will provide a better understanding of the effects of $\Delta G°$ on rates and mechanisms.

The nobelium and mendelevium redox couples differ from those of the lighter actinides in that they involve readily accessible 2+ ions and are thus much more like the europium couple, which has been fairly well studied. These two actinide couples, however, span a very wide potential range, so that a variety of reactants can be studied.

Studies of redox chemistry in neutral or basic solutions require the presence of complexing agents. The species present, the redox potentials, and probably the rate laws will be different. Thus, the range of conditions can be extended from aquo ions to a variety of complex ions.

It is expected that kinetic studies will be made using tracer concentrations of the actinides and a wide range of macro concentrations of the other reactants. This will minimize radiolytic effects and requirements for elements available in only small amounts.

For multidentate ligands involving "softer" sites (e.g., N in EDTA), there is thermodynamic evidence for enhanced covalency in the 5f elements that increase with Z. Kinetics of exchange studied with tracer techniques have shown the Am-N bond rupture to be slow. Kinetic studies of the actinides and analogous lanthanides with nitrogen donor ligands could provide direct evidence for the extent of covalency in the heavy 5f elements. For long-lived species such as ^{248}Cm and ^{249}Cf, fast techniques could be employed to study the complexation formation kinetics to obtain further information on the hydration states of these cations. Studies of Am-aminoylcarboxylato complexes by stopped-flow spectrometry have demonstrated the feasibility and value of such studies.

Complex Formation

For the investigation of aqueous actinide complexes, it is important to have the long-lived isotopes. In studies of the carbonato complexes of the lighter actinides, for example, the production of peroxide and carbonate radical ions resulting from self-radiolysis causes problems in identification of spectral characteristics of these metal ions. Carbonato complexes have been useful for extending studies of the lighter actinides to alkaline solutions and should also be investigated for the heavier (transplutonium) actinides.

The types of ligands that provide considerable promise for developing the aqueous complex chemistry of the transplutonium elements are alpha hydroxy acids (lactic, hydroxyisobutyric, citric, and many others). Other effective ligands for the trivalent (and divalent) states are the higher analogs of EDTA (such as DTPA and TTHA) and some of the new phenolic ligands that have proved effective for Ga(III), Fe(III), and the trivalent lanthanides. The 4+ oxidation state of the transplutonium elements may be selectively stabilized by the catechol and hydroxamic acid ligands, which have proved effective for some of the lighter actinides. The lower oxidation states may be stabilized by crown ethers and oxygen-containing cryptands. To maximize metal ion stabilization the macrocyclic crown ethers and macrobicyclic cryptands currently available may be modified to accommodate the larger ionic radii of the transplutonium elements with longer bridges (larger cages) and by replacement of some of the oxygens with nitrogen or sulfur. Comparison of lanthanide behavior with such ligands could reflect the extent of additional covalency in the transplutonium systems. It should be emphasized that the higher specificities of the cryptate, macrocyclic, and other cage-like ligands relative to the conventional ligands offer the best opportunity for discrimination between closely related transplutonium ions of the same charge, which differ only slightly in ionic radii and related properties.

The cryptand and macrocyclic ligands offer distinct advantages for separation methods because the inherent rigidity of the ligand cages makes them sensitive to small differences in ionic radii. Thus, a specially designed cryptand or crown ether could be used for selective extraction of transplutonium ions from aqueous complexes into an appropriate organic phase. Conversely, immobilized cryptands and macrocycles could be employed for selective ion-exchange adsorption and elution processes. Certain types of cage structures may offer problems involving the kinetics of metal exchange, and for that reason the more flexible macrocyclic ligands may provide more reasonable rates. Both macrocyclic and macrobicyclic types should be investigated, however, since kinetic problems may be solved in many cases by appropriate ligand design. Because of the fact that the cage-like ligands have been developed relatively recently, the need for comparisons with the preplutonium actinides and the lanthanides will require parallel equilibrium and kinetic studies for those elements.

Thermodynamics of Complex Formation

With rare exception, studies of the complexation thermodynamics of transplutonium elements have been limited to tracer-level studies of the trivalent state. Thermodynamic measurements on aquo and complexed ions of Cm-Es are required in some cases. Aqueous calorimetry will complement known ΔG° data and provide important aquo ion entropy data. Participation of 5f orbitals in complex stabilization mandates study of ΔH° and ΔG° of complex formation in solution. Similar ΔG° values for complexation between An(III) and Ln(III) ions are often associated with rather surprising differences in ΔH° and ΔS°. These results need to be confirmed by direct calorimetric determination of ΔH° using ^{248}Cm and ^{249}Cf. Other complexes need to be studied by tracer techniques from Am(III) through Fm(III) to determine whether these differences in ΔH° and ΔS° are general. If these effects are verified for the actinide(III) complexes relative to the analogous Ln(III) species, an explanation must be sought in covalency and/or relativistic effects.

Knowledge of the actinide ion hydration state is basic to an understanding of the solution chemistry of these elements for both fundamental and applied reasons. The use of "hypersensitive" f-f transitions offers a rather simple and sensitive technique. However, elucidation of the relation between such hypersensitive spectra and coordination symmetry, covalent perturbation, etc., is needed before these spectra can be used for such purposes. Defining the local coordination symmetry of $^{248}\mathrm{Cm}^{3+}$(aq) by neutron and X-ray scattering could provide such calibration. The hypersensitivity could then be used for cations available only at more dilute levels, e.g., Bk, Cf, and Es.

NONAQUEOUS ENVIRONMENTS

Organometallic Chemistry

Until only a few years ago the chemistry of the lanthanides and actinides was restricted to the ions in combination with hard ligands, such as halides, oxide, or water. The break with tradition began with the lanthanides and has now extended to the lighter actinides [Th(IV), U(IV)]. An extensive organometallic chemistry of thorium and uranium is being developed, with more and more ligands typical of those in the organometallic chemistry of the transition elements being incorporated. Cyclopentadienyl compounds have already been prepared with elements up to Cf. There are reasons for preparing these molecules besides their intrinsic interest and novelty. Many show chemical reactivity involving H_2, CO, and organic molecules that is much greater than that exhibited by their transition metal analogs--reactivity that is germane to understanding catalysis. For the 3+ oxidation state, comparisons can be made between the lanthanides and actinides; they are significant in the context of differences in 4f versus 5f participation in bonding. Moreover, for the actinides the 4+ oxidation state is accessible for some of the transplutonium elements and comparisons with the lighter actinides are significant in the same connection.

Four general classes of organoactinide compounds have been investigated: (1) sandwich complexes of Th, Pa, U, Np, and Pu with two cyclooctatetraene ligands; (2) tris(cyclopentadienyl) complexes of Th-Cf (inclusive); (3) compounds of tetravalent Th and U containing two pentamethylcyclopentadienyl ligands; and (4) derivatives of tetravalent Th and U with two bis(trimethylsilyl)amide groups. The thermal stability of these compounds appears to be attributable to a high degree of coordinative saturation brought about by bulky ligand arrays that impede decomposition pathways. Although extremely air sensitive, these material are now easily handled using established high-vacuum and inert-atmosphere techniques. The relatively high volatility and solubility in nonpolar solvents contrast with the properties of actinide compounds containing "hard" ligands.

These recent advances indicate that numerous stable organoactinide compounds of the transplutonium elements should be obtainable. These are desirable in that systematic studies of analogous compounds along the actinide series could be conducted, comparing the new information with that already in hand for lanthanides and early transition metals.

Since organoactinides are expected to be among the most covalent actinide compounds, it is desirable to examine the variations in covalency and 5f character of the actinide-carbon bond as one proceeds from the lighter (early-transition metal-like) actinides to the heavier (lanthanide-like) ones. Although covalency and 5f orbital participation in bonding are difficult to quantify, electronic spectroscopy, esr, and photoelectron spectroscopy, as well as chemical reactivity (e.g., reactivity of cyclopentadienylactinides toward $FeCl_2$), could serve as useful probes.

In view of the availability of the divalent oxidation state for many of the transplutonium elements, it will be of interest to establish whether these oxidation states are more readily accessible with "soft," organic ligand systems. Organometallic compounds of several divalent lanthanides have been prepared. Divalent organometallic compounds of the transplutonium elements could exhibit 5f-π-dative interactions with ligands, such as CO, CNR, and olefins. In this regard there are the interesting effects of lower valency and contracted 5f orbitals as one proceeds to the heavier transplutonium elements. The possibility that transplutonium elements might form stable, low-valent compounds with "soft" donors such as phosphines should also be explored; the surprising observation that tetravalent uranium complexes prefer phosphines to amines is encouraging.

The scale for the preparation, isolation, and characterization of the light organoactinide compounds is commonly >100 mg. Lesser amounts could probably be tolerated for comparative reaction chemistry and spectroscopy; however, several tens of micrograms is probably the minimum sample size for meaningful experiments. Thus, preparations of new organometallic derivatives of Np, Pu, and the transplutonium elements Am, Cm, Bk, and Cf appear to be practical at this time.

Molecular (Volatile) Compounds

Although the bonds that the actinides form tend to be highly ionic, it is possible to prepare molecular species with them. A scientific rationale for proceeding in this direction is to provide a matrix in which the metal ions are isolated from each other, a feature that can be important in refined studies of magnetic properties; a practical rationale is to enhance solubility in nonaqueous solvents and to enhance volatility.

Work on the tetraborohydrides of the earlier actinides is already in progress, and with derivatization the volatilities can be increased over those of the parent compounds. Molecularity in the series depends on the bulk of the borohydride group and on the internal charge balancing. The same ends can be achieved by alkoxides and amides that bear sterically demanding substituents. This chemistry has been widely developed for transition metal ions with remarkable results. The use of bulky alkoxide and amide ligands in the preparation of volatile molecular compounds should be expanded considerably for the more accessible actinides and eventually extended to the later elements of the series.

Oxidation State Stabilization

The much greater availability and longer half-lives of the four elements following plutonium, i.e., Am, Cm, Bk, and Cf, allow an increased scale and scope of experiments over that possible with the transcalifornium elements, which have considerably shorter half-lives. The study of these latter elements requires more specialized techniques and/or facilities at an accelerator.

The number of oxidation states of Am-Cf that can be stabilized in aqueous media is limited by the redox behavior of water. These limits of redox behavior can be extended by the use of nonaqueous solvents. Pertinent to this point, the recent report of evanescent AmF_6 suggests that pentavalent americium as the yet unknown AmF_6^- ion might be stable in anhydrous HF, in parallel with the properties of the known UF_6^- and PuF_6^- ions.

We know that 8-coordinated solids of high-lattice energy, e.g., AnO_2 and AnF_4, stabilize the tetravalent states of the actinides. In still higher oxidation states, diminished ion size and increased acidity suggest that basic solvents such as oxide donors will provide the needed stabilization for these high-oxidation states.

The difficulty of obtaining Am(II) versus Eu(II) and the enhanced accessibility of Bk(IV) versus Tb(IV) imply that a wider variety of higher oxidation states than is now known is to be found for the transplutonium elements.

For stabilization of the lower-oxidation states, larger, more polarizable anions such as Cl^- and I^- in solvents capable of accepting electrons (e.g., liquid NH_3) should be investigated in conjunction with electrochemical studies.

There is intense interest in the lowest-oxidation states (II, even I) of elements of $Z > 96$. Media displaying low-solvating power are expected to enhance the stability of ions in low-oxidation states because of the low-charge density of these ions. Examples include molten mixtures of $AlCl_3$ and organic chlorides (e.g., alkyl pyridinium chloride), which are liquid near room temperature. These solvent systems are compatible with electrochemical measurements and have the additional advantage of displaying a broad electroactivity range. Experiments show that U(III) and Np(III) are stabilized over their corresponding tetravalent states with increasing chloroacidity (high $AlCl_3$ content and low free-chloride concentration). Similarly, Sm(II) and Yb(II) have been observed in these media, which therefore are likely to be particularly suited to studies of Cf(II) and Es(II). It is less certain whether Bk(II) could be similarly stabilized.

The significance of this area of endeavor is found primarily in determining the bounds of chemical oxidation-state stability. However, the data also have implications for the long-range oxidation-state stability in media proposed for storage of nuclear wastes containing actinides.

THERMODYNAMIC DATA

Thermochemical measurements, complemented by structural and spectroscopic studies, are essential for obtaining quantitative information on the relative stabilities of the various species of the elements with $Z > 96$ because:

o The stability of their divalent, trivalent, and tetravalent ions must be used to extrapolate to the heaviest actinides.

- The understanding and prediction of properties throughout the actinide series, including the trivalent and tetravalent ions of lighter actinides, mandate a knowledge of the $Z = 96-99$ region.
- The prediction of favorable parameters to obtain pure compounds for solid-state studies requires good thermodynamic data.

An example of an area whose thermodynamics has been elucidated is that of the stability relationships among the crystalline metals, their vapors, and the trivalent aquo ions. Enthalpies of sublimation have been determined for all actinide metals through einsteinium as well as enthalpies of formation of $An^{3+}(aq)$ through californium. These data systematically correlate the most fundamental species of these elements and provide a powerful predictive tool for heavier actinides.

In contrast with the above, no parallel data exist for the thermodynamic properties of the binary oxides (M_2O_3, MO_2, and intermediate phases) with $Z > 96$, with the exception of a recent result of $^{248}Cm_2O_3$. In addition, such measurements will help resolve systematic discrepancies in the stability relationships of lighter actinide oxides. Thermochemical data for other classes of compounds (e.g., dihalides and trihalides) are totally lacking. Such measurements will lead to more detailed understanding of electronic structure and to predictions for new classes of compounds (monoxides, chalcogenides, etc.).

Other thermodynamic data needs are discussed elsewhere, in particular those on complex formation in aqueous solution discussed earlier in this chapter and on solid-state properties (Chapter 5).

SEPARATIONS CHEMISTRY

Opportunities and Challenges

Separation of the transplutonium elements from one another and from source materials (e.g., reactor fuels, target materials, reprocessing wastes, etc.) is a sine qua non to elucidation of their chemical and physical properties and to practical applications. The entire broad field of transplutonium element research is based on the availability of relatively pure isotopes on a reasonably assured schedule. This implies the disciplined application of established separations processes and techniques and, in some cases, development of new or improved separations methods. The large number of transplutonium elements and their isotopes, and the very large number of fission-product elements and target elements that exist with them when they are produced, pose some of the most difficult inorganic chemical-separation problems ever faced.

Beyond the chemical separations required for production of pure transplutonium elements are the separations often required to obtain a pure isotope, e.g., the isolation of ^{248}Cm from ^{252}Cf. With the expected synthesis of the transactinide elements will come a new set of chemical properties, perhaps significantly different from those of the expected chemical analogs, and thus a new set of chemical-separation challenges. Even more challenging are the chemical separations often required for the very rapid isolation and identification of small numbers of atoms of new elements.

All of the above separations require substantial chemical information about many or all of the elements present. In some important cases the presence of significant amounts of radiation imposes an additional major burden on the separations chemist. Since many practical separation processes are carried out in combined aqueous and organic systems, radiolysis effects may strongly influence the processes and reagents chosen.

Thus, the separations chemist must rely on other researchers for knowledge of the basic chemical and radioactive properties of transplutonium elements to assist him in devising practicable processes for the isolation of each transplutonium element for its use in research.

Research Needs and Special Problems

Considering that kilogram amounts of long-lived isotopes of Am and Cm have been available for over 30 years, it is not surprising that efficient and workable aqueous-based processes for separation of Am and Cm from fission products, from other actinides, and from each other have been developed and applied. An important, still unresolved problem, however, is development and demonstration of a separation process (e.g., continuous countercurrent liquid-liquid extraction) for removing Am^{3+} and Cm^{3+} from strongly acidic nitrate solutions. Such solutions are routinely generated in reprocessing irradiated defense and commercial reactor fuels and contain kilogram amounts of ^{241}Am, ^{243}Am, and ^{244}Cm that could be isolated for disposal or for beneficial use. Solvent extraction and other separations processes for recovery of trivalent Am and Cm from acidic nitrate solutions have been only partially developed; additional bench-scale work is needed to develop those schemes to the point where they can be applied on a large scale.

Separation (recovery) of transuranium elements from Purex process high-level waste may, in some instances at least, greatly simplify and facilitate ultimate disposal of such wastes. A case in point is the high-level waste that will be generated at the U.S. Department of Energy's Purex plant in Hanford, Washington from future processing of fuel for their N-Reactor. Preliminary engineering analyses indicate that removal of ^{241}Am, and perhaps other transuranium elements, coupled with removal of the high-heat-producing by-product nuclides ^{90}Sr and ^{137}Cs, from these wastes could have a favorable economic impact on their disposal. Recovered transuranium elements (and associated fission product lanthanides) could be either purified further or converted to an immobile form (e.g., by incorporation in borosilicate glass) for disposal in a deep geologic repository. Wastes depleted in transplutonium elements, ^{90}Sr, and ^{137}Cs could probably be suitably deposited in near-surface facilities. Economic benefits accrue by virtue of the greatly reduced repository space required for disposal of a small volume of transuranium waste.

This latter example further emphasizes the continuing need for better understanding of the fundamental separations chemistry of Am and Cm from aqueous nitrate solutions and for developing and testing new and improved separation schema that can be satisfactorily scaled up. Availability of ^{248}Cm from the HFIR/TRU complex will substantially facilitate rapid development of the required curium separations processes.

There are important isotopes that are obtainable in adequately pure form only through special separations operations in the TRU facility.

These include ^{248}Cm, ^{249}Cf, and, perhaps, ^{254}Es. The first two are derived from decay of their respective parents and require clean areas and special operations for their final isolation. At present the separations are carried out through combinations of solvent extraction and ion-exchange processes in aqueous and organic systems. The use of new techniques should be explored for reducing the number of special operating steps. The new techniques examined should include selective organic reagents and nonaqueous systems, such as molten salts. Similar observations may be made about ^{254}Es if it should become a significant isotope in TRU production.

Use of volatile compounds in separations processes is well known and widely practiced. These compounds include halides, borohydrides, organometallic compounds, and perhaps others. Sorption-desorption techniques on carefully selected solids permit extraordinary chemical separations of gaseous compounds. Such methods should be developed for obtaining the very high degree of purity sometimes needed for transplutonium element isotopes, e.g., ^{248}Cm, which must be scrupulously free of ^{244}Cm, and ^{249}Cf, which must be free of ^{252}Cf.

Radiolysis of solvents and reagents is a major consideration in chemical-separation processes, both for production and research activities. Both aqueous and organic systems are vulnerable. Therefore, nonaqueous, inorganic systems should be studied. This implies study of molten salts and metals, anhydrous HF, and other systems.

TRANSEINSTEINIUM ($Z > 99$) CHEMISTRY

The elements to be considered consist of the heaviest actinides and the known transactinides as well as the undiscovered but predicted elements thought to be relatively stable in the region of $Z = 110$–120.

Scientific Basis for Study

The chemistry of elements 100 through 109 is important because the actinide series ends at lawrencium ($Z = 103$), and a new type of series begins at element 104. Thus, there is the important question as to the continuation of the periodicity observed in the lighter elements into the region of the heaviest elements. If the conventional periodicity continues, element 104 should be the first member of a 6d transition series extending to eka-mercury, element 112. Eka-iridium, Z = 109, the heaviest known element, was just recently discovered in Darmstadt, West Germany. The chemical properties of this 6d series will be heavily influenced by relativistic effects. These effects will be seen most clearly in the s and $p_{1/2}$ electrons. For example, eka-mercury will probably be a very volatile, noble liquid or even a gas, and eka-lead will have similar properties. The new series will almost certainly have significant deviations from the lighter homologs, and these differences need to be experimentally determined for as many elements in the series as possible.

Similarly, the unexpected trend toward divalency, discovered in the latter part of the actinide series, suggests the need for more studies in the Z = 101-103 region. Especially mendelevium in oxidation state I, which has been reported but not confirmed, requires more effort. In a similar vein the possibilty that relativistic effects may cause lawrencium to have the $5f^{14}7s^27p$ configuration, rather than the $5f^{14}6d7s^2$ configuration, suggests the need to establish whether oxidation states lower than III can exist for the last member of the actinide series.

Thus, the reasons for studying elements 100-109 are strongly intertwined: (1) the extent to which the symmetry of the known periodic table can be applied in the heaviest element region and (2) the determination of relativistic influence on chemical properties and reactions.

Techniques, New Approaches, and Research Goals

Ion exchange and solvent extraction have been applied successfully to studies of the chemical properties of the actinides and transactinides, even on a one-atom-at-a-time basis. From a simplified point of view, this is due to the one atom going through many reactions in these types of processes to give statistically significant results. Methods potentially involving only one atom and one reaction, such as coprecipitation, often given erroneous results.

Methods based on aqueous chemistry for alpha emitters are relatively slow, because the solvents must be evaporated before counting. Isotopes with half-lives as short as 30 seconds have been studied by these aqueous methods.

Methods based on gas transport (thermochromatography) are more rapid and have been applied to transactinide isotopes with spontaneous fission half-lives down to a few seconds. These techniques could be extended to shorter half-lives. For example, for the easily detectable gamma emitters, centrifugal contactors have allowed solvent extraction studies of isotopes with half-lives of only a few seconds. Such work suggests the development of scintillation counting of alpha emitters and perhaps thin-layer liquid chromatography for fission counting using mica track detectors.

Another approach might be to develop the chemistry of these elements, using their analogs, in solvent-extraction systems composed of highly volatile solvents that can be evaporated rapidly.

For reactor-produced gamma emitters, gas-phase methods have allowed studies of isotopes with half-lives as short as a few tenths of a second. Although atoms produced with the aid of accelerators require time to achieve their full complement of electrons, much faster methods of studying the chemistry of transactinides than have been used in the past may be possible.

A particularly exciting approach may involve laser-based spectroscopy in few-atom experiments. For example, the 77-min isotope ^{256}Md can be made in yields of about 10^6 atoms. This element may be a good candidate for an attempt at such spectroscopic studies.

So little is known about the chemistry of these heaviest elements that priority should be given to studies of the most fundamental properties, such as attainable oxidation states and their relative stabilities, ionic radii, polarizabilities, and simple gaseous and aqueous species. Perhaps properties of the metal atoms themselves could be obtained through thermochromatography in a strongly reducing atmosphere (using perhaps hydrogen or, if necessary, even sodium vapor as the carrier gas).

Mendelevium(I) has been reported, but careful experiments have not confirmed its existence. New approaches--e.g., the use of nonaqueous solvents and/or the appropriate crown ether--should be employed to promote the stabilization of the univalent state. But first it would be worthwhile to determine the ionic radius of divalent mendelevium.

Similarly, the ionic radius of lawrencium(III) should be measured by determining its elution position from an exchange column relative to the elution positions of other trivalent lanthanides and actinides whose ionic radii are known. The production of 3-min ^{260}Lr at the level of 10 to 100 atoms per experiment is now possible, giving a distinct advantage over previous experiments carried out with 26-s ^{256}Lr, which yielded only one or two atoms per chemistry experiment.

Nobelium-259, with a 1-hr half-life, can now be made in the thousand-atom-per-experiment range, allowing more definitive chemical studies than could be done in the past with 3-min ^{255}No. The III/II and II/0 reduction potentials should be confirmed. Also the polarizability and more detail on the relation of nobelium(II) to other divalent elements is needed in view of its apparent remarkably close similarity to the alkaline earth ions.

The chemistry of element 104 carried out by solvent extraction and thermochromatographic techniques has established it as the first member of a new transition series. It is particularly important to determine the oxidation states that element 104 can attain and the species it forms in binary compounds and in aqueous media. Faster, continuous solvent-extraction systems, perhaps using liquid scintillation counting or highly volatile solvents, should be developed for this purpose since 1-min ^{261}104 will probably have to be employed in these experiments.

The chemistry of element 105 can be extended by working with 35-s ^{262}105 rather than the 2-s isotope used in Soviet experiments. Experiments based on gas transport are desirable; early emphasis might involve carbonyl chemistry. Chemical studies of the higher atomic member elements will depend on the development of reactions yielding longer-lived isotopes at reasonable production rates.

The chemistry in the superheavy element region will magnify the relativistic effects expected in the 6d transition series. This will produce interesting contrasts with the lighter elements. For example, (113)Cl is expected to be soluble in aqueous ammonia, whereas the homologous compound, TlCl, is not. Eka-mercury is expected to be so much more noble than mercury that its oxide, fluoride, and bromide are expected to be unstable. Similarly, eka-lead should be more noble than lead because of its $7p_{1/2}^2$ closed shell.

Knowledge of the chemistry of the heaviest existing elements is necessary to extrapolate with confidence to the chemical properties of the superheavy elements. Accurate forecasting of these properties is probably essential to the discovery of superheavy elements, as was the case for the first two transplutonium elements.

CONCLUSIONS

Chemistry is based on establishing interrelations in the behavior of the different elements. Each element with its unique features, when its chemistry is compared with that of others, helps knit the fabric of theory that transforms the subject from a compilation of observations into a science. The chemistry of the actinides provides significant and direct comparisons with that of the lanthanides and the transition metals. These comparisons are incomplete unless the chemistry of the transplutonium actinides is more fully explored. The mysteries that remain to be probed in studies of the transactinide elements are perhaps even more exciting than are those to be uncovered for the heavier actinides. It is recognized that relativistic effects influence the chemistry of all the heavier elements. These effects are expected to be especially important in the transactinides. In establishing the relation between chemical behavior and electronic structure for the heaviest elements, we will be in a better position to understand how relativistic effects are manifested in the chemistry of the better-known elements.

The members of this panel conclude that continuing the HFIR/TRU facility and studying the chemistry of the immediate and derived products of the facility are important to the chemical community.

In preparing our report we made a broad survey of the kind of research being done on the actinides in relation to that being done with other metallic elements. Gaps in knowledge exist not only for the transplutonium elements but also for the more accessible members of the series. Some of these gaps are exposed here in the hope that it will alert our colleagues to the need for greater research efforts on the actinides as a whole.

4

SPECTROSCOPY

EXECUTIVE SUMMARY

The availability of transplutonium elements affords the opportunity, via analysis of their spectra, to expand our understanding of electronic structure throughout the periodic table. A particularly important issue to be elucidated will be the involvement of the 5f orbitals in bonding. Since 5f orbitals, which are progressively filled through the actinide series, are intermediate in their properties between the 4f orbitals and the 3d orbitals, the insights gained from actinide spectroscopy can be expected to illuminate the behavior of the lanthanides and the transition metals.

The study of the heavy actinides is particularly important since the progressive lowering of the 5f orbital energies leads to a simplification of the spectra, which will aid in the interpretation of the more complex spectra of the lighter actinides. It will be desirable to develop chemistry for the study of molecules with maximum covalency across the actinide series. The intermediate extension of the 5f orbitals should also lead to interesting excitonic and mixed-valent properties of actinide compounds, which can fruitfully be studied spectroscopically.

The first priority is to interpret the spectra of both free atoms and free ions of the elements. Comprehensive intensity measurements of free-ion spectra, now possible for the first time, are required for further interpretation, and studies need to be extended to more highly ionized species. The spectra of the actinide ions in solution and in ionic lattices provide unique opportunities for studying the effects of crystal fields. Such studies have been extremely fruitful in the understanding of transition-metal chemistry.

Because the 5f levels are relatively sharp and well defined but still sensitive to the chemical environment, the actinide ions are likely to be excellent spectroscopic probes of chemical structure and dynamics. Applications might include the probing of structure in amorphous materials and at specific ion sites in biological molecules and the analysis of phonon or vibronic coupling.

Aside from provision for the elements themselves, this research requires the availability of sophisticated spectroscopic equipment in laboratories able to handle substantial quantities of highly radioactive nuclides. Currently envisaged studies of the heavier actinides require microgram to milligram quantities and the regular availability provided by the HFIR/TRU facility. However, the recent development of laser-excitation spectroscopy promises a dramatic decrease in the amount of material required for many studies and opens the prospect of obtaining spectra of low-abundance molecules or ions and of elements beyond einsteinium. Indeed the sensitivity available with the latest techniques can extend to single atoms, and it is possible that spectroscopy will play an important role in the search for new elements. To apply the new techniques, the energies of the spectral lines must be reasonably predictable. Progress in the general spectroscopic understanding of the heavy elements is crucial in this connection.

INTRODUCTION

Spectroscopy is the primary source of information about electronic structure and therefore contributes importantly to our understanding of chemical and physical properties. The crystal-field interpretation of spectra has been the most important concept of the last 30 yr in the development of transition-metal chemistry. A similar approach is now being applied to the actinide elements, with the promise of expanding our understanding of electronic structure throughout the periodic table.

In actinide spectra the role of the 5f electrons is dominant and can be delineated, especially as more data on transplutonium elements become available. The recent concept that the behavior of 5f electrons is intermediate between that of 3d and 4f electrons provides an interpretive framework, and further studies promise to throw more light on transition metal and lanthanide as well as actinide chemistry. In addition, relativistic effects come to the fore in heavy-element spectra and can be specifically explored.

Spectroscopy is of particular importance to the study of transplutonium elements since optical methods are readily adaptable to these materials, which are difficult to handle and available only in small amounts. Indeed, the new techniques of laser-excitation spectroscopy should be applicable to the very few atoms of the heaviest elements that may become available for study.

ATOMIC SPECTROSCOPY

Energy Levels and Configurations

The electronic and nuclear-structure properties of the heavy elements provide the key to understanding the chemistry and stability of these elements. The presence of the 5f electrons is proved unequivocally by the identification of the electronic ground-state configuration and higher configurations derived from atomic spectroscopy. The stabilization of the 5f electron in higher valence states can be monitored by various resonance spectroscopic methods.

As of now, the elements from americium to einsteinium have been surveyed (see Appendix G) and the ground configuration identified. The next step is to move toward locating the energy levels associated with higher configurations. To do this it is necessary to observe these spectra by more refined techniques. For the scarce elements beyond einsteinium, entirely new techniques will be required. It is worth noting that these new techniques would also find tremendous interest and application in various analytical spectroscopic methods of scientific and commercial value.

Energy values and total angular momentum quantum numbers are necessary for calculations of the thermodynamic properties of the elements. It is important to identify all the possible levels below at least 20,000 cm^{-1} for such calculations to have meaning.

The grouping of the levels by configuration is accomplished by the study of isotope shifts, since each configuration has a somewhat unique isotope shift. Isotope-shift data are also of interest to nuclear physics because the isotope shift is a measure of nuclear volume effects. Zeeman-effect and hyperfine-structure studies are useful for assigning quantum numbers to levels within a configuration.

Studies of the hyperfine structure obtained in optical-emission spectroscopy yield values for the nuclear dipole and quadrupole moments that are of interest in nuclear physics. Laser spectroscopy techniques can improve the precision of hyperfine and isotope-shift measurements by a factor of 10 or more for specific transitions. These laser measurements may allow hyperfine anomaly studies to be made, if appropriate isotopes are available in sufficient quantities.

Energy-level analyses of the higher stages of ionization are needed because of their importance to the interpretation of solution and solid-state spectra. This will require development of new techniques usable with very small samples.

Ionization Energies

Ionization energies are important for understanding the systematics of the actinide elements. Techniques are well established for the determination of accurate ionization energies of the neutral species by observation of extensive Rydberg series through laser-excitation methods.[1] The accuracy of 1 part in 10^5 that can be realized allows clear distinction of trends and good tests of theoretical calculations and their reliability for extrapolation. For elements beyond Es, extrapolated values may be the only values ever available. In the actinide series, accurate experimental values are not available for Ac, Th, Pa, Am, Cm, and for transcurium elements. Sufficient materials and techniques are available to obtain ionization energies of the neutral atoms up to and including Am. Development of better handling techniques and beam sources requiring smaller amounts of metal are required for series members beyond Am. (The exact limit on the amount of metal needed is not known, but tens of milligrams may be required for assured success using present-day technology.)

Laser techniques have the potential to determine the ionization energies of singly ionized elements and possibly doubly and more highly ionized species. The experiments become much more difficult at each degree of ionization, and considerable spectroscopic information about each species is needed.

Theory

Relativistic effects for these high-Z elements are of course large and dictate use of relativistic (Dirac-Fock) rather than nonrelativistic (Hartree-Fock) theory. The principal relativistic effect is a contraction of inner-shell orbits, especially for s and $p_{1/2}$ electrons. This results in magnification of isotope shifts and hyperfine-structure splittings, which are already large at these high values of Z.

As an indirect result of the s- and p-electron contractions, these electrons shield the outer 5f and 6d electrons from the nucleus more completely, so that the 5f and 6d orbits actually move outward rather than inward, with the following consequences:

o Electrons in the 5f and 6d orbits are computed to be bound less tightly than in Hartree-Fock theory, and the 5f-6d excitation energy is likewise decreased. This is part of the reason that 5f electrons are less localized than the 4f electrons in lanthanides and why 6d electrons are a more important aspect of the electronic structure of the actinides (and of actinide compounds) than are 5d electrons in the lanthanides.

o Electron-electron Coulomb energies of 5f and 6d electrons are reduced, and spin-orbit-interaction energies are decreased even more strongly, so that the tendencies toward jj coupling (especially pronounced at the high-Z end of the actinide series) are decreased somewhat relative to the nonrelativistic predictions.

- The absolute accuracy of Dirac-Fock calculations is not well established at these high values of Z, and checking against experimental data is required. It is important that these comparisons be carried to as high Z as possible. The closer one can come experimentally to the end of the actinide series (Z = 103), the simpler the electronic structure and spectra become, thereby reducing the uncertainties in comparison between experiment and theory. The accuracy of theoretical predictions of the electronic structure of superheavy elements can then be better assessed.

Anomalous Element Abundances in A_p (Peculiar A-type) Stars

It is conceivable that the anomalous abundances in these stars may also involve transuranium elements. The abundance of elements with Z above 26 (iron) in the sun, and most other stars decreases exponentially with increasing Z (and hence yttrium is far more abundant than lanthanides, rhodium more abundant than bismuth, etc., and thorium and uranium barely detectable). (Fortunately for inorganic chemists, the Earth's crust contains 0.15 percent by weight of elements with Z above 31 and in roughly comparable amounts, typically 1 to 10 ppm.)

In 1913 a star was discovered in Canes Venatici with very strong Fraunhofer lines of europium. This was the first case of an A_p star, a group that constitutes about 10 percent of all A-type stars and that is characterized by the presence of a single element or a few elements in very high abundance, strongly variable with time. (The Twenty-third International Colloquium on Astrophysics [held in Liege in 1981] dealt with this subject.) One star shows a strong maximum of rare earth every 23 yr, another contains a million times more bismuth than the sun,[2] and another shows great amounts of osmium and uranium.[3] The most remarkable feature is perhaps the short time scale of a few years.

There is a serious lack of atomic spectral-line positions and relative intensities of transuranium elements, M^o, M^+, and M^{+2}, for comparison with numerous unidentified Fraunhofer lines of A_p stars.

These objects may involve very heavy elements and are among the most enigmatic of all stars.

CONDENSED-MATTER SPECTROSCOPY

Because of their electronic configurations, the transplutonium elements couple to their environment with a strength that is intermediate between that of the lanthanides (weak) and the 3d transition metal series (strong). The spectra that result when 5f ions are placed into various insulating hosts generally consist of relatively sharp transitions. These lines may be traced to their free-ion origins. The pure electronic transitions (zero phonon lines) provide (1) a unique tool with which to investigate the effects of the environment (symmetry, bonding type, valency) on the ionic levels and (2) a probe for investigating various dynamic effects produced by the collective excitations and reactions occurring in the environment itself.

The development in recent years of new techniques based on tunable dye lasers has allowed the study of spectroscopic features in a much more fundamental manner, since laser spectroscopy can be conducted in such a way as to yield site- and energy-specific information about intrinsic properties of electronic transitions. This feature constitutes an advance that cannot be overemphasized, because these techniques provide a way to suppress extrinsic spectral features that often obscure those spectral aspects that are of principal interest.

The transplutonium series is attractive to study because it provides numerous transitions that span a region of the spectrum in which laser sources are readily available. The larger "crystalline" effects on the 5f levels also lead to larger separations between Stark components. This decreases the probability of nonradiative processes and thus leads to a considerable number of fluorescence transitions that can be used as probes.

A number of areas where the above techniques can and are being applied to actinides to study various chemical and physical effects through their spectroscopic signatures are outlined below.

Structure Effects

In the area of energy level structure analysis, which requires the close interaction of theory and experiment, significant progress has been made in the characterization of the free-ion and crystal-field parameters of the trivalent actinides in $LaCl_3$.[4] Spectra in lower symmetry sites should be studied both experimentally and theoretically in order to reveal subtle symmetry-related differences. Heavy actinides in the trivalent state have recently been shown to be excellent candidates for treatment by the Judd-Ofelt theory of transition intensities.[5] Extension of this work to crystals with well-characterized site symmetries should be pursued as an avenue that will open up uncharted territory. The ability to compute line intensities consistent with experimental values would be exceptionally valuable as a new tool for classifying observed transitions.

In solid compounds of the heavier actinides it is known that the divalent state is progressively stabilized with increasing number, and from available data it can be expected that f-f transitions will be observed in absorption over a large energy range before the onset of more intense f-d transitions. Such spectra provide unique and entirely new information on the nature of electronic structure and the influences of bonding on structure. It is also clear from the results of recent research efforts, including work with divalent lanthanide systems, that 2-photon excitation techniques provide the key to greatly extending the energy range over which the structure of the f^N configuration can be explored.[6] Use of these techniques results in the f-f transitions assuming a parity-allowed character, so that they can be detected in an energy range normally masked by f-d absorption bands or by charge-transfer bands. Two-photon spectroscopy should be especially valuable in studies of heavy actinides, where f-f transitions in 4+ and in some cases 3+ valence states are increasingly susceptible to masking by charge-transfer transitions.[7]

Mixed-valence compounds seem well established in the actinide series, in complex oxide phases, beginning with the uranium-oxygen system. Mixed valency may be a useful concept in interpreting experimental data for the heavier actinide (mixed) oxides. Mixed- valence compounds are at the forefront of solid-state science and should be amenable to study by spectroscopic techniques, including absorption and selective excitation.

The strength of the ion-lattice coupling in the actinide series leads to the formation of well-developed and well-defined vibronic side bands adjacent to the pure electronic transitions. These vibronic side bands reflect the vibrational structure of the molecular complex or lattice in the vicinity of the active ion. As such they can be used as a probe of local dynamics. For this probe to be most effective, it is convenient to use ions that possess simple electronic structure (e.g., the $^5D_0$-$^7F_0$ transition in Eu^{3+}; both Am^{3+} and Cm^{4+} have equivalent transitions). Americium, curium, and berkelium in different valence states can serve as well in this regard. The variation in the valence state allows the incorporation of actinide probes into molecular complexes and lattices of different charge without the complicating need of charge compensation.

Because the actinide f-orbital energies are sensitive to their chemical environment, they are amenable to site-selective spectroscopies. Recent studies of various types of centers in amorphous and vitreous hosts have demonstrated that they can yield information on the microscopic (bonding, valence, coordination) and macroscopic constitution of disordered systems.[8] Generally, no comprehensive studies exist of actinide ion-activated glasses in which these techniques have been used. The panel believes that it would now be timely to consider a study of the optical properties of some common glasses and ceramics activated by actinides up to Bk^{3+}. The emphasis of these studies should not only be on the structural details but also on the dynamical changes that may occur in the structure owing to the effects of intense radioactivity. This information coupled with advances in spectroscopic monitoring from a distance may prove to be important in waste-disposal technologies.

Relativistic effects, which are important for the actinides, should be explored in condensed-phase as well as in free-ion spectra. The approach would be to explore the systematic variation of physical parameters as a function of increasing Z, comparing the results of relativistic with nonrelativistic calculations. A suitable candidate for study may be the 5f-6d excitation energy, for which the relativistic effect might be sufficiently large to be established experimentally (greater than 20 percent). Such an investigation may be helpful in the analyses of the more complex emission spectra of free ions.

In the heavier actinide elements the lower-density electronic states in the 0 to 20,000 cm^{-1} range have been exploited to demonstrate fluorescence at 25° in solution. In the case of Cm^{3+} this emission offers an exceptionally sensitive, and environmentally applicable, mode of detection in aqueous media.* Fluorescence can also be used to monitor formation of complexes in solution. The "hypersensitive" electronic transitions also are of interest in studies of solution chemistry; they have been observed in trivalent actinides and deserve detailed investigation. For the heavier actinides these transitions are in an energy range that is amenable to experimental investigation.

Spectroscopy in nonaqueous solutions, including molten salts, can be expected to be productive in terms of stabilization of unusual oxidation states and of exploring the effects of different coordination environments. Likewise, spectroscopic and photochemical studies of volatile actinide molecules, particularly organometallics, should be highly informative.

Site-selective spectroscopy may also be used to good advantage in the study of the incorporation of actinides in biological complexes, where they may be expected to occupy specific ion sites in the structure to be probed. The panel believes that initial studies of actinide ion complexes of this type should be considered, as they promise to yield information on biological and medically related processes.

Relaxation and Dynamics

Environmental collective excitations and interionic interactions are principally responsible for the relaxation and equilibration processes

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* Detection at the environmentally relevant level of approximately 10^{-10} M has been estimated.

that affect the electronic states of the active ion in a complex or in a host. No relevant relaxation measurements have been made on transplutonium elements to date, even though the relaxation parameters are accessible to various laser-based techniques through their influence on the intrinsic transition-line width. Such measurements should be attempted in order to elucidate the nature of environment-ion coupling.

Site-selective spectroscopy can be conducted in a time-resolved fashion. The spectra obtained will contain information on various dynamic processes that affect the optically excited state of the active ion.[9] Processes of this type include ion-ion interactions that result in energy diffusion or chemical reactions that may change the valency or bonding of the ion. The less-shielded 5f electrons of the transplutonium elements should yield stronger ion-ion coupling, which is expected to differ considerably from the lanthanide coupling. It is likely that these interactions will include an exchange component and that their strength will be sufficient to bridge the transition between incoherent and coherent transfer, a matter of high current interest.[10] Considerable work has been carried out on the lanthanides using time-resolved techniques, and it has been demonstrated in this series that the time-resolved spectra can be used as a powerful analytical tool to monitor chemical reactions in solid solutions. Such experiments are feasible and desirable for the actinides. This is especially the case for transplutonium elements, for which either short lifetimes or small sample quantities preclude comprehensive reaction studies in solid solutions.

NEW TECHNIQUES

The possibility of carrying out spectroscopy on increasingly heavy elements depends strongly on the sample requirements for the techniques in use. In this connection the recent development of laser-excitation spectroscopy, with fluorescence or mass-spectrometry detection, promises a dramatic decrease in the amount of sample required. These techniques are so sensitive that it is reasonable to think in terms of extensive studies on 10^{12} atoms (~2 ng) in beams and 10^5 atoms or less in neutral or ion sources. Indeed the recent success in exciting the spectrum of francium atoms recoiling from an accelerator target indicates the ultimate few-atom potential of these methods. Of course the energy of the spectral lines must be reasonably predictable if laser excitation is to be successfully applied, and the progress of general spectroscopic understanding of the actinides will be crucial in this connection.

With these extremely high sensitivities potentially available, laser-excitation spectroscopy should be seriously considered as a detection method in the search for new elements. As the accuracy of spectral prediction improves, the possibility of searching for specific resonance lines of new element atoms or ions should be considered as an adjunct to chemical separations and nuclear detection. The use of a mass detector in the resonant laser-ionization scheme can result in ion implantation of a few to many of the ionized species for retrieval and study. The large isotope shifts of the actinides give scope to laser-isotope separation methods as a way to prepare pure samples of otherwise hard to separate materials for spectroscopic study.

MATERIAL AND FACILITY REQUIREMENTS

To perform most of the spectroscopic studies outlined here and in Appendix G, the products of the HFIR and TRU are required either as samples or as starting materials for synthesizing new elements or isotopes. For the former purpose, the elements ^{249}Bk, ^{250}Cf, ^{251}Cf, ^{253}Es, ^{254}Es, and ^{257}Fm are uniquely available from the HFIR/TRU. Present optical spectroscopy techniques have been successfully used with samples as small as 50 μg. Five hundred μg are preferred for thorough emission-spectral studies of each element. Ionization energies have been determined on 500 mg samples using laser-spectroscopy techniques. Beam-source developments will have to result in the reduction of the required sample size by orders of magnitude in order to permit the extension of these studies to einsteinium and beyond.

Existing laboratories equipped for investigation of laser-isotope separation parameters (and certain other laser facilities) contain most of the equipment necessary for ionization-energy, hyperfine-structure, and isotope-shift measurements. The cost of one such facility (excluding buildings) is about $500,000. Operating charges for building space alone are at least $200,000 per year. Currently these facilities are fully committed to laser-isotope separation and will be for about 2 or more yr, and their future commitment is unknown. Moreover, there is no firm manpower commitment at these facilities for investigations of the heavier actinides. (Less than 10 percent of laboratory manpower for these facilities, or about 1.5 man-years, was committed to studies of the lanthanides and Np[1] over a 6-yr period.) Certainly more support for manpower and for the facilities (or like facilities) is required if the ionization energies and high-resolution hyperfine-structure studies are to be extended to the heavier actinides. Development of efficient beam sources and facilities to convert the higher actinides to metals will be needed as well.

In the field of optical-emission spectroscopy there has been a marked decrease in the number of workers and in financial support for energy-level analyses of the actinide elements. Successful analysis of presently observed spectra and observation of spectra beyond einsteinium will require new manpower and support commitments.

Advances in observation techniques, especially large Fourier transform spectrometers, allow improvements of about a factor of 10 in wavenumber (energy) accuracy and vast improvement in determination of relative line intensity. For investigation of the transplutonium elements there is a clear need for a facility consisting of a high-resolution Fourier transform spectrometer and heavy-element handling capabilities.

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5

SOLID-STATE PHYSICS AND CHEMISTRY OF THE TRANSPLUTONIUM ELEMENTS

INTRODUCTION

The central issue in the solid-state science of the actinides is the quantum mechanics of the 5f electrons and the roles they play in binding energy, thermodynamics and phase stability, electronic structure, and collective states of actinide solids. In the early part of the actinide series the 5f electrons are located largely outside the atomic core and change their character to less extended states only after plutonium. They thereby give rise to many important effects that are less evident for the lanthanide elements and the transition elements but that are nevertheless extremely important to their chemical and physical properties. Moreover, the character of the 5f electrons can be affected by their contact with adjacent atoms in the solid, by pressure, by temperature, and by the formation of dilute solutions, alloys, and compounds.

Research on the actinides is important, not only for its intrinsic scientific interest but also for the light it throws on solid-state science in other parts of the periodic table.

The most important issue this panel has addressed is how far along the actinide series beyond plutonium it is feasible, necessary, and worthwhile to go in order to discover the essential experimental facts about 5f electron behavior in solids.

In the formation of a solid, free atoms are brought close to each other, and the discrete energy levels of the outer electrons broaden into bands. Because of the large radial extent of the d-electron wave function in transition elements, the d-electrons hybridize with the s- and p-electrons to form a relatively broad conduction band, and the localized atomic character of the d-electrons is generally considered to be lost in metallic solids. At the other extreme, in the lanthanides other than cerium the 4f electrons are localized with the maxima in radial charge density occurring well inside the usual interatomic distances in solids. Thus, atomic-like 4f-electron behavior is retained in metallic as well as in ionic lanthanide solids. The only rare-earth metal that does not fit this picture is cerium, where the 4f level is not yet fully stabilized. For the early part of the actinide series the 5f electrons have a greater radial extent than their 4f counterparts, with the result that they influence to a much greater extent the coupling of neighboring atoms and the solid-state properties.

As the nuclear charge increases along the series for a given oxidation state, the fact that the 5f electrons remain outside the core means that the 6d and 7s electrons experience a greater nuclear attraction due to imperfect shielding. This results in contraction of the atomic radius, which is reversed only when the 5f electrons are localized into the atomic core beyond plutonium. The effects of this actinide contraction are clearly shown in the properties of the actinide metals that begin as f-bonding d-like transition metals and cross over to localized f-electron lanthanide-like behavior at americium (see Figure 1); this is the reason why the actinides were not recognized as a second f-transition series until the discovery of the transuranium elements. The chemistry of conducting compounds is not understood well enough to assert that the crossover occurs at the same place as in the elements or to know whether the crossover is affected by the ligand atoms. This is an instructive example of the importance of understanding the systematics of extended series of elements in the periodic table.

In the crossover regions (for the actinide elements from uranium to curium and beyond, and for the lanthanides the isolated element cerium), the energies and wave functions of the outer 4f or 5f electrons are in delicate balance. Small perturbations can therefore cause transfer of electrons from localized f states to itinerant band states and vice versa. Thus, the solid can be made to exhibit a richness of solid-state phenomena not seen so vividly and in such variety in other regions of the periodic table. These include unusual crystal structures; unusual

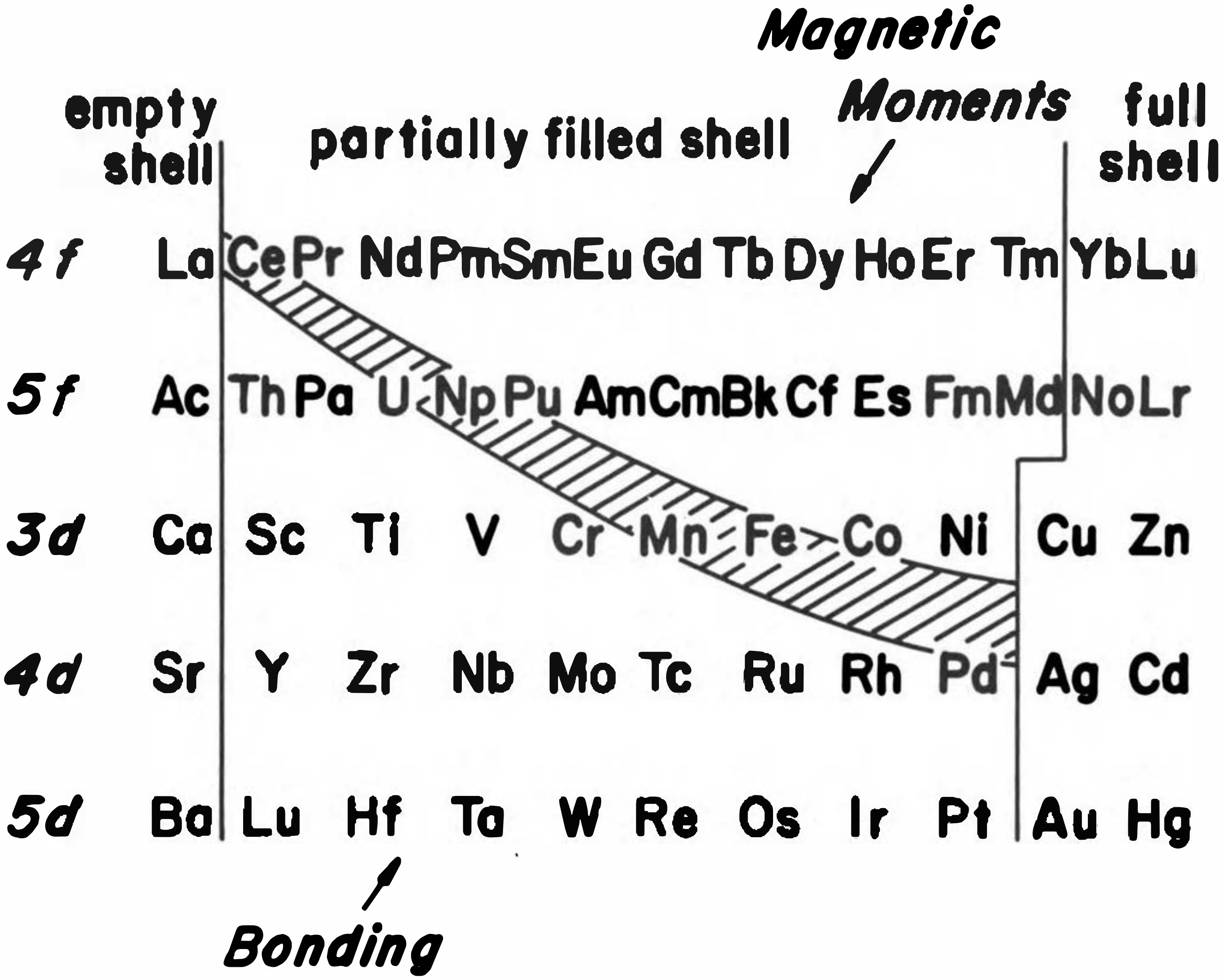

FIGURE 1. A nearly periodic table of transition metals showing the crossover to localized d- and f-electron behavior.

mechanical and thermodynamic properties; a wide variety of valence states; and many collective phenomena such as magnetism, superconductivity, and valence fluctuation in forms that contrast in important ways with the same phenomena as they occur with the transition elements and lanthanides (see Figure 2). The electron theory of solids is currently not capable of accounting in detail for all these behaviors. Successful development of a theory that can accurately describe the electronic structure of the actinide solids in the crossover region is an important goal of solid-state physics since the resultant theory should throw light on the behavior of crystalline solids formed by all the elements in the periodic table. Thus, experimental and theoretical research performed to obtain a better understanding of the diverse phenomena exhibited by the actinide elements and compounds in the crossover region is indispensable for the development of the general electron theory of solids. Confirmation of the mid-series transition to localized 5f behavior can be supported only by experiments on materials containing the heavier elements, i.e., curium, berkelium, and californium.

Understanding the diverse physical and chemical properties of plutonium and the other actinides in the crossover region and its immediate vicinity not only provides valuable insights into the necessary elements of a unified electron theory of solids but also contributes to a deeper understanding of the unique properties of plutonium as well as of uranium that are of critical importance to nuclear applications.

SOLID-STATE PHYSICS

The experimentally obvious change from metallic 5f bonding into local-moment, nonbonding configurations taking place between plutonium and americium is a unique situation in the periodic table and is at the very heart of the basic understanding of electronic structure--i.e., how atomic levels develop into extended states in a solid. To pinpoint both how this transition takes place and what specific factors determine the changeover from one behavior to the other is, then, not only a question about actinide electronic structure but also one about electronic

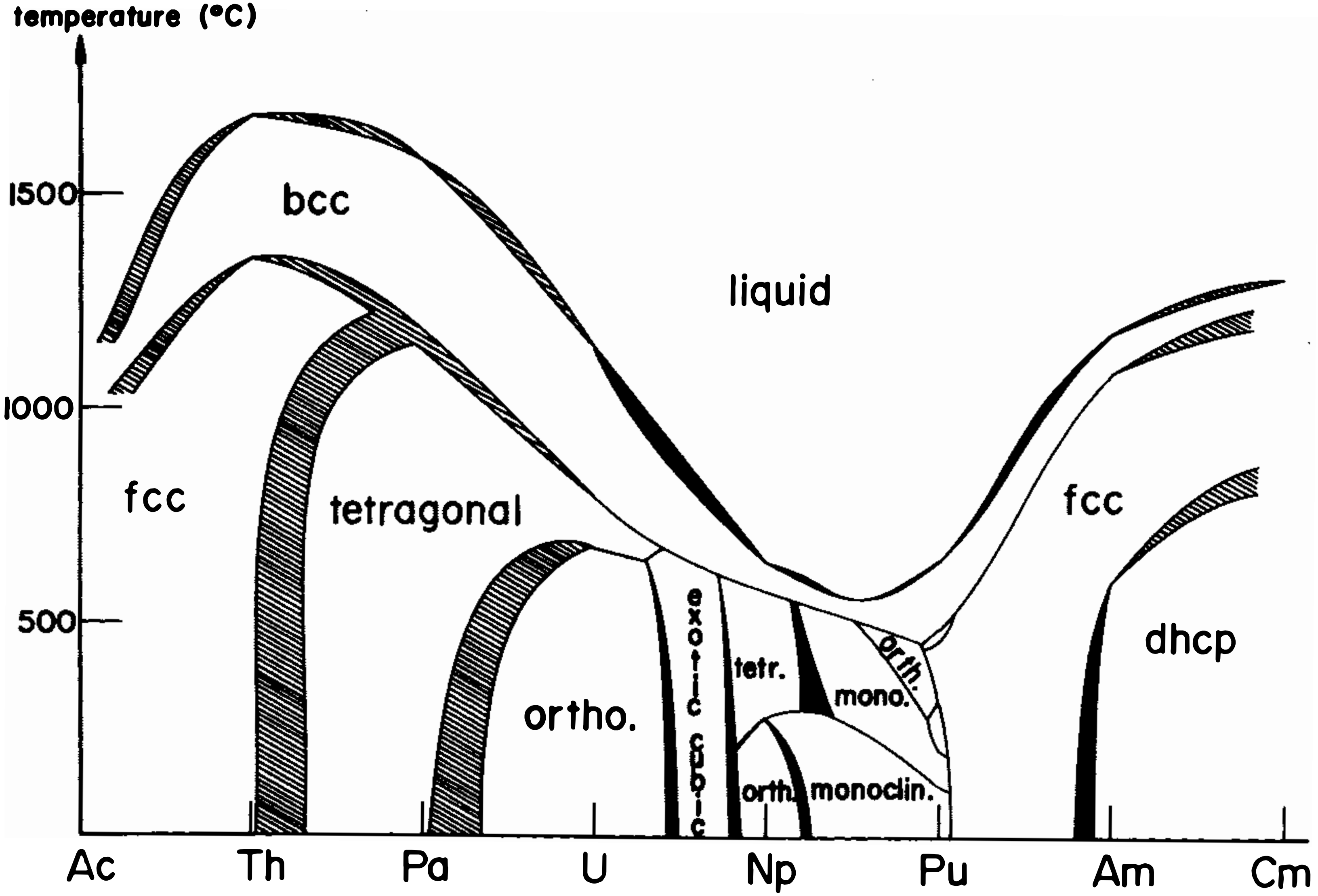

FIGURE 2. Schematic binary alloy phase diagram of the actinides showing the crossover region.

structure in general. Thus, every means available to investigate this crossover region should be applied, and high-pressure experiments in particular are especially appropriate. To make the most of such research it is important that the ranges before and after the transition region are well characterized and understood. It is in this respect that investigations of the transplutonium elements find their importance, since their physical properties serve as a reference for behavior outside the critical range.

Present data suggest that transamericium metals behave most like the lanthanides. The room-temperature crystal structure for the metals from Am to Cf is double-hexagonal close packed (dhcp), as it is for the light lanthanides. For a complete analogy with the lanthanides there should be an actinide body-centered cubic (bcc) phase before melting. This is currently neither confirmed nor disproved. Furthermore, present data seem to show a significant decrease in melting temperature between curium and berkelium, which, if correct, could reflect an unexplained transition region. More research is needed.

With pressure, americium metal changes structure from dhcp to face-centered cubic (fcc). This transition also occurs for the early lanthanides. Studies of curium, berkelium, and californium metals will show whether this is also a general characteristic for the heavier actinides. Furthermore, it has recently been shown that the lanthanides at still higher pressures undergo a transition to a distorted fcc phase. This possibility should be explored for the actinides, since it will show in detail to what extent the heavier actinides can be regarded as a second lanthanide series.

The fact that americium metal is trivalent instead of being divalent, like its corresponding lanthanide-element europium, will help explain why europium and yttberium are divalent, an aspect that can be clarified in great detail by studies of the heavier actinides. Since the f-d separation increases onward from berkelium, understanding of which element first becomes a divalent metal provides an assessment of the critical f-d separation necessary for an actinide to exhibit a divalent state. Present data indicate that this occurs between californium and einsteinium, which makes high-pressure studies of einsteinium particularly interesting, since even very small compressions should induce a transition to a trivalent metal. Extremely interesting is the possibility that this valence change might proceed via an intermediate valence state involving fluctuation between f^{11} and f^{10} configurations, something never encountered among the rare earth metals. Chemical manipulation could also bring californium into a mixed-valence state (between f^{10} and f^{9}), again a completely new situation. Such studies could have a great impact on our understanding of the mixed-valence phenomenon.

Similarly, it is possible that berkelium under pressure may show a valence transition from three to four. For terbium, its corresponding element among the rare earths, no such transition has ever been observed. Once more, this may involve the possibility of a mixed-valence state between f^{7} and f^{8}, with no correspondence among the lanthanides. For intermetallic compounds of berkelium with heavy 4d-transition elements there is, once more, a possibility for a valence change. At still higher pressures elemental berkelium should transform into a metallic 5f state, i.e., be forced into the itinerant 5f regime.

It seems clear that critical f-d separations for valence change are concentrated in the elements following plutonium, i.e., those elements that can be made in sufficient amounts for solid-state investigations with the presently available reactor techniques. Studies of these elements will provide detailed information about the relation between electronic structure and crystal structure, which is a central question in solid-state physics. Furthermore, a wide variety of electronic transitions are expected and they should have unique features. Extensions into surface studies of these elements should be illuminating, since atoms in the selvage region can be expected to reconstruct and exhibit electronic changes of state. Californium is a candidate element for such an electronic transition.

Magnetic ordering for the transplutonium elements promises to be most interesting since the Ruderman-Kittel-Kasuya-Yosida (RKKY) parameters will be different from those for the corresponding lanthanide elements. The fact that Am^{3+} ($5f^{6}$) has zero angular momentum ($J = 0$) in its ground-state multiplets makes it difficult to take advantage of the magnetic properties as a sensitive probe for seeing any change in 5f electronic behavior on the heavy side of plutonium. This means that any confirmation of a model of plutonium 5f electronic behavior based on the behavior of heavier elements calls for work on curium, which fortunately also has the virtue of having long-lived isotopes (especially ^{248}Cm).

The first round of experiments on curium and curium compounds would be magnetic susceptibility and high-field magnetization measurements. One would probably proceed by looking at a family of compounds, such as the monopnictides or sulfides, in addition to pure curium. Susceptibility measurements are of interest to see if the Curie-Weiss law gives a paramagnetic moment with gadolinium-like behavior. Existing measurements do not define this to better than 10 percent. These measurements could be performed on polycrystalline ^{244}Cm, but high-field measurements of magnetization on single crystals would be more definitive. This is because the anisotropy that might be shown in such experiments is very characteristic of the degree of localization of the 5f electrons (PuSb, for example, shows behavior remarkably similar to CeSb and CeBi). For these experiments one would want to have ^{248}Cm available because the anisotropy must be measured at liquid-helium temperatures along with other properties, such as specific heat. To carry out experiments on a family of compounds, requires single crystals of about 20 mg each, and therefore a total requirement of 200 mg of ^{248}Cm, one year's total output, to grow the crystals needed for a single family of compounds, such as the monopnictides. In addition, pressure experiments are extremely valuable for exploring the 5f-localization question. The same crystals used for magnetic measurements can be used for X-ray diffraction studies of structural changes and for conductivity measurements under pressure to observe changes associated with increased delocalization.

The early actinide materials through plutonium are most unusual in their mechanical properties, having a large number of low-symmetry structures. Studies of americium by ultrasonic and heat-capacity measurements of sound velocity and by other techniques, such as photoacoustic absorption, can be used to see if it has returned to "normal" behavior.

Regarding equilibrium behavior, elastic neutron-scattering experiments to observe magnetic structure are an important class of experiments valuable for confirming particular models of 5f behavior. These experiments can also be done with samples of the size described above. However, inelastic neutron-scattering experiments to observe dynamic behavior are much more demanding on sample size. Minimal material demand for inelastic neutron-scattering experiments is single crystal material containing at least 500 mg of ^{248}Cm, for one compound. A strong argument for interest in these experiments rests on existing research on excitation spectra of the uranium monopnictides. Both the dispersion and relaxation behavior of those materials are exceedingly unusual. The very strong relaxation broadening observed is probably characteristic of the localization of the 5f electrons in the atom core. It will be important to see if this phenomenon disappears at curium. The phonon spectrum would be obtained as a bonus of inelastic neutron-scattering.

The techniques of photoemission spectroscopy (such as XPS, UPS, ARPES, CIS, CFS, BIS, and resonant photoemission, which can all be performed with a synchrotron light source) can be applied to transplutonium elements to obtain direct information about the electronic structure. Information about the occupied and unoccupied electronic density of states, electronic-band structure, mixed valency, and hybridization of f electrons with other conduction electrons can be obtained with milligram-size samples. The effects of self-radiation damage on the sample is not critical, and the interference of daughter products in short half-life isotopes can be tolerated in these experiments. The logical experiments to perform now are the determination of total density of states for the transplutonium metals, Am, Cm, Bk, and Cf. The localization of the 5f electron and the amount of hybridization of 5f electrons with other conduction electrons can be determined under favorable conditions. These experiments will be important for a full understanding of the point along the transplutonium-element series where the 5f electrons first behave like 4f electrons in lanthanides. The possibility of a divalent surface on Cf metal similar to that found in the rare-earth series on Sm can easily be investigated. Stability of actinide monoxide (especially in the heavy actinides) can be studied by photoemission techniques. The valence state of metallic transplutonium elements can also be studied by the relatively new techniques of heavy-ion fluorescence spectroscopy and electron energy-loss spectroscopy. Here again small, thin film samples can be used. Another microscopic technique, X-ray absorption spectroscopy (both XANES and EXAFS), can be applied to study the valence state, local atomic coordination, and near-neighbor vibrational properties in small crystalline and amorphous solid samples of transplutonium elements.

SOLID-STATE CHEMISTRY

Introduction

Studies of metals and compounds of the transplutonium elements offer a number of opportunities for establishing principles that will be transferable to other parts of the periodic table. The occurrence of relatively localized 5f electrons close to the Fermi level, characteristic of the transplutonium elements, offers extraordinary opportunities not found in the heavy lanthanides where the 4f levels are more deeply buried. Examples include berkelium (f level < 2 eV), a prime candidate for a cerium-type collapse under pressure, and californium, whose metal properties mimic samarium and for which both trivalent and divalent states have been observed. A collapse in berkelium would be especially attractive in that high-symmetry structures should be encountered, which would simplify the experimental work. Only the metals have been considered to date; the f levels in compounds are not known, and the chemistry is therefore undetermined and needed.

Metals

Although appreciable experimental data have been acquired for the transplutonium metals, significant questions still exist about their systematics as a function of atomic number. Two examples are the melting points and phase behavior. The sharp drop in melting point observed for the transcurium metals is not consistent with the gradual increase in melting points for the lanthanide metals (excluding divalent europium and ytterbium). Although the values for californium and einsteinium metals can be rationalized by the onset and final attainment of divalency, the reason for the lower melting point of berkelium is not clear. The first step should be the confirmation of the melting points for these metals. Furthermore, the phase behavior of these metals needs additional investigation. The apparent substitution, or addition, of a fcc "high-temperature" phase for the actinides, as opposed to the bcc phase of comparable lanthanide metals, has significant implications for comparing the 4f–5f bonding.

Alloy studies offer opportunities for modifying crystal structures and valencies. In the lanthanides the initial dhcp structures pass through the α-Sm structure before forming hcp metals beginning at gadolinium. The α-U structure has been found in cerium and americium and, recently, in praseodymium under pressure. The details of the correspondence of various structures between the lanthanides and actinides is not yet completely clear. Yet the unique structures in these two series offer the possibility of understanding how rather small changes of electronic structure can influence such crystal structures. A first step would be to alloy yttrium or heavy lanthanides with curium to obtain the α-Sm structure (or an actinide equivalent). This could be begun with Cm on a milligram scale and followed with other appropriate actinides at both ambient and high pressures. Since the α-U structure in praseodymium has only recently been observed, there are opportunities in both f series for alloy studies, including application of pressure.

Although californium remains trivalent in the divalent host europium, einsteinium, which has recently been shown to be a divalent metal, could possibly become trivalent in a trivalent host. Similarly, americium or berkelium could form compounds with noble metals that would force them to be tetravalent in the metallic state, something that does not occur in the lanthanides. Alloys with heavy actinides offer a possibility to alter valence in metallic systems to an extent not seen before.

Compounds

Principal examples of compounds currently known for the transplutonium elements are as follows:

Am, Cm	Bk, Cf, Es
3^+ and 4^+ oxides and halides; pnictides and chalcogenides; Am dihalides except for the fluoride	3^+ oxides and halides; BkF_4, CfF_4, BkO_2, Cf and Es dihalides except for the fluorides; some chalcogenides and pnictides (Bk, Cf)

Generally, the basic properties (such as X-ray structures) are known and fragmentary thermodynamic data are available. Vapor-pressure studies have been made on all the metals through Es and on the Cm oxides.

The following studies involving synthesis and characterization of various compounds should be undertaken to map out the rudiments of the solid-state chemistry of the transplutonium elements:

o Reactions of most of the trivalent compounds (or where known divalent) with their respective metals should be investigated in order to examine the possible formation of new metallic compounds with an oxidation state of two or below. This is an unexplored region for which the results cannot be well predicted; analogies with either the lanthanides or the transition (d) elements would yield quite different results.

o Metallic oxides and sulfides such as AmO, CfS, and EsO are of interest for possible valence fluctuations and better characterization of the divalent state. These particular compounds would clarify the oxidation-state relationships with lanthanides.

o Americium and curium hydrides have been investigated. More work is necessary on the transcurium hydrides to determine whether they are similar to those of the lanthanides. Einsteinium(II) dihydride is particularly interesting because Es metal is divalent, as are Eu and Yb metals that form salt-like dihydrides, whereas the analogous HoH_2 is metallic. This comparison also applies to EsS. These are extremely difficult experiments.

- At least four types of carbides have been reported for the lanthanides, but except for some Am carbide data nothing is available for the trans-Pu elements.

- An important but incompletely understood high-energy permanent-magnet material which forms the basis of a small but rapidly growing business, $SmCo_5$ is a member of a class of intermetallic compounds represented as RCo_5, where R is a rare earth. The coupling systematics of the RCo_5 family are clear: ferromagnetic for light rare earths and ferrimagnetic for heavy rare earths. Improved understanding of the nature of the exchange that generates these coupling systematics is a significant undertaking since this underlies the utility of $SmCo_5$.

It is of considerable interest to ascertain whether the coupling systematics of the RCo_5 and $AnCo_5$ are the same. Synthesis and magnetic studies of the $AnCo_5$ systems should be undertaken, as these might well prove useful in providing an improved understanding of exchange in RCo_5 systems. There is special interest in two compounds of the $AnCo_5$ series: $PuCo_5$ and $CfCo_5$. If because of the separation of Pu atoms in $PuCo_5$ the 5f electrons of Pu are localized, Pu is the electronic counterpart of Sm. If the 5f electrons remain delocalized in $PuCo_5$, Cf might prove to be the analog of Sm. Studies of magnetic anisotropy of $AnCo_5$ compounds may prove useful in elucidating the truly extraordinary magnetic anisotropy of $SmCo_5$.

- The higher oxidation states of Am are well characterized (except for the Soviet report of the 7+ state which needs to be verified). Compounds involving Cm(V), Cm(VI), Bk(V), and Cf(V) need to be explored as ternary fluorides and oxides, a known way of stabilizing higher oxidation states. To date, Es(IV) is not known from a macroscopic experiment. The oxidation states of 5+ or above are unique for an f-element series, and any series of compounds 4+ or above would provide a valuable comparison.

- The nearness of the 5f band to the Fermi level in the metals indicates that the application of pressure should lead to an increase in valence of metals or to a semiconductor-metal transition, perhaps quite generally. Californium(II) sulfide and AmI_2 are obvious candidates for the latter, analogous to SmSe and NdI_2 in the lanthanides, where the transformation is relatively rare.

- Generally, transplutonium materials should be characterized by the determination of structures, magnetic and optical properties, conductivity, and thermodynamic and phase relationships. Anomalous results should be carefully examined to determine whether they originate with experimental problems, e.g., the recent reports of temperature-dependent magnetic susceptibility for the $5f^6$ compounds CmO_2 and CmF_4.

This list is not all-inclusive but is a beginning for the comparison and classification of the solid-state chemistry of these elements relative to the rest of the periodic table.

Heterogeneous Catalysis

Heterogeneous catalysis studies in actinide metals, alloys, or compounds may be unique in that the 5f orbitals determine catalytic properties, in contrast to the other transition metals, where catalysis is a d-electron phenomenon. Thus, there exists the totally new opportunity for an understanding of catalysis in terms of a different electronic system. Catalysis with the early actinides, like the early 3d metals, is greatly affected by the extent of metallic bonding. Therefore, the transplutonium elements and compounds offer the opportunity to study f-electron catalysis with relatively localized f orbitals having energies near the Fermi level. Additionally, the phenomenon of continuously damaged, and therefore highly defect-laden surfaces appears to satisfy some of the prime criteria for successful catalysis. The questions of specificity for these materials and the effects of high-radiation fields have never been addressed.

Thermodynamic Considerations (Solid-State)

The vapor pressures and thermodynamic properties of the elements americium through einsteinium have been determined, and calorimetric studies have been made on the metals through californium. However, the thermodynamic properties of transplutonium alloys and compounds have not been studied, with the exception of the curium-oxygen system. Of particular interest are the oxides, carbides, and perhaps nitrides, which would be the products found in the reprocessing of fuels from high-performance (e.g., fast-breeder or gas-cooled) reactors. An understanding of the relative stabilities of these transplutonium compounds would also come out of thermodynamic studies and would be most helpful in clarifying the stability of earlier actinide compounds.

Single Crystal Growth

Although a number of studies can be successfully carried out on polycrystalline materials, in some instances it is imperative to have single crystals for investigation. Numerous methods have been used for growing single crystals, but only three appear promising for the transplutonium elements, compounds, and alloys: (1) vapor transport in a temperature gradient; (2) growth in a metal solvent with subsequent removal of solvent by etching; and (3) solution growth (e.g., from molten ternary oxides for oxide single crystals). These techniques have the virtues of being adaptable to small amounts of radioactive materials and to the removal of impurities.

THEORY

The central question of solid-state physics is how outer electrons in atoms serve to bond those atoms together so as to form a well-ordered crystalline lattice. The actinides provide the only situation in the periodic table where one can follow a well-defined class of atomic electrons, the 5f electrons, as they change over from localized/nonbonding to delocalized (itinerant/band-like) bonding behavior. The presently accepted view sees this changeover as occurring at plutonium and going from the heavy toward the lighter actinides. Our understanding is not yet at a state where it is known how sharply this transition occurs. Recently, however, theory has made sufficient progress to give hope of fully quantifying this concept. On the practical side, such progress gives promise of understanding the unique structural allotropic forms of elemental plutonium and thereby of enhancing our ability to predict and control stabilization of particular phases through alloying. The occurrence of the transition (localized to delocalized) will depend not only on the particular element being considered, e.g., Pu, Am, or Np, but also on the lattice spacing. Thus, an important task of theory is to relate to changes in behavior within an isostructural family of compounds, e.g., monopnictides, for the same element.

The central aspect of theoretical/calculational capability to carry out this program is the ability to combine state-of-the-art self-consistent relativistic band calculations and model (e.g., Anderson model) calculations, including correlated electron behavior for a lattice.

The nature of intra-atomic electronic correlation depends on the relative importance of relativistic effects, i.e., where the physics lies between the L-S and j-j coupled limits. Very recent self-consistent calculations for an Anderson model involving hybridization of an fcc lattice of $5f^5$ (Pu^{3+}) ions with free-electron bonds shows that magnetic phenomenology can be used as a very sensitive diagnostic tool to recognize the amount of intermediate (between L-S and j-j) coupling. Through hybridization with band electrons as the 5f electrons become delocalized, the intra-atomic correlation affects bonding with neighboring 5f ions and thus determines the choice between competing lattice structures, slightly different in energy. Thus, for the first time, a situation exists in the actinides (centering around the behavior at elemental plutonium) where we might understand how electron correlation effects (i.e., effects beyond one-electron band theories) affect bonding and lattice structures in solids.

To quantify fully this theoretical framework for the changes in bonding, and consequences thereof, as the 5f electrons delocalize, we need self-consistent relativistic band calculations. The reason for relativistic calculations is evident. To treat relativistic effects properly for the 5f electrons as they delocalize, we have to include such effects for the band electrons with which the hybridization occurs. The need for self-consistency in the band calculations results from the requirement for high-quality wave functions for the treatment of bonding and lattice structure.

We note that in treating the electronic behavior of a specific material by use of a hybridization-mediated lattice-coupling model, some aspects of the behavior may depend on specific features of the band behavior. For example, in examining hybridization-mediated magnetic coupling, predicted exchange splitting of bands may be larger than the energy width of the band features dominating the hybridization, giving rise to "nonlinear" hybridization behavior of a characteristic type. Furthermore, judging from the observed behavior of magnetic excitation in uranium metallic compounds (via inelastic neutron scattering), the dynamic behavior tends to "pick out" different parts of the band structure with which important 5f hybridization occurs. For example, in uranium monopnictides a working hypothesis is that the peculiar dispersion observed, e.g., in USb, results from hybridization with anion-derived p bands, while the remarkably strong relaxation effects result from hybridization with uranium-derived d electrons. Thus, a definitive test of the proposed hybridization model calculations, involving mixing of correlated 5f atomic electrons with self-consistent relativistic band electrons, is to predict the excitation behavior and the nature of changeover of this behavior as the 5f electrons localize on going to the elements heavier than plutonium.

LEVEL OF EFFORT IN TRANSPLUTONIUM RESEARCH IN SOLID-STATE PHYSICS AND CHEMISTRY

The panel has made its best estimates of the current level of effort in transplutonium-element research in solid-state physics and chemistry and finds a very serious mismatch between the scientific opportunities perceived in the field and the number of scientists who see actinide physics and chemistry as their major area of research. There are five institutions carrying on research in this field: Lawrence Berkeley Laboratory, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Argonne National Laboratory, and Oak Ridge National Laboratory. Among these 5 institutions we have identified approximately 24 individuals performing transuranium-actinide-element research, and, of these, fewer than one-third are working on transplutonium-element research. The data on financial support for this research area are very sparse, and the best estimate the panel can make is that approximately $1M is spent per year by the U. S. Department of Energy on transplutonium-element research by BES and OMA combined. This is not inconsistent with the small number of identified scientists in this field.

There are 2000 to 4000 active solid-state physicists in the United States, judging by recorded attendance at the major annual meeting devoted to this field, and there are considerably fewer solid-state chemists. Any reasonable appraisal of the scientific opportunities for research on the actinide elements and their potential technological importance compared with solid-state science research in other areas of the periodic table would suggest that a few hundred scientists should be performing research in the field. Our best estimate, therefore, is that the field is underfunded and undermanned by a factor of 10.

PRINCIPAL CONCLUSIONS

Research on the actinide elements is important not only for its intrinsic scientific interest but also for the light it throws on solid-state science in other parts of the periodic table.

Research on the actinide elements is at a more elementary level than corresponding research in other areas of materials science. This lag may represent a cumulative deficit of 10 yr of research. It results from:

o The unavailability, until recently, of transplutonium elements in sufficient quantity.

- A sharp downturn around 1975 in funding of materials science research in the actinide elements.
- The general inconvenience and expense of carrying on research on the actinide elements.

The panel has identified approximately 24 scientists in the United States involved in transuranium solid-state science research, of whom fewer than one-third are involved in transplutonium-element research. In view of the scientific opportunities perceived by the panel, this may be too small by a factor of 10. The small number of scientists involved in transplutonium-element solid-state science research has led to a smaller requirement for supplies of curium-248 and californium-249 than would have been the case if the level of effort in the field had been in better balance with the scientific opportunities.

It is the view of the panel that solid-state science research should be actively pursued beyond americium and curium to berkelium and californium. The reasons for this conclusion are as follows:

- Research on berkelium and californium must be performed to understand fully the distinction between the light and heavy actinide metals and compounds.
- Californium-249 is the last element in the periodic table for which bulk solid-state experiments can be conducted without extraordinary effort.
- Berkelium-249 is available as the parent in the production of californium-249. Similarly, pure curium-248 is available as the daughter of californium-252.

APPENDIX: OTHER USES OF HFIR

The principal and original reason for the construction of the HFIR was the production of isotopes of the heavy elements, but HFIR has since become one of the leading neutron-scattering centers of the western world. Many of the basic problems discussed above, such as localization of f electrons and the competition between superconductivity and magnetism, have been the object of extensive research at the HFIR, utilizing the neutron-scattering facility. Most of the work to date has focused on the rare-earth elements and compounds, but the results have had a major impact on our understanding of the actinides. Although the programs for isotope production and for neutron scattering are separate, the overall value of the HIFR has been greatly enhanced by the neutron-scattering program, and both programs should be considered together in judgments of the HFIR's future.

APPENDIXES

APPENDIX A

Department of Energy
Washington, D.C. 20545

December 20, 1982

Dr. Gerhart Friedlander, Chairman
Workshop on Transplutonium Element Research
c/o Office of Chemistry and Chemical Technology
National Research Council
2101 Constitution Avenue, NW
Washington, DC 20418

Dear Dr. Friedlander:

The advance materials have arrived for the February 27-March 2, 1983 Workshop on Transplutonium Element Research, being sponsored by the Committee on Chemical Sciences and the Subcommittee on Nuclear and Radiochemistry, and it seems appropriate to record in this letter our views on it, including thoughts which we brought to the discussions which led to its being organized.

First, we are greatly pleased that you agreed to chair the Workshop. Your outstanding scientific reputation, insights, objectivity, firmness of purpose and tact bring to it precisely the needed qualities.

Among the areas in which basic research is supported by the Department of Energy, the transplutonium element area has increasingly received special attention because of its high costs relative to those of other areas.

Earlier in the year the Subcommittee on Nuclear and Radiochemistry published the report of "A Review of the Accomplishments and Promise of U.S. Transplutonium Research -- 1940-1981." This presented, thoroughly and competently, the impressive achievements which have been made over the years in this area, including contributions to understanding in neighboring fields. It provided a useful part of the basis for our own review of the same area.

Now the forthcoming Workshop should provide a very useful and timely further step. What we hope for is a distillation of broad, expert views on the importance and future promise of research on the transplutonium elements compared to those of the overall field of chemistry (and related physics). By bringing together experts in transplutonium research and experts in other areas who can be expected to project, in a broad-visioned and objective way, the comparative values of the transplutonium element area, and by organizing their discussions as you have planned, you have provided the basis of a valuable result: a well reasoned placing of this area of research in proper perspective.

We are looking forward to a stimulating and productive Workshop, and to the report issuing from it.

Sincerely,

Elliot S. Pierce, Director
Division of Chemical Sciences
Office of Basic Energy Sciences

cc: Dr. D.C. Hoffman
Dr. J.L. Kinsey
Dr. A. Schriesheim
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APPENDIX B

Workshop on Future Directions in Transplutonium Element Research
February 28 to March 2, 1983

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Panel Organization

Workshop Chairman: Gerhart Friedlander, Brookhaven National Laboratory

Panel 1 Nuclear Reactions and Synthesis of New Species

Chairman: Günter Herrmann, University of Mainz
Rapporteur: Patricia Baisden, Lawrence Livermore Laboratory
Resource Paper: Glenn T. Seaborg, Lawrence Berkeley Laboratory

John M. Alexander, State University of New York
Paul R. Fields, Argonne National Laboratory
Albert Ghiorso, Lawrence Berkeley Laboratory
Richard L. Hahn, Oak Ridge National Laboratory
Darleane C. Hoffman, Los Alamos Scientific Laboratory
E. Kenneth Hulet, Lawrence Livermore National Laboratory

Panel 2 Nuclear Properties of the Transplutonium Elements

Chairman: Joseph Weneser, Brookhaven National Laboratory
Rapporteur: Victor E. Viola, Jr., Indiana University
Resource Paper: Arnold M. Friedman, Argonne National Laboratory
Jerry E. Wilhelmy, Los Alamos Scientific Laboratory

Sven Björnholm, University of Copenhagen
Richard R. Chasman, Argonne National Laboratory
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Jack S. Greenberg, Yale University
Joseph H. Hamilton, Jr., Vanderbilt University
Richard L. Hoff, Lawrence Livermore Laboratory
Herve A. Nifenecker, CENG, France
J. Rayford Nix, Los Alamos Scientific Laboratory

Panel 3 Chemical Properties of the Transplutonium Elements

Chairman: Henry Taube, Stanford University
Rapporteur: Joseph R. Peterson, University of Tennessee
Resource Paper: Gregory R. Choppin, Florida State University
Robert A. Penneman, Los Alamos Scientific Laboratory

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Jesse M. Cleveland, U.S. Geological Survey
Jean Fuger, University de Liege
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O. Lewis Keller, Oak Ridge National Laboratory
Arthur E. Martell, Texas A&M University
Lester R. Morss, Argonne National Laboratory
Werner Müller, European Institute for Transuranium Elements
Thomas W. Newton, Los Alamos Scientific Laboratory
Wallace W. Schultz, Rockwell Hanford Operations
James C. Sullivan, Argonne National Laboratory
Raymond G. Wymer, Oak Ridge National Laboratory

Panel 4 Spectroscopy of the Transplutonium Elements

Chairman: Thomas G. Spiro, Princeton University
Rapporteur: J.P. Young, Oak Ridge National Laboratory
Resource Paper: William T. Carnall, Argonne National Laboratory
John G. Conway, Jr., Lawrence Berkeley Laboratory

Robert G. Cowan, Los Alamos Scientific Laboratory
C. Klixbul Jorgensen, Universite de Geneva
Donald S. McClure, Princeton University
Jack L. Ryan, Battelle Memorial Institute
Earl F. Worden, Jr., Lawrence Livermore Laboratory
William M. Yen, University of Wisconsin

Panel 5 Solid-State Physics and Chemistry of the Transplutonium Elements

Chairman: Albert M. Clogston, Tesuque, New Mexico
Rapporteur: Daniel J. Lam, Argonne National Laboratory
Resource Paper: Norman Edelstein, Lawrence Berkeley Laboratory
James L. Smith, Los Alamos Scientific Laboratory

Bernard R. Cooper, West Virginia University
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Edward F. Janzow, Monsanto Research Corporation
Yosh Maruyama, University of Kentucky Medical Center
Robert B. Pagett, E.I. du Pont de Nemours & Co., Inc.

APPENDIX C

THE OAK RIDGE TRANSPLUTONIUM PRODUCTION PROGRAM*

O. Lewin Keller, Jr.

Oak Ridge National Laboratory

The objective of this Workshop is to determine future directions in transplutonium elements research to be emphasized over the next few years. As part of the background for achieving this objective, an outline is presented in this paper of the budgetary, organizational, and production support structure that exists today for work in this area. A brief glimpse is also given into some of the motivations and developments of the past that caused the production facilities to be built.

As is well known, quite often in the history of science, the invention of a new device or technique or a fundamental scientific discovery will dictate new directions and spawn still newer discoveries. As an example (Table 1), it is worthwhile to trace the discoveries of neptunium and plutonium, the first of the transuranium elements, from their beginnings in the invention of the cyclotron by Ernest Lawrence, the discovery of the neutron by Sir James Chadwick, and the discovery of artificial radioactivity by the Joliot-Curies. The work of Enrico Fermi is particularly interesting in this regard because he thought that the nuclear reactions he was inducing with neutrons were producing new transuranium elements. Otto Hahn showed that actually Fermi was producing a new type of nuclear reaction called fission. Finally, in 1940, McMillan and Abelson bombarded uranium with neutrons, furnished by the Berkeley

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*Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

60-inch cyclotron, to discover neptunium. Seaborg, McMillan, and co-workers used the same cyclotron to discover plutonium.

TABLE 1

KEY STEPS TO THE DISCOVERY OF TRANSURANIUM ELEMENTS

Discovery	Discoverer	Year of Nobel Prize
Cyclotron	Ernest Lawrence (U.S.)	1939 (Physics)
Neutron	Sir James Chadwick (England)	1935 (Physics)
Artificial Radioactivity	Irene and Frederic Joliot-Curie (France)	1935 (Chemistry)
Neutron Induced Nuclear Reactions	Enrico Fermi (Italy)	1938 (Physics)
Nuclear Fission	Otto Hahn (Germany)	1944 (Chemistry)
Transuranium Elements	Edwin McMillan (U.S.) Glenn Seaborg (U.S.)	1951 (Chemistry)

Similarly, new theoretical developments in nuclear and solid state physics, the recent addition in a number of countries of heavy ion accelerator capabilities, and other new additions of instrumentation and technique can be suggestive for this Workshop for promising avenues in chemistry, physics, medicine, and industry for transplutonium research.

The international character of nuclear chemistry and physics, as illustrated by Table 1, dictates that these new avenues will continue to be developed on a worldwide basis. For example, the recent discovery of element 109 by German scientists at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt brings the number of known elements to 108 — 45 more than the 63 known in 1869 when Mendeleev announced the first periodic table. The periodic table of today (Fig. 1) contains much more basic chemical and physical information than Mendeleev's, because the 45 new elements that have been discovered since 1869 contain the whole family of the noble gases, most of the lanthanides and actinides, and a new transactinide series, each with their own unique electronic configurations and familial chemical properties. This is a good time to have this Workshop because the discovery of element 109 gives renewed hope that the periodic table will be further extended into the eka-platinum (Z = 110) through eka-radium (Z = 120) region through the added stability predicted for magic nuclei in that part of the chart of the nuclides. On the basis of current theory, it thus appears reasonable to believe that the approximately 150 isotopes now known in the transplutonium region (Fig. 2) may be joined by some of still higher atomic number in the "superheavy" region of $Z = 110\text{-}120$ and $N \cong 184$.

In the early 1930's, the periodic table contained 88 elements, 25 more than the original table, and it was universally accepted that any new elements that might be discovered would be members of a 6d series (Fig. 3). The discovery of plutonium and its production on an industrial scale in World War II were to change this perception. In the latter days of the wartime Manhattan Project, Seaborg, Ghiorso, and co-workers discovered americium and curium using Seaborg's newly devised actinide concept to develop the requisite chemistry for the separation of these new elements from the targets. The actinide concept was first known only inside the classified Manhattan Project where it was received with great skepticism. In Seaborg's periodic table of 1945 (Fig. 4), he boldly moved uranium, protactinium, and thorium from their long accustomed places to the new actinide series then populated also by

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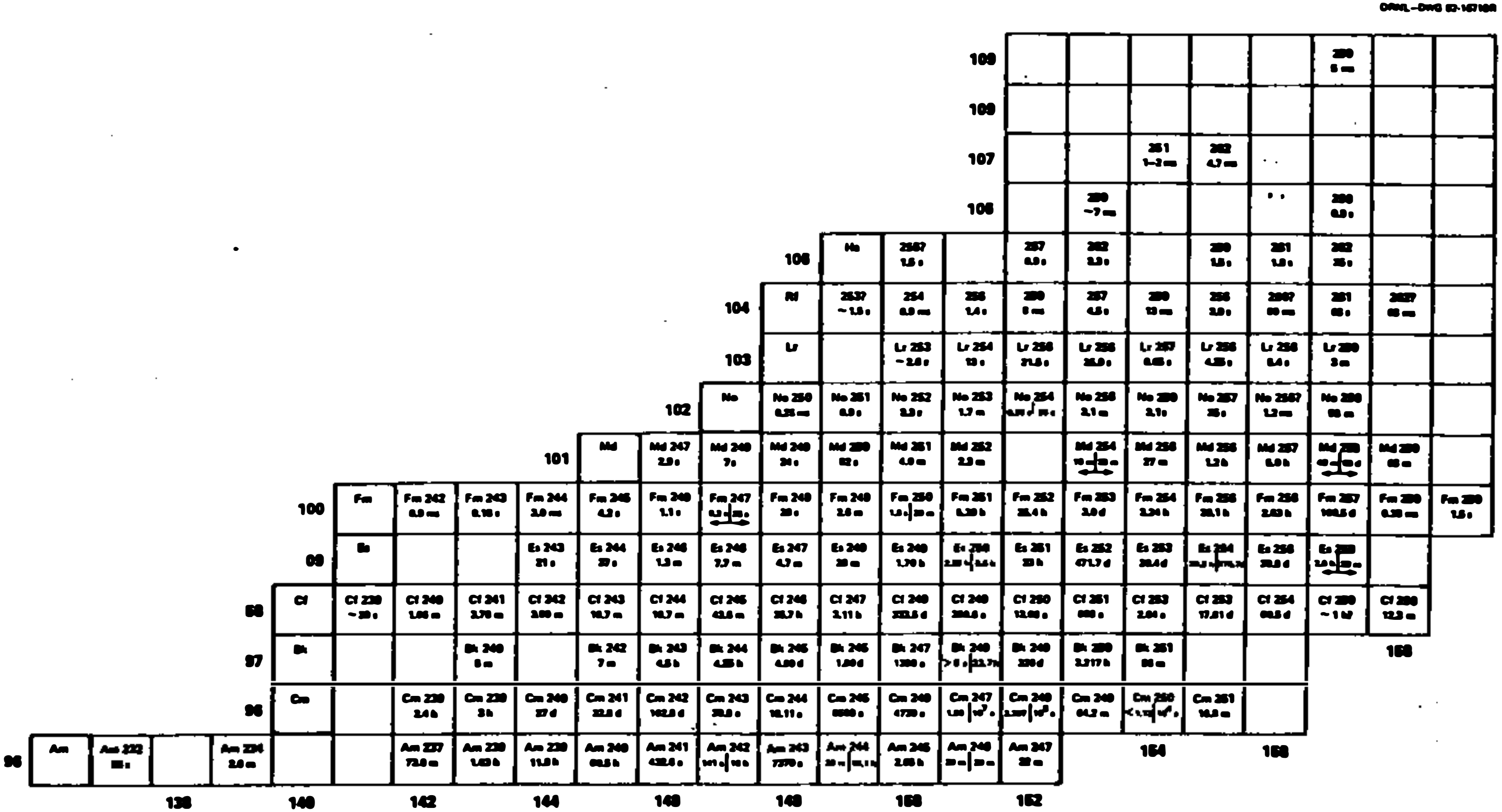
IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIA	VIIIA	IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIII
H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Rf 104	Ha 105	106	107	(108)	109	(110)	(111)	(112)	(113)	(114)	(115)	(116)	(117)	(118)

LANTHANIDE SERIES	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
ACTINIDE SERIES	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

Figure 1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108
107
106
105
104
103
102
101
100
99
98
97
96
95
Md
No
Lr
Rf
Ha
Fm
Es
Cf
Bk
Cm
Am
138
140
142
144
146
148
150
152
154
156
158

Figure 2

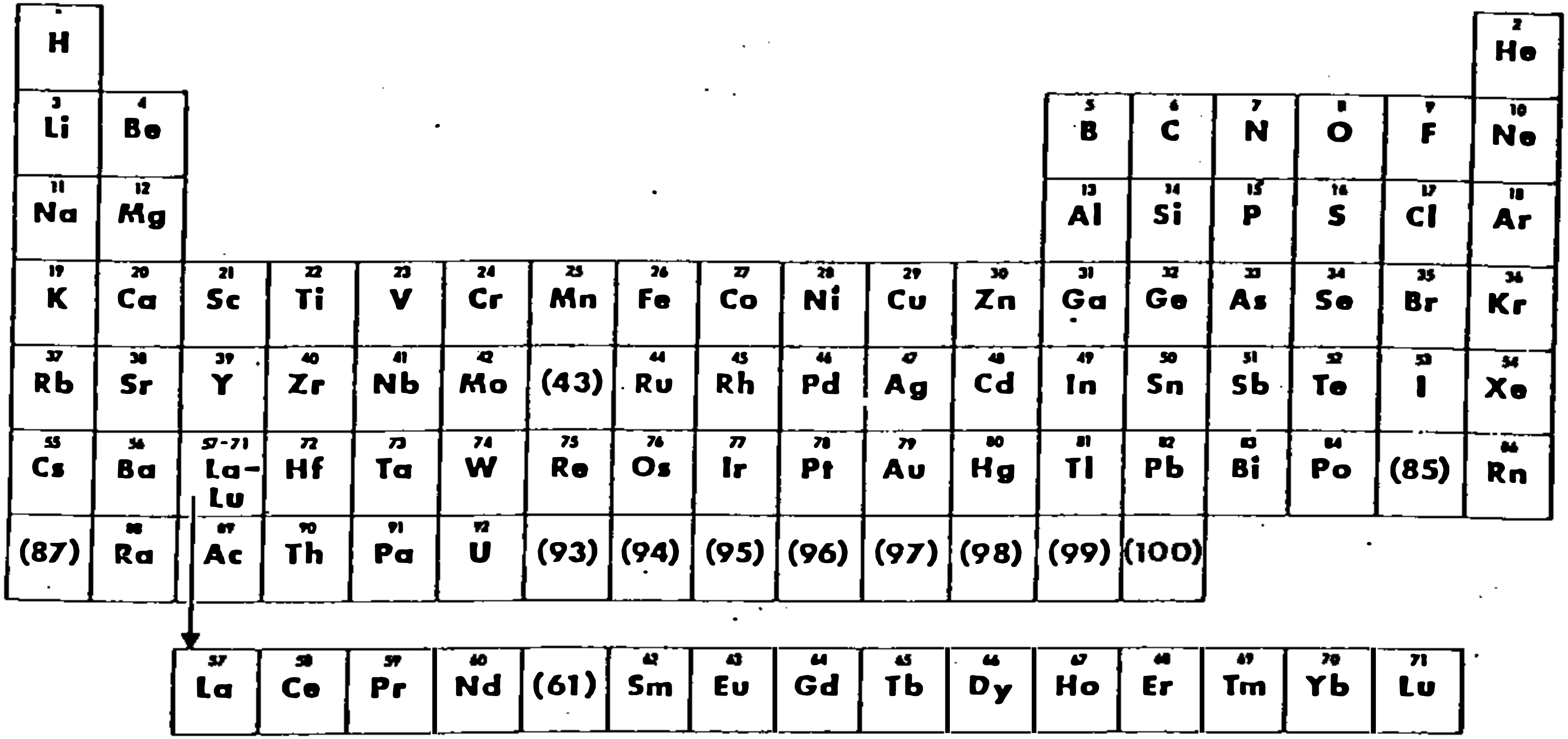

H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
(43)
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
57-71 La–Lu
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
(85)
86 Rn
(87)
88 Ra
89 Ac
90 Th
91 Pa
92 U
(93)
(94)
(95)
(96)
(97)
(98)
(99)
(100)
57 La
58 Ce
59 Pr
60 Nd
(61)
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu

Figure 3

ORNL–DWG 83-9515

PERIODIC TABLE SHOWING HEAVY ELEMENTS AS MEMBERS OF AN ACTINIDE SERIES

Arrangement by Glenn T. Seaborg

1945

1 H 1.008																1 H 1.008	2 He 4.003
3 Li 6.940	4 Be 9.02											5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.997	12 Mg 24.32	13 Al 26.97										13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 A 39.944
19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 Xe 131.3
55 Cs 132.91	56 Ba 137.36	57 La 138.92 58-71 see La series	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po	85	86 Rn 222
87	88 Ra	89 Ac see Ac series	90 Th	91 Pa	92 U	93 Np	94 Pu	95	96								

LANTHANIDE SERIES	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99
ACTINIDE SERIES	89 Ac	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np 237	94 Pu	95	96							

Figure 4

neptunium and plutonium. One of the major motivations for many years in the pursuit of transuranium research was to experimentally verify the actinide concept. This concept today continues to give a useful framework for current and future research as it has in the past. After the discovery of americium and curium, Seaborg and his co-workers continued to discover more new elements which, in addition to their chemical importance as actinides, also gave a unique opportunity to study spontaneous fission. In the pursuit of investigations in various of these nuclear and chemical areas, it became apparent that the production of larger amounts of the more stable isotopes of curium, berkelium, californium, einsteinium, and fermium was needed if rapid and reliable research was to proceed. These isotopes were needed for chemical and nuclear studies and as targets for the discovery of new elements and isotopes at accelerators. Also, the discovery of californium-252, the strong neutron emitter, demanded its exploration for applications in cancer therapy and industry. It was in this atmosphere (Table 2) that the concept of a major transplutonium element production facility was born, and the reactor and chemical processing facilities were constructed in Oak Ridge in the 1960's for this purpose.

TABLE 2

SOME MOTIVATIONS FOR BUILDING HFIR/TRU

1. New Element Discovery
2. Proof of Actinide Concept
3. Spontaneous Fission Research
4. Medical and Industrial Applications of Californium-252 as a Neutron Source

First of all, a reactor producing a very high neutron flux was needed in order to produce reasonable quantities of isotopes from curium-248 through fermium-257 (Fig. 5). The path up from the target element plutonium involves neutron capture to increase the mass (A) alternating with β-decay to increase the atomic number (Z). For example, the very high neutron flux allows the production from curium-244 of curium-249, which then β-decays to berkelium-249 and so on. After fermium-257, the half-life for decay by spontaneous fission is so unfavorable that no further elements can be produced by neutron irradiation in this manner and resort must be made to accelerators. For example, elements 104-106 were discovered at Berkeley using californium-249 targets from the Oak Ridge facility and beams from their Heavy Ion Linear Accelerator.

The High Flux Isotope Reactor (HFIR) is a light water moderated reactor using 93% enriched uranium-235 as a fuel (Fig. 6 and Table 3). The target rods in HFIR now contain not only plutonium but also the higher Z elements americium and curium after many cycles of irradiation, so the HFIR today is more efficient than in earlier years for production of the heavier elements.

Also, HFIR's reliability is an important plus to the research community. Since achieving full power in 1966, HFIR has operated more than 90% of the time. The original cost of HFIR was $14,718,000.

The targets for the production of the transuranium elements are fabricated for HFIR in a special chemical processing plant called TRU (Transuranium Processing Plant) (Table 4). It is here also that the highly irradiated HFIR targets are processed and the transplutonium elements are separated, purified, and distributed to the research community. The Transuranium Processing Plant is the only facility of its kind in the world that has been capable of carrying out its very difficult mission. Its original cost was $8,818,000.

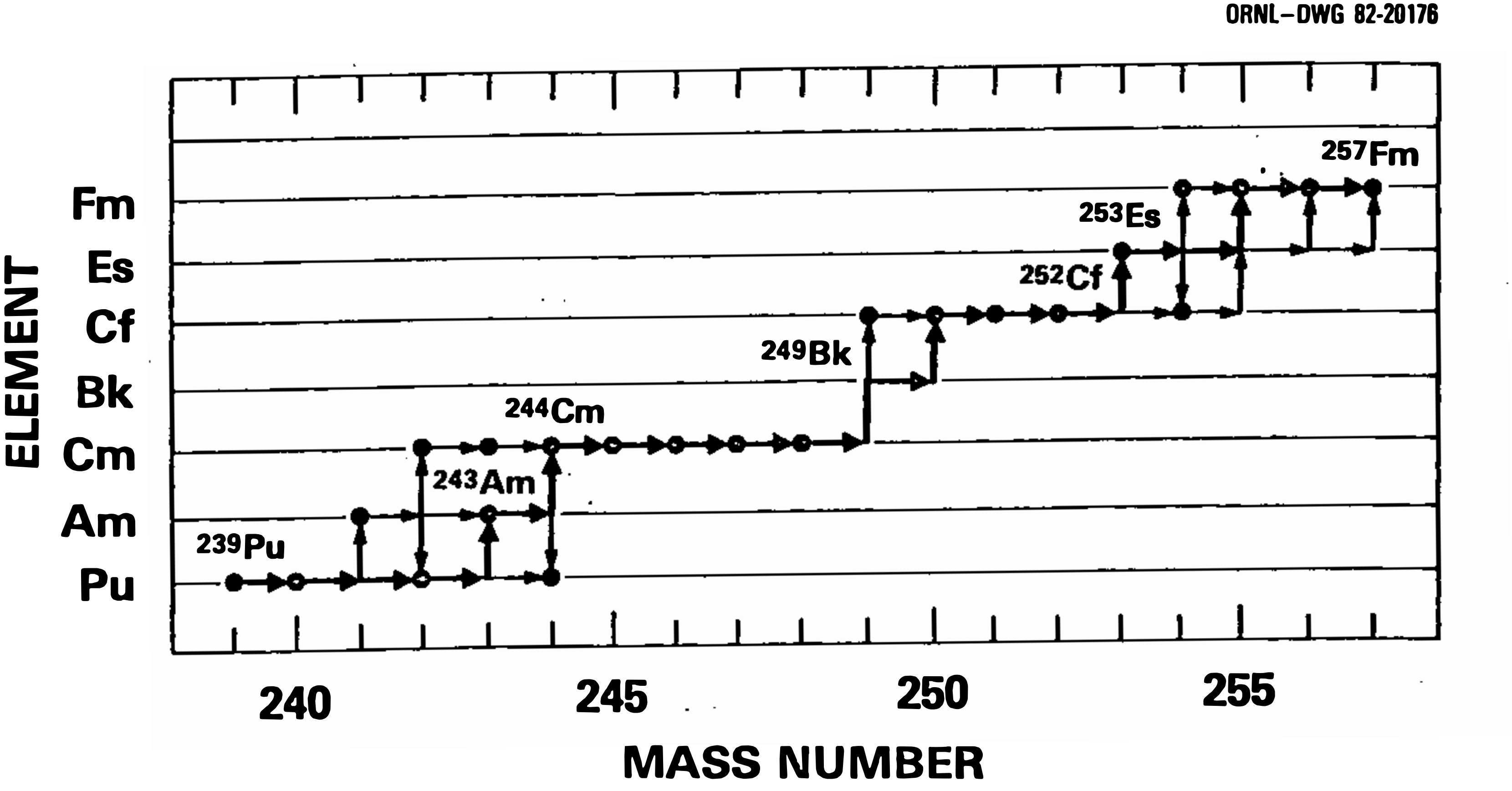
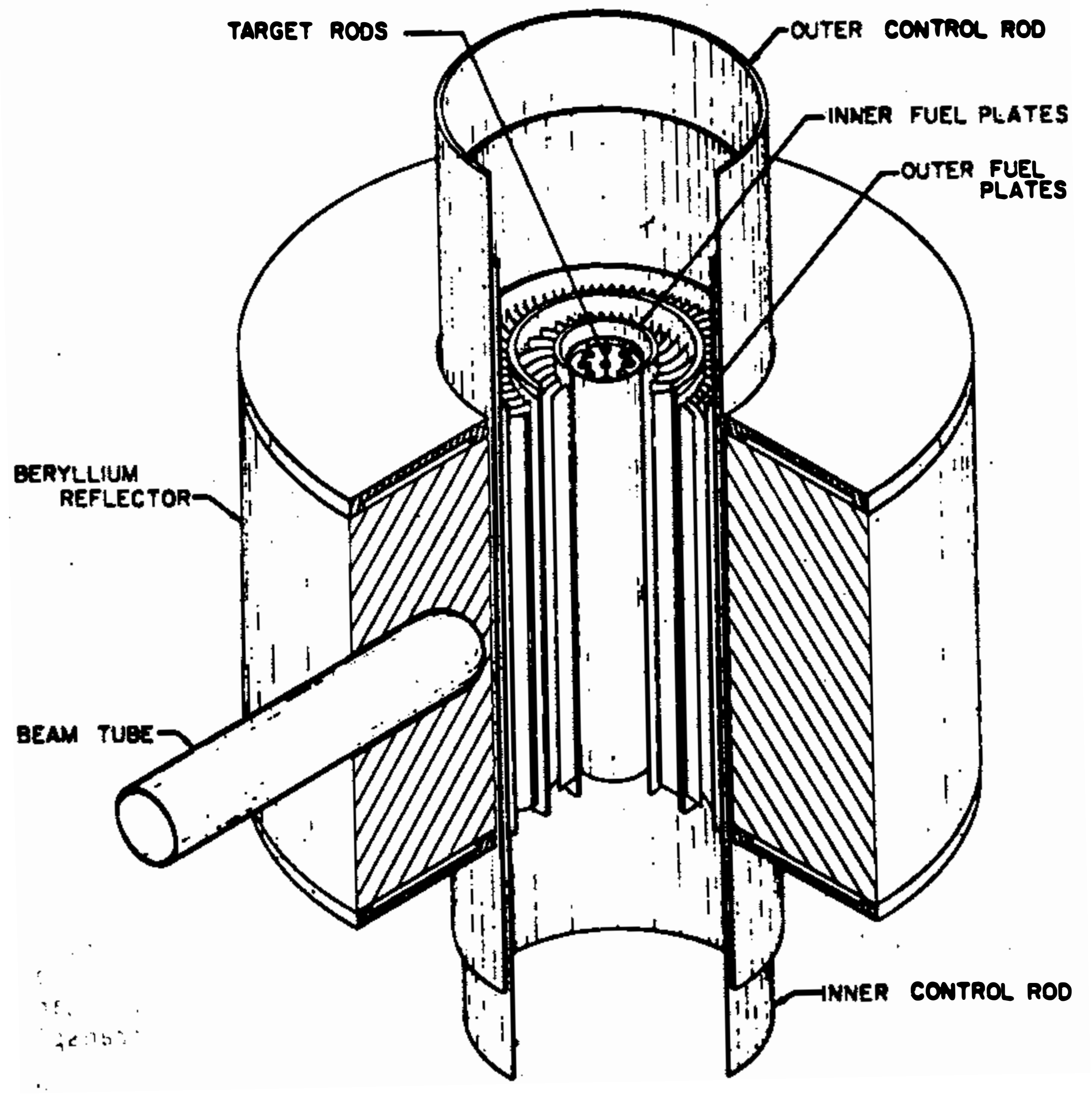

ORNL–DWG 82-20176
ELEMENT
Fm
Es
Cf
Bk
Cm
Am
Pu
257Fm
253Es
252Cf
249Bk
244Cm
243Am
239Pu
240
245
250
255
MASS NUMBER

Figure 5

ORNL-LR-DWG-65776



Schematic of High Flux Isotope Reactor core.

Figure 6

TABLE 3

HIGH FLUX ISOTOPE REACTOR (HFIR)

Commencement of construction	1961
Criticality achieved	1965
100 Mw (thermal) full power achieved	1966
Fuel	93% enriched ^{235}U
Fuel load	9.4 kg ^{235}U
Moderator	H_2O
Reflector	Be
Thermal neutron flux	
unperturbed	5×10^{15} n cm^{-2} sec^{-1}
perturbed	$2\text{-}3 \times 10^{15}$ n cm^{-2} sec^{-1}
Functions	Transplutonium isotope production Special isotope production Neutron diffraction Small angle neutron scattering Neutron activation analysis
Cost	$14,718,000

TABLE 4

TRANSURANIUM PROCESSING PLANT (TRU)

Commencement of construction	1963
Commencement of "hot" operations	1966
First processing of HFIR targets	1967
Functions	Fabrication of Am-Cm HFIR targets Isolation of transplutonium elements from irradiated HFIR targets Preparation of special transplutonium isotopes Special projects for DOE
Cost	$8,818,000

The routine production of HFIR/TRU includes isotopes of elements from curium-248 through einsteinium-253 in multimilligram quantities with smaller amounts of einsteinium-254 and fermium-257 (Table 5).

TABLE 5

ROUTINE HFIR/TRU PRODUCTION

Isotope	Half-Life	Amount/Year
^{248}Cm	3.397 x 10^5 yr	150 mg
^{249}Bk	320 d	50 mg
^{249}Cf	350.6 yr	from ^{249}Bk decay
^{252}Cf	2.64 yr	500 mg
^{253}Es	20.4 d	2 mg
^{254}Es	275.7 d	3 µg
^{257}Fm	100.5 d	1 pg

In addition, the engineers and chemists of TRU have been adept at working with the research community on special isotope production and sample fabrication problems. Some examples of these efforts include production, with the help of Calutron enrichment, of plutoniums 240 and 244, curiums 243 and 245, and californium 254 (Table 6).

A current example of great importance for the research community is the proposed production of einsteinium-254 as a target for the superheavy elements search and for the synthesis of increased amounts of neutron-rich isotopes of elements 101 to 103 (and perhaps above) for chemical and nuclear studies (Table 7). Compound nucleus, incomplete fusion, and transfer reactions are currently being studied in this region by nuclear chemists in order to attain basic understanding of the nuclear phenomena involved.

TABLE 6

EXAMPLES OF SPECIAL HFIR/TRU PRODUCTION

Isotope	Amount	Purity (Atom %)	Use
^{240}Pu	20 g	99.930	Fast spectrum neutron dosimeter
^{244}Pu	60 mg	99.423	Isotope dilution mass spec.
^{243}Cm	60 mg	57.78	γ Cm tracer; isotope dilution mass spec.
^{245}Cm	90 μg	99.12	Fission studies
^{254}Cf	200 pg	0.0914*	Fission studies

*Furnished 99% of the fission in the sample

TABLE 7

PROPOSED HFIR/TRU SYNTHESIS OF ^{254}ES

Requestor: G. T. Seaborg

Amount Requested: 40 μg

Purpose: Target for superheavy elements search and for synthesis of elements 101 to 103 and perhaps above for chemical and nuclear studies.

Background: ^{254}Es (T 1/2 = 276 d) is probably the heaviest nuclide producible in μg quantities. In standard production, its yield is 0.7% of ^{253}Es (T 1/2 = 20 d). After nine months, the activities of the two isotopes are equal and several μg targets of ^{254}Es can be prepared. Perhaps irradiation in a harder spectrum might enhance ^{254}Es over ^{253}Es. Studies of this possibility are now underway at ORNL. If so, much larger targets of ^{254}Es, even of 40 μg, may be possible.

Also, the TRU has value beyond its use in separation and purification of heavy elements for research and sale. It is a unique hot cell facility which provides alpha containment, and as such is a valuable training ground for hot cell operators. Its great versatility, deriving from the ease with which equipment racks can be replaced in a totally contained mode, makes it useful for carrying out development studies on the nuclear fuel cycle. The outstanding example of this type of use is in nuclear reactor fuel reprocessing. It has been used to carry out Purex (solvent extraction) flow sheet studies and off-gas cleanup studies for the U. S. Consolidated Fuel Recycle Program. In this connection it has also served to train and provide experience to fuel reprocessing specialists. There are only a few facilities in the United States currently operating with irradiated fuel where such experience may be obtained; young scientists and engineers trained in fuel reprocessing will be scarce indeed in the next decade in the United States.

Other fuel cycle uses could include developing chemical and engineering methods for separating and purifying valuable isotopes from spent nuclear fuel elements. It may, for example, be possible to obtain substantial quantities of nonradioactive fission product palladium and rhodium from such spent fuel elements. Finally, it should be pointed out that some of the materials separated and purified in TRU have defense-related applications.

Organizationally, the HFIR/TRU and its associated Heavy Element Chemistry Research Programs are under the Processes and Techniques Branch, Chemical Sciences Division, Office of Basic Energy Sciences (Table 8).

This program interacts strongly with other programs in the Department of Energy (DOE), especially those under the Office of Defense Programs and the Office of High Energy and Nuclear Physics (Table 9). We will be

TABLE 8

LOCATION OF HFIR/TRU AND HEAVY ELEMENT CHEMISTRY IN DOE

OFFICE OF ENERGY RESEARCH (OER)
Director - Alvin Trivelpiece
Deputy Director - James S. Kane

OFFICE OF BASIC ENERGY SCIENCES (BES)
Associate Director - Richard H. Kropschot
Deputy Associate Director - Donald K. Stevens

CHEMICAL SCIENCES DIVISION
Director - Elliot S. Pierce

PROCESSES AND TECHNIQUES BRANCH
Chief - F. Dee Stevenson

HFIR/TRU AND HEAVY ELEMENT CHEMISTRY
John Burnett

TABLE 9

OTHER DOE PROGRAMS HAVING COORDINATIONS AND INTERACTIONS WITH THE HEAVY ELEMENT CHEMISTRY PROGRAM

OFFICE OF HIGH ENERGY AND NUCLEAR PHYSICS - OER
Nuclear Physics Division
Enloe T. Ritter

OFFICE OF DEFENSE PROGRAMS

OFFICE OF TERMINAL WASTE DISPOSAL AND REMEDIAL ACTION - ASSISTANT SECRETARY NUCLEAR ENERGY
Division of Waste Repository Deployment
Thomas Longo

OFFICE OF HEALTH AND ENVIRONMENTAL RESEARCH - OER
Division of Ecological Research
Robert Watters

hearing of much work carried out under the auspices of these two other parts of DOE during this Workshop, as well as about their plans for the future.

DOE also has a Transplutonium Program Committee (Table 10), which:

(a) Advises on the transplutonium production and research program, including its direction and scope;

(b) Identifies isotopes of particular value to the program and sets production goals and schedules for them;

(c) Recommends distribution of isotopes from the production program.

TABLE 10

DOE TRANSPLUTONIUM PROGRAM COMMITTEE (1983)

J. L. Burnett	Chairman	D. G. Karraker	SRL (Savannah River)
J. W. Nehls	Secretary	Seymour Katcoff	BNL (Brookhaven)
W. T. Carnall	ANL (Argonne)	O. L. Keller	ORNL (Oak Ridge)
D. E. Ferguson	ORNL (Oak Ridge)	R. A. Penneman	LANL (Los Alamos)
Albert Ghiorso	LBL (Berkeley)	C. W. Reich	EG&G (Idaho)
R. W. Hoff	LLNL (Livermore)		

DOE Chemical Sciences Division funding of the Transplutonium Elements Research and Production Program over the last five years is given in Table 11. The first line gives the Chemical Sciences Division budget for research at various national laboratories and universities carried out with HFIR/TRU products and the related actinides and lanthanides. In addition to Chemical Sciences, research is also funded through DOE's Office of Defense Programs and Office of High Energy and Nuclear Physics. The latter is expected to support approximately $600,000 of research in FY-83 requiring the use of

TABLE 11

FUNDING: TRANSPLUTONIUM ELEMENTS RESEARCH AND PRODUCTION

Operating ($M)	FY-79	FY-80	FY-81	FY-82	FY-83 (est.)
Heavy Element Chem. Research (Chem. Sci.) (HEC)‡	3.1	3.4	3.6	4.2	4.5

‡Additional research with transplutonium elements is funded by the Office of High Energy and Nuclear Physics, and the Office of Defense Programs. (See text)

HFIR					
Total	4.7	5.0	5.6	6.3	7.2
Chem. Sci.	3.0	3.4	3.5	3.6	5.7**
Other OER*	0.9	1.0	1.0	1.6	-0-

*Magnetic Fusion, Materials Sciences, OHER

TRU					
Total	4.0	4.5	4.7	5.3	5.9
Chem. Sci.	3.1	3.3	3.7	4.2	4.8
Total Chem. Sci. for Transuranium Elements	9.2	10.1	10.8	12.0	15.0**
BES (Total Budget)	173	196	209	226	261

**includes HFIR charges for total OER

HFIR/TRU isotopes. In addition to Chemical Sciences, DOE funding of research requiring the use of HFIR/TRU isotopes was about $2M in FY-82. Also, in addition to research sponsored in the United States, researchers throughout the free world are dependent on HFIR/TRU for transplutonium elements. In Appendix I, a listing of papers published during the last five years with participation by foreign countries is given to indicate this wide interest. At the UNILAC accelerator in Darmstadt, for example, ^{248}Cm has been used for nuclear reaction studies (mainly deep inelastic processes), searches for superheavy elements, Coulomb excitation, searches for positron and x-ray emission from superheavy quasi atoms, and Coulomb fission. Work on fission and fission products was carried out in Mainz on ^{249}Cf and ^{250}Cf samples. In addition, special isotopic samples of ^{242}Pu and ^{244}Pu were made available for work at the UNILAC from the HFIR/TRU (with the help of Calutron enrichment). Countries represented in the publication list include the Federal Republic of Germany, France, Israel, Belgium, Taiwan, Sweden, Finland, Holland, and Lebanon. Of course, in each case, these countries are allocating some of their research dollars to these studies.

Research and applications involving ^{252}Cf as a neutron source also are not reflected in the Chemical Sciences budget. Dr. Yosh Maruyama, for example, who will make a presentation to this Workshop, leads a group that began applying ^{252}Cf (loaned by DOE) as a neutron source for cancer therapy about six years ago at the University of Kentucky Medical Center. So he has data on patients going back beyond the five year limit considered adequate to declare a treated person cured of cancer. The cure rate achieved by Dr. Maruyama's group for advanced stage cervical tumors is 37%. Dr. Maruyama, an M.D., and Dr. Larry Beach, a Ph.D. physicist, have combined their talents to successfully develop methods for irradiating the cancerous tissue while adequately protecting the medical personnel. Their approach to cancer therapy has exploited the unique properties of ^{252}Cf as a high intensity source of neutrons (as distinct from gamma rays) in treating cancerous tumors and other types of cancer. As these new approaches developed recently at the

University of Kentucky become more widely recognized, other hospitals in the United States and abroad can be expected to begin applying them as well. In addition to the support represented by the loan of ^{252}Cf from DOE to Dr. Maruyama's group, they have also received support from the National Cancer Institute and the American Cancer Society.

The HFIR operation (Table 11) is funded from several sources, with the principal funding coming from the DOE Office of Energy Research (OER). Until FY-83, this funding from OER was separated into contributions from Chemical Sciences, Materials Sciences, Magnetic Fusion, and Office of Health and Environmental Research (OHER). These budget categories reflect the fact that HFIR is a multipurpose neutron facility and has unique uses in areas of research besides the production of transplutonium elements. The other major area of research at HFIR, commensurate with the transplutonium elements production program, is the use of the neutron scattering facilities there for materials research. The characteristics of HFIR that make it ideal for transplutonium elements production simultaneously give it the highest thermal neutron flux in the world for neutron scattering research. There are only two other comparable facilities in the free world, one at the Brookhaven National Laboratory and the other at the Institut Laue-Langevin in Grenoble. In addition to extensive neutron diffraction facilities, HFIR also is the site of the only national Small Angle Neutron Scattering (SANS) facility. The SANS is supported by both the National Science Foundation (NSF) and DOE for work by university, industrial, and national laboratory researchers.

In the past, funding for HFIR operations was somewhat arbitrarily divided among the several participating groups in OER. Beginning in FY-83, however, all OER funding for HFIR is allocated through Chemical Sciences.

(Incidentally, also beginning in FY-83, all OER funding for the High Flux Beam Reactor (HFBR) at Brookhaven is allocated through the Materials Sciences Division of BES.) The fraction of OER funding for HFIR to be assigned to the transplutonium elements program is thus ill-defined considering the commensurate importance of the other programs.

In the case of the TRU, funding is principally from Chemical Sciences with some from the U. S. Consolidated Fuel Recycle Program (CFRP). In FY-83, it is expected that the Chemical Sciences program will be about $4.8 M and the CFRP about $1.1 M.

In summary, for FY-83, the overall total $15 M estimated budget from BES/ Chemical Sciences Division for research and production must be reduced by several millions to reflect the other uses of HFIR. The allocation of BES resources to the transplutonium program is thus less than the 5.7% that the $15 M represents. On the other hand, the $4.5 M under Heavy Elements Chemical Research in Table 11 is too low by several millions because it does not include programs of other parts of DOE, other government and private agencies, and foreign countries that use HFIR/TRU products.

The laboratories receiving isotopes directly from TRU over the last four years are given in Table 12, and the details of the shipments are given in Appendix II. This listing does not include most of the distributions of californium-252 which are made from Savannah River and Monsanto Research.

TABLE 12

LABORATORIES DIRECTLY RECEIVING TRU DISTRIBUTION (1977 - 1982)

Argonne National Laboratory

Batelle Memorial Institute - Columbus

Brookhaven National Laboratory

EG&G, Idaho

GSI - Darmstadt, FRG

Hanford Engineering Development Laboratory

Kernforschungszentrum Karlsruhe, FRG

Lawrence Berkeley Laboratory

Lawrence Livermore National Laboratory

Liege, University of

Los Alamos National Laboratory

Lovelace Biomedical and Environmental Research Institute, Inc.

Michigan, University of

National Bureau of Standards

New Brunswick Laboratory

Oak Ridge National Laboratory

Princeton Plasma Physics Laboratory

Sandia National Laboratory

Savannah River Laboratory

Savannah River Ecology Laboratory

Yale University

APPENDIX I

WORK INVOLVING FOREIGN COLLABORATORS EMPLOYING ISOTOPES FROM THE U. S. TRANSPLUTONIUM PRODUCTION PROGRAM (1977 - 1982)

A. Journal Articles

1. "Γ_n/Γ_f in Heavy Actinides." A. Gavron, H. C. Britt, P. D. Goldstone, R. Schoenmackers, J. Weber, and J. B. Wilhelmy. Phys. Rev. C 15, 2238 (1977).

2. "Determination of Γ_n/Γ_f at 12-20 MeV Excitation from Evaporation-Residue Cross Sections." P. D. Goldstone, H. C. Britt, R. Schoenmackers, and J. B. Wilhelmy. Phys. Rev. Letters 38, 1262 (1977).

3. "Fission Properties of the Heavy Actinides." J. B. Wilhelmy, H. C. Britt, D. C. Hoffman, W. R. Daniels, E. Cheifetz, A. Gavron, J. Weber, E. K. Hulet, H. J. Landrum, R. W. Lougheed, and J. F. Wild. S.-Afr. Tydskr. Fis. 1, 116 (1978).

4. "Identification of Short-Lived Ruthenium and Rhodium Isotopes in Fission by Rapid Chemical Separations." G. Franz and G. Herrmann. J. Inorg. Nucl. Chem. 40, 945 (1978).

5. "Three-Particle Exclusive Measurements of the Reactions $^{238}U + ^{238}U$ and $^{238}U + ^{248}Cm$. P. Glässel, D. v. Harrach, Y. Civelekoglu, R. Männer, H. J. Specht, J. B. Wilhelmy, H. Freiesleben, and K. D. Hildenbrand. Phys. Rev. Letters 43, 1983 (1979).

6. "Electrochemical Study of Mendelevium in Aqueous Solution: No Evidence for Monovalent Ions." K. Samhoun, F. David, R. L. Hahn, G. D. O'Kelley, J. R. Tarrant, and D. E. Hobart. J. Inorg. Nucl. Chem. 41, 1749 (1979).

7. "Americium Ditelluride." John H. Burns, Daniel Damien, and Richard G. Haire. Acta Cryst. B35, 143 (1979).

8. "Techniques of Preparation and Crystal Chemistry of Transuranium Chalcogenides and Pnictides." D. A. Damien, R. G. Haire, and J. R. Peterson. J. de Physique, Supplement C4, 95 (1979).

9. "Curium-248 Monopnictides and Monochalcogenides." D. Damien, R. G. Haire, and J. R. Peterson. J. Less-Common Metals 68, 159 (1979).

10. "Preparation and Lattice Parameters of Berkelium-249 Monopnictides." J. Inorg. Nucl. Chem. 42, 995 (1980).

11. "Californium-249 Monoarsenide and Monoantimonide." D. Damien, R. G. Haire, and J. R. Peterson. Inorg. Nucl. Chem. Letters 16, 537 (1980).

12. "Spontaneous Fission Properties of the Neutron-Deficient Fm Isotopes, 1.2 s ^{246}Fm and 38 s ^{248}Fm." D. C. Hoffman, D. Lee, A. Ghiorso, M. J. Nurmia, and K. Aleklett. Phys. Rev. C 22, 1581 (1980).

13. "Spontaneous Fission of ^{259}Fm." E. K. Hulet, R. W. Lougheed, J. H. Landrum, J. F. Wild, D. C. Hoffman, J. Weber, and J. B. Wilhelmy. Phys. Rev. C 21, 966 (1980).

14. "12.3 min ^{256}Cf and 43 min ^{258}Md and Systematics of the Spontaneous Fission Properties of Heavy Nuclides." D. C. Hoffman, J. B. Wilhelmy, J. Weber, W. R. Daniels, E. K. Hulet, R. W. Lougheed, J. H. Landrum, J. F. Wild, and R. J. Dupzyk. Phys. Rev. C 21, 972 (1980).

15. "Experimental Confirmation of a Scaling Law for the 1sσ Excitation Probability for $Z_1 + Z_2 > 120$, and Its Breakdown in Pb + Cm Collisions at Very Small Internuclear Distances. D. Liesen, P. Armbruster, F. Bosch, S. Hagmann, P. H. Mokler, H. J. Wollersheim, H. Schmidt-Böcking, R. Schuch, and J. B. Wilhelmy. Phys. Rev. Letters 44, 983 (1980).

16. "Fission Barriers for ^{255}Es, ^{256}Es, and ^{255}Fm." H. C. Britt, E. Cheifetz, D. C. Hoffman, and J. B. Wilhelmy. Phys. Rev. C 21, 761 (1980).

17. "Fission Properties of the 1.5-s Spontaneous Fission Activity Produced in Bombardment of ^{248}Cm with ^{18}O." Darleane C. Hoffman, Diana Lee, Albert Ghiorso, M. J. Nurmia, Kjell Aleklett, and Matti Leino. Phys. Rev. C 24, 495 (1981).

18. "Comparison of ^{252}Cf Spontaneous Fission with ^{250}Cf(t,pf)." J. Weber, H. C. Britt, and J. B. Wilhelmy. Phys. Rev. C 23, 2100 (1981).

19. "Fission Probabilities for Actinide Nuclei Excited by the $(^{12}C, {}^{8}Be_{g.s.})$ Reaction." E. Cheifetz, H. C. Britt, and J. B. Wilhelmy. Phys. Rev. C 24, 519 (1981).

20. "Electrochemical Studies of Trivalent Californium and Selected Trivalent Lanthanides in Aqueous Solution." C. Musikas, R. G. Haire, and J. R. Peterson. J. Inorg. Nucl. Chem. 43, 2935 (1981).

21. "A New Determination of the Enthalpy of Solution of Berkelium Metal and the Standard Enthalpy of Formation of Bk^{3+} (aq)." J. Fuger, R. G. Haire, and J. R. Peterson. J. Inorg. Nucl. Chem. 43, 3209 (1981).

22. "A Procedure for a Fast Separation of Berkelium and Cerium." Y.-F. Liu, C. Luo, H. R. von Gunten, and G. T. Seaborg. Inorg. Nucl. Chem. Letters 17, 257 (1981).

23. "Actinide Production in Collisions of ^{238}U with ^{248}Cm." M. Schädel, W. Brüchle, J. V. Kratz, K. Sümmerer, G. Wirth, G. Herrmann, R. Stakemann, G. Tittel, N. Trautmann, J. M. Nitschke, E. K. Hulet, R. W. Lougheed, R. L. Hahn, and R. L. Ferguson. Phys. Rev. Letters 48, 852 (1982).

24. "The Preparation of Curium Metal Targets for the Synthesis of Superheavy Elements." R. W. Lougheed, E. K. Hulet, R. L. Landingham, J. M. Nitschke, H. Folger, J. V. Kratz, W. Brüchle, and H. Gäggeler. Nucl. Instr. and Meth. 200, 71 (1982).

25. "Production of Heavy Actinides from Interactions of ^{16}O, ^{18}O, ^{20}Ne, and ^{22}Ne with ^{248}Cm." D. Lee, H. von Gunten, D. Hoffman, B. Jacak, M. Nurmia, Y.-F. Liu, C. Luo, and G. T. Seaborg. Phys. Rev. C 25, 286 (1982).

26. "Decay Properties of Neutron-Rich Silver Isotopes." W. Brüchle and G. Hermann. Radiochimica Acta 30, 1 (1982).

27. "Experimental Features of Coulomb Fission." G. Himmele, H. Backe, P. A. Butler, D. Habs, V. Metag, J. B. Wilhelmy, and H. J. Specht. Nucl. Phys. A (1982) (in press).

28. "Nuclear Charge Distribution in Fission: Fractional Cumulative Yields of Isotopes of Krypton and Xenon in ^{249}Cf(n_{th},f) and ^{250}Cf(sp.f)." H.-H. Meixler, K. Wolfsberg, and H. E. Denschlag. Canad. J. Chem. (1982) (in press).

B. Proceedings and Presentations

1. "Neutron Rich Fragments from Spontaneous Fission of ^{254}Cf." H. A. Selic, E. Cheifetz, A. Wolf, and J. B. Wilhelmy. Proc., Conf. on Nuclear Spectroscopy of Fission Products, Grenoble, France, 21-23 May 1979, Ed. Till von Egidy, The Institute of Physics, Bristol and London, p. 316.

2. "Even-Even Neutron Rich Isotopes." E. Cheifetz, H. A. Selic, A. Wolf, R. Chechik, and J. B. Wilhelmy. Proc., Conf. on Nuclear Spectroscopy of Fission Products, Grenoble, France, 21-23 May 1979, Ed. Till von Egidy, The Institute of Physics, Bristol and London, p. 193.

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APPENDIX II

Part 1. Distribution of Heavy Elements from the Transuranium Processing Plant During the Period October 1, 1978 - September 30, 1980

Major Nuclide	Date Shipped	TRU file Number	Shipped to:	
			Recipient	Site
^{240}Pu, g				
0.134	01-10-79	1004	IRML[a]	HEDL
0.167	11-02-79	1032	R. W. Hoff	LLNL
0.049	11-02-79	1033	C. W. Reich	EG&G Idaho
29.01	11-06-79	1068	IRML[a]	LANL and HEDL
29.360				
^{242}Pu, g				
0.151	12-11-79	1075	S. Katcoff	BNL
^{241}Am, g				
17.64	02-16-79	988	Isotopes Sales	ORNL[b]
^{243}Am, g				
0.10	02-16-79	1016A	Isotopes Sales	ORNL[c]
2.03	02-22-79	1014B	IRML[a]	LLNL
0.16	03-09-79	1014A	R. W. Hoff	LLNL
0.05	03.15-79	1017	C. W. Reich	EG&G Idaho
2.3	03-27-79	1029	IRML[a]	LLNL
5.94	04-05-79	1020	Operations Div.	Karlsruhe
20.0	05-31-79	986B	L. R. Morss	U. of Liege
0.10	08-01-79	1019	Isotopes Sales	BCNM, Belgium
10.14	11-06-79	1018	IRML[a]	LANL
2.08	09-26-80	1105	R. L. Hahn	ORNL
42.90				
Curium (mixed), g				
142.4	10-13-78	987	A. R. Boulogne	SRL
0.040	02-01-79	1006	L. W. Reynolds	SRL
0.002	05-02-79	1030	S. E. Dismuke	ORNL
0.57	09-04-79	1047	Isotopes Sales	ORNL[c]
0.032	09-11-79	1048	G. W. Beall	ORNL
0.010	10-16-79	1062A	S. Katz	ORNL
0.010	01-14-80	1062C	S. Katz	ORNL
2.093	03-03-80	1046A	IRML[a]	ORNL
10.75	03-05-80	1045	R. W. Hoff	LLNL
0.002	04-22-80	1091	M. M. Abraham	ORNL
155.55				

Major Nuclide	Date Shipped	TRU file Number	Shipped to:	
			Recipient	Site
^{243}Cm (56%), mg				
5.0	01-29-79	1008A	J. J. Thompson	Lovelace Found.
10.0	02-02-79	1008B,C	J. J. Thompson	Lovelace Found.
0.1	02-02-79	1009	W. T. Carnall	ANL
1.0	02-02-79	1010	R. A. Penneman	LANL
(1.1 ng)	11-15-79	1073	J. F. Emery	ORNL
1.0	07-02-80	1090A	M. M. Abraham	ORNL
5.2	09-26-80	1011	IRML[a] for	HAIE[d]
22.3				
^{245}Cm (99%), μg				
92	01-25-79	991	R. W. Hoff	LLNL
2.2	06-05-79	1037	J. K. Dickens	ORNL
94.2				
^{248}Cm (97%), mg				
20.4	05-31-79	986A	L. R. Morss	Univ. of Liege
0.52	05-31-79	1034A	IRML[a]	Yale Univ.
13.42	06-14-79	985B	R. G. Haire	ORNL
0.507	06-29-79	1034B	IRML[a]	Yale Univ.
0.101	07-30-79	1042	J. H. Hamilton	Darmstadt
0.802	09-18-79	1034C	IRML[a]	Yale Univ.
0.097	10-08-79	1064	J. M. Peele	ORNL[c]
0.489	10-09-79	1034E	Isotopes Sales	GSI-Darmstadt
19.95	11-12-79	1055	W. T. Carnall	ANL
19.95	11-12-79	1057	R. W. Hoff	LLNL
0.036	11-28-79	1039	D. W. Hayes	SRL
19.95	11-28-79	1056	N. M. Edelstein	LBL
23.8	12-18-79	1071	R. W. Hoff	LLNL[e]
0.478	01-10-80	1034F	Isotopes Sales	GSI-Darmstadt
19.95	01-12-80	1059	R. G. Haire	ORNL
140.090				
^{249}Bk, mg				
6.296	03-05-79	1022	W. T. Carnall	ANL
6.296	03-05-79	1023	N. M. Edelstein	LBL
6.296	03-06-79	1024	R. W. Hoff	LLNL
6.693	05-25-79	1035	R. G. Haire	LANL[f]
6.374	05-25-79	1036	R. G. Haire	ORNL[f]
3.0[f]	07-09-79	1040A	J. W. Ward	LANL
0.001	08-03-79	1038	Isotopes Sales	India
8.879	05-20-80	1085	W. T. Carnall	ANL
8.879	05-20-80	1087	R. W. Hoff	LLNL
7.419	06-02-80	1086	N. M. Edelstein	LBL
9.164	07-05-80	1089	R. G. Haire	ORNL
69.297				

Major Nuclide	Date Shipped	TRU file Number	Shipped to:	
			Recipient	Site
^{249}Cf, mg				
17.538	11-02-78	1000	R. G. Haire	ORNL[f]
0.245	01-09-79	1001	C. W. Reich	EG&G Idaho
2.56	01-19-79	996	W. T. Carnall	ANL
2.56	01-19-79	997	N. M. Edelstein	LBL
2.56	01-19-79	998	R. W. Hoff	LLNL
1.0	07-09-79	1040B	J. W. Ward	LANL[f]
1.23	12-03-79	1072	J. K. Dickens	ORNL
0.001	06-30-80	1094	Isotopes Sales	IPL[g]
27.694				
^{250}Cf (85%), mg				
0.232	08-20-79	1051	J. G. Conway	LBL
^{252}Cf, mg				
0.0118 (NSD-105)	12-08-79	980	E. H. Gupton	ORNL
0.010	01-17-79	1005	IRML[a]	Germany
1.623 (NS-100)	02-27-79	929	V. Spiegel	NBS
0.0117	03-21-79	1027	IRML[a]	Karlsruhe
0.0112	03-21-79	1028	IRML[a]	ORNL
1.909 (NSD-106)	05-04-79	989	S. Untermeyer	HEDL
42.414	05-23-79	975	A. R. Boulogne	SRL
0.0026	07-30-79	1031	IRML[a]	HEDL
42.900	08-17-79	1041	A. R. Boulogne	SRL
37.312	09-18-79	1052	A. R. Boulogne	SRL
36.764	10-04-79	1053	A. R. Boulogne	SRL
36.499	10-15-79	1054	A. R. Boulogne	SRL
38.018	11-09-79	1069	W. H. Brotherton, Sr.	SRL
37.741	01-04-80	1070	W. H. Brotherton, Sr.	SRL
0.206 (NZD-31)	01-24-80	1079	F. J. Muckenthaler	ORNL
0.001	01-25-80	1065	IRML[a]	ORNL
21.821 (NSD-107)	02-05-80	1074	J. F. Schulze	SNL
0.088 (NSD-78)	04-07-80	1063A	J. H. Eaves	UNC Ind.
0.00137 (Sr-Cf-260C)	04-07-80	1063B	J. H. Eaves	UNC Ind.
0.0275	04-24-80	1092	IRML[a]	ORNL
0.567	06-18-80	1080	R. J. Gehrke	EG&G Idaho
0.00016 (FS-3)	07-03-80	1099	J. T. Nihalczo	ORNL

Major Nuclide	Date Shipped	TRU file Number	Shipped to: Recipient	Site
1.240 (NZD-44)	07-17-80	951	R. C. Hagenauer	NBL[h]
0.00045 (FS-4)	07-22-80	1100	J. T. Mihalczo	ORNL
29.715	08-12-80	1101	P. B. Pagett	SRL
14.189 (NSD-102)	09-10-80	943A	R. J. Cloutier	ORAU
15.729 (NSD-103)	09-10-80	943B	R. J. Cloutier	ORAU
359.824				
^{253}Es (mixed), μg				
110	02-13-79	1012	W. T. Carnall	ANL
414	02-13-79	1013	R. G. Haire	ORNL
451	02-08-80	1081	W. T. Carnall	ANL
248	02-20-80	1082A	R. G. Haire	ORNL
400	02-29-80	1082B	R. G. Haire	ORNL
5	06-27-80	1096	R. W. Hoff	LLNL
1628				
^{254}Es, μg				
0.0009	10-15-79	1066	R. G. Haire	ORNL
3	11-27-79	1060	M. M. Abraham	ORNL
0.22	06-19-80	1097	R. W. Hoff	LLNL
3.2209				
^{257}Fm, pg				
1	06-27-80	1098	R. W. Hoff	LLNL

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[a] Isotopes Research Materials Laboratory (ORNL). In some instances, material was forwarded to another site.

[b] Not a TRU product. Material purified and returned to inventory.

[c] For dispensing small orders

[d] Joint US/UK Higher Actinides Irradiation Experiment.

[e] Material contained more ^{244}Cm (0.165%) than typical high-purity ^{248}Cm.

[f] Contains some material previously allocated to LANL and ORNL.

[g] Isotope Products Laboratories.

[h] New Brunswick Laboratory of the DOE at Argonne, IL.

Part 2. Distribution of heavy elements from the Transuranium Processing Plant During the Period October 1, 1980 - September 30, 1981

Major Nuclide	Date Shipped	TRU file Number	Shipped to:	
			Recipient	Site
Curium (mixed), g				
2.08	10-01-80	1046B	IRML[b] for	HAIE[c]
0.206	10-06-80	1103	IRML[b] for	HAIE[c,a]
4.393	10-06-80	1104	IRML[b] for	LANL[a]
12.29	10-10-80	1046C	IRML[b] for	HAIE[c]
18.969				
^{243}Cm (8%), mg				
10.0	09-02-81	1144	R. A. Guilmette	Lovelace[d]
^{243}Cm (58%), mg				
1.0	03-06-81	1090B	M. M. Abraham	ORNL
^{244}Cm (>99%), mg				
3.2	02-02-81	1115	R. W. Hoff	LLNL
^{248}Cm (92%), mg				
9.25	03-06-81	1117	IRML[b] for	HAIE[c]
^{249}Bk, mg				
9.174	01-12-81	1110	W. T. Carnall	ANL
9.174	01-12-81	1111	W. T. Carnall for	LBL
9.174	02-03-81	1112	R. W. Hoff	LLNL
9.174	02-20-81	1113	R. G. Haire for	LANL
9.174	02-20-81	1114	R. G. Haire	ORNL
7.593	08-03-81	1124	W. T. Carnall	ANL
7.593	08-03-81	1125	N. M. Edelstein	LBL
7.593	09-03-81	1126	R. W. Hoff	LLNL
68.649				
^{249}Cf, mg				
1.83	09-09-81	1129	W. T. Carnall	ANL
1.83	09-09-81	1130	N. M. Edelstein	LBL
3.66				
^{252}Cf, mg				
0.0115	03-06-81	1119	IRML[b]	LANL
0.0715 (NSD-76)	03-19-81	1118	R. L. Stevenson	EG&G Idaho
2.062 (NBS-108)	04-02-81	1095A	E. D. McGarry	NBS

Major Nuclide	Date Shipped	TRU file Number	Shipped to:	
			Recipient	Site
3.328 (NBS-109)	04-02-81	1095B	E. D. McGarry for	U. of Mich.
0.0136 (FS-5)	06-09-81	1134	J. T. Mihalczo	ORNL
29.102	06-17-81	1136	R. B. Pagett	SRL
0.0054 (FS-7)	06-23-71	1135	J. T. Mihalczo	ORNL
0.165 (NSD-27)	07-16-81	1137	C. E. Clifford	PPPL[e]
1.645 (NSD-73)	09-22-81	1149	W. M. Lysher	HEDL
0.0613 (NSD-77)	09-23-81	1139	R. W. Barnes	Battelle-Ohio[f]
36.4653				
^{253}Es (mixed), μg				
297	10-30-80	1107A	R. G. Haire	ORNL
316	11-11-80	1106	W. T. Carnall	ANL
369	11-24-80	1107B	R. G. Haire	ORNL
88.8	12-16-80	1107C	R. G. Haire	ORNL
388	03-31-81	1120	W. T. Carnall	ANL
819	04-13-81	1121	R. G. Haire	ORNL
2277.8				
^{257}Fm, pg				
1 (est)	11-11-80	1109	R. W. Hoff	LLNL
0.9 (est)	04-28-81	1123	R. W. Hoff	LLNL
1.9				

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[a] Material contained 67% ^{246}Cm.

[b] Isotopes Research Materials Laboratory (ORNL). In some instances material was forwarded to another site.

[c] Joint US/UK Higher Actinides Irradiation Experiment.

[d] Lovelace Biomedical and Environmental Research Institute, Inc., Albuquerque, NM.

[e] Princeton Plasma Physics Laboratory, Princeton, NJ.

[f] Battelle Memorial Institute, Columbus, OH.

Part 3. Distribution of heavy elements from the Transuranium Processing Plant During the Period October 1, 1981 - June 30, 1982

Major Nuclide	Date Shipped	TRU file Number	Shipped to:	
			Recipient	Site
^{244}Pu, mg				
3.25	10-22-81	1143	R. W. Hoff	LLNL
^{243}Cm (8.4%), mg				
2.06	02-12-82	1156	R. A. Guilmette	Lovelace[a]
^{243}Cm (58%), mg				
0.11	10-16-81	1150	W. B. Farrell	SREL[b]
0.001	02-17-82	1157	Isotopes Sales for	ANL
0.65	03-02-82	1158	N. M. Edelstein	LBL
0.761				
^{248}Cm (97%), mg				
19.95	11-06-81	1058	R. G. Haire	ORNL
17.8	03-11-82	1160	W. T. Carnall	ANL
37.75				
^{249}Bk, mg				
7.284	04-02-82	1167	R. W. Hoff	LLNL
7.284	04-19-82	1169	R. G. Haire	ORNL
7.284	04-22-82	1165	W. T. Carnall	ANL
7.284	04-22-82	1166	W. T. Carnall for	LBL
29.136				
^{249}Cf, mg				
1.83	10-20-81	1131	R. W. Hoff	LLNL
10.93	02-18-82	999B	R. G. Haire for	LANL
1.83	02-18-82	1132	R. G. Haire for	LANL
1.83	02-18-82	1133	R. G. Haire	ORNL
7.68	02-26-82	999A	R. G. Haire for	LANL
1.05	03-02-82	1159	K. Wolfsberg	LANL
25.15				
^{252}Cf, mg				
34.724	10-22-81	1145	R. B. Pagett	SRL
0.00867 (NS-2)	11-09-81	1151	J. T. Mihalczo	ORNL
0.000345 (NSD-24)				
0.00042	12-01-81	1152	IRML[c]	ORNL
6.892 (NSS-111)	03-02-82	1161	J. E. Bigelow	ORNL

Major Nuclide	Date Shipped	TRU file Number	Shipped to: Recipient	Site
46.188	03-22-82	1146	R. B. Pagett	SRL
1.787 (NS-110)	03-31-82	1140	E. D. McGarry	NBS
56.621 (LSD-112)	04-23-82	1162	J. B. Wray	SNL
0.219 (SR-Cf-167)	06-02-82	1178	F. Levert	TEC[d]
0.0112	06-24-82	1154A	IRML[c]	ORNL
146.452				
^{253}Es (mixed), μg				
312	03-05-82	1163	W. T. Carnall	ANL
498	04-19-82	1164	R. G. Haire	ORNL
810				
^{253}Es (milked), μg				
76.7	04-19-82	1170A	R. G. Haire	ORNL
^{254}Es, μg				
2.95	12-21-81	1153	R. W. Lougheed	LLNL

[a] Lovelace Biomedical and Environmental Research Institute, Inc., Albuquerque, NM.

[b] Savannah River Ecology Laboratory, Aiken, SC.

[c] Isotope Research Materials Laboratory (ORNL).

[d] Technology for Energy Corporation, Knoxville, TN.

APPENDIX D

NUCLEAR REACTIONS AND SYNTHESIS OF NEW TRANSURANIUM SPECIES

Glenn T. Seaborg

At the time of this writing (late 1982) 16 transuranium elements are known (atomic numbers 93 to 107, inclusive, and number 109). Distributed among these 16 elements are nearly 200 nuclear species. Those with atomic numbers 93 to 101, inclusive, were first synthesized and identified (i.e., discovered) through the use of neutrons, deuterons or helium ions. The half-lives became shorter and shorter with increasing atomic number, until at elements 107 and 109 these are in the range of milliseconds.

Three of the transuranium elements (numbers 104, 105 and 106) and a large proportion of the transfermium (beyond number 100) nuclear species discovered during the last 15 years have utilized actinide isotopes produced in the high flux isotope reactor/transuranium processing plant (HFIR-TRU) facilities at Oak Ridge National Laboratory (ORNL) as the target material. Present indications are that most of the future disoveries of new transuranium nuclear species and the discovery of superheavy elements, if successfully accomplished, will utilize such target material.

In this short review, I shall describe the special aspects of heavy ion nuclear reaction mechanisms operative in the transuranium region, the role of new techniques, possible nuclear reactions for the production of additional transuranium elements and nuclear species and the importance of work in this region for the development of nuclear models and theoretical concepts. This discussion should make it clear that a continuing supply of elements and isotopes, some of them relatively short-lived, produced by the HFIR-TRU facilities, will be a requirement for future synthesis of new elements and isotopes.

In this short account, I shall not cover the historical aspects except for some brief references that are indispensable to an understanding of the theme. A compilation[1] of reprints of the original publications, accompanied by explanatory material, covers very thoroughly all aspects of the historical background of the transuranium elements through atomic number 106. This includes such information on the discovery of these elements, including accounts of the competing claims for the discovery of elements 104, 105 and 106 by scientists at the Dubna Laboratory in the Soviet Union, as well as original information on many isotopes, nuclear reactions for their production, radioactive properties, chemical properties of the elements, etc. The discovery of all elements beyond atomic number 100 (fermium) has been made on a one-atom-at-a-time basis and this will surely continue to be the case. It has been crucial to the claim of discovery that the atomic number of the reaction product be clearly identified using chemical or physical techniques. Criteria for establishing that such an identification has been made have been published[2] by an international group of experts and these criteria will guide the discussions in the review.

Nuclear stability considerations and radioactivity decay properties, which are of central importance in devising experiments for the production and identification of new elements and new isotopes, are the subject of another paper[3] prepared for this workshop.

However, for the convenience of the reader, I shall briefly summarize some salient information about superheavy elements (SHE). Simple extrapolations of radioactive decay properties for elements beyond atomic number 109 suggest that the half life, especially that for decay by spontaneous fission, shall become so short as to make detection very difficult and soon impossible. However, in the period from 1966 to 1972, a number of calculations[4] based on modern theories of nuclear structure showed that in the region of proton number Z = 114 and neutron number N = 184 the ground states of nuclei should be stabilized against decay by spontaneous fission. This stabilization is due to the complete filling of major proton and neutron shells in this region and is analogous to the stabilization of chemical elements such as the noble gases by the filling of their electronic shells. Such superheavy elements are predicted to form an island of relative stability extending both above and below Z = 114 and N = 184 and separated from the peninsula of known nuclei by a sea of instability.

Some more recent calculations,[5] based on careful consideration of the effect of mass asymmetry on the fission barrier and a reduced spin-orbit coupling strength, have indicated that the Z = 114 shell effect is not very large. These calculations do confirm the existence of a shell at N = 184, but also suggest less stability for species with N < 184; that is, the island of stability has a cliff with a sharp drop-off for N < 184. If these considerations are correct, it would become considerably more difficult to synthesize and detect the superheavy elements. A premium would be placed on producing a nucleus with N = 184 or very close to this, N = 183, in order that it might have a half life sufficiently long to make it detectable.

During the last 15 years, numerous attempts have been made to synthesize and identify superheavy elements through the bombardment of heavy target nuclei with heavy ions. None of these experiments has been successful. A summary and analysis[6] suggests that this failure is not due to the failure to produce superheavy intermediate nuclei, but is due to the low survival probabilities of these superheavy precursors.

NUCLEAR REACTION MECHANISMS

Nuclear reactions designed to produce isotopes in the transplutonium region are dominated by the competing fission reaction, which diminishes the yield of the desired products. This diminution in yield is usually very drastic and is greater the higher the atomic number and degree of excitation of the intermediate nucleus. The tendency toward undergoing this unwanted fission also increases with increasing angular momentum imparted to the intermediate nucleus. (Angular momentum increases with the increasing mass of the bombarding projectile nucleus and with the increasing magnitude of the impact parameter, the lateral distance between the centers of the target and projectile nuclei.) Thus, the name of the game is to produce intermediate nuclei with a minimum of excitation (cold nuclei) and a minimum of angular momentum so they can reach the ground state (usually through the emission of neutrons and gamma-rays) with the minimum of loss from the competing fission reaction.

There are a number of heavy ion reaction mechanisms that might lead to the identification of new isotopes and, in one case, possibly new elements, through the production of cold nuclei in sufficient yields to be detectable. The compound nucleus mechanism, known and understood for the longest time, offers the best and, probably the only, hope for the production and identification of new elements; this seems to be operable with heavy element target nuclei (lead and bismuth) only for heavy ion projectiles with atomic number up to 26 (iron) - for transplutonium targets, this limitation produces no roadblock to the possible production of superheavy elements.

The other heavy ion nuclear reaction mechanisms cover a range of categories whose definition is not always unambiguous and which tend to merge at the boundaries of the definitions one into the other. An oversimplified categorization into two types will serve our present purposes. One type is well described as simple transfer reactions and is applicable for our purposes (transplutonium targets) with light heavy ions - up to atomic number 10 (neon) or somewhat higher. The other can be described as deep inelastic transfer reactions, whose importance increases with the increasing atomic number of the heavy ion projectile, with uranium projectiles the most interesting for transplutonium targets.

Compound Nucleus Mechanism. This mechanism involves the complete amalgamation (complete fusion) of the heavy ion projectile with the target nucleus, followed by the de-excitation of this compound nucleus through the emission (usually) of neutrons and gamma-rays in competition with the more prevalent fission reaction. The most central collisions (smallest impact parameter) which impart only a small amount of angular momentum to the system, lead to such complete fusion of the projectile and target nuclei. The product nuclei are strongly focused in the forward (i.e., the projectile beam) direction due to momentum conservation. The classical method of preparing transuranium nuclei has been through the use of the complete fusion reaction. A typical example is the synthesis of element 106 by Ghiorso *et al.*[7], who bombarded ^{249}Cf with 95 MeV ^{18}O and observed the ^{249}Cf (^{18}O, 4n) $^{263}106$ reaction with a cross section of $\sim$0.3nb. The $^{263}106$ atoms ($t_{\frac{1}{2}} = 0.9 \pm 0.2$ sec) were identified by observing the previously known daughter, ^{259}Rf, and granddaughter, ^{255}No, through the decay sequence $^{263}106 \xrightarrow{\alpha} {}^{259}Rf \xrightarrow{\alpha} {}^{255}No \xrightarrow{\alpha}$. The $^{263}106$ atoms were isolated using a helium jet and deposited on the rim of a wheel. The deposit was then rotated in front of a sequence of surface barrier detectors which then detected the primary alpha-decay of $^{263}106$. These primary detectors were then moved to face another series of secondary detectors which detected the decay of the previously known daughter atoms implanted in the primary detectors by recoil in the intial decay. The time correlated decay information was recorded using an on-line computer. A total of 14 time-correlated events was observed.

However, despite successes such as this, if we look at the cross sections for complete fusion reactions such as the X (heavy ion, 4n) Y reaction, we find a sharp decrease in the magnitude of these cross sections as the (Z,A) of the heavy ion projectile increases. As a further constraint, the limits on availability of target materials with $Z > 98$, presents great, but no insurmountable, difficulties in synthesizing new transuranium nuclei with complete fusion reactions. A number of workers, particularly those in the Soviet Union, have pointed out that if some heavy ion projectiles with $40 \leqslant A \leqslant 60$ are used in combination with tightly bound target nuclei containing closed shells of nucleons, it is possible to form extremely "cold" compound nuclei whose survival probabilities might be high enough to compensate for the decreased complete fusion cross sections.

A number of experimental studies involving the magic lead and bismuth nuclei have shown that the possibility of such "cold fusion" reactions is, in fact, a reality. Flerov et al.[8] observed the production of ^{252}No using the ^{206}Pb (^{48}Ca, 2n) reaction, while Nitschke et al.[9] found ^{254}No to be produced with a surprisingly large cross section of 3.4 ± 0.4 μb in the ^{208}Pb (^{48}Ca, 2n) reaction. In this same manner, Gäggeler et al.[10] observed the production of ^{244}Fm in the ^{206}Pb (^{40}Ar, 2n) reaction.

The principal development, however, that has pushed "cold fusion" reactions to the forefront in efforts to synthesize new transuranium nuclei was the work of Münzenberg et al.[11,12] using the velocity filter (separator for heavy ion reaction products) (SHIP) at Gesellschaft für Schwerionenforschung mbH (GSI). They have observed unambiguous evidence for the occurrence of the ^{207}Pb (^{50}Ti, 2n) ^{255}Rf and ^{209}Bi (^{50}Ti, 2n) ^{257}Ha reactions at a bombarding energy of 4.85 MeV/u. Most interestingly, at a ^{50}Ti energy of 235 MeV (4.70 MeV/A), they observed the ^{208}Pb (^{50}Ti,n) ^{257}Rf reaction. Since SHIP is a velocity separator, "transfer" and "deep inelastic" products are strongly suppressed since the products from these binary reactions have a wide angular distribution and do not move with the velocity of the complete fusion evaporation residues. The separator accepts recoils only from a limited range of angles near 0°; thus, these reactions are quite probably cold complete fusion reactions.

Of special interest is the use of cold fusion reactions to synthesize, and thus discover, element 107[11] and element 109.[13] For the former, ^{209}Bi was bombarded with 4.85 and 4.95 MeV/u ^{54}Cr, and the ^{209}Bi (^{54}Cr,n) ^{262}107 reaction was observed. The identification of the ^{262}107 ($t_{\frac{1}{2}} = 4.7^{+2.3}_{-1.6}$ ms) was based upon the observation of a set of correlated alpha particle decays which end in the known ^{250}Fm decay. No complete decay chains were observed due to the small yield and the 50% efficiency of the detector system, but two partially complete chains ending in ^{250}Fm were observed, and one chain ending in ^{254}Lr was observed. The velocity of the ^{262}107 atoms was determined two different ways, by the velocity separator itself and by a time-of-flight measurement. The energy of the evaporation residue was measured and agreed with expectations for the cold fusion mechanism. Similarly, element 109 was identified[13] as the result of the bombardment of ^{209}Bi with 5.15 MeV/u ^{58}Fe ions according to the reaction ^{209}Bi (^{58}Fe,n) ^{266}109. A single atom of ^{266}109 (which decayed after a time interval of 5 ms) was identified through the observation of correlated alpha particle and spontaneous fission decays involving previously known products.

Transfer Reactions. In this type of nuclear reaction there is transfer of nucleons from the projectile to the target nucleus leading (of interest to us) to products with atomic numbers all the way from that of the target nucleus to that of the compound nucleus. (The transfer of just a couple of nucleons is also referred to as quasielastic scattering and the transfer of a large part of the projectile is alternatively referred to as "massive transfer" or "incomplete fusion".) These reactions seem to result from the more peripheral collisions (those with larger impact parameters) and higher angular momentum. The product nuclei are not so strongly focused in the forward direction as in the case of the compound nucleus mechanism. For light heavy ions and heavy target nuclei, of primary interest to us, the protons transfer preferentially from the projectile nucleus to the target nucleus, a tendency that can be understood by considering the potential energies of the systems near contact.[14]

One of the first and more careful studies of these heavy ion "transfer" reactions involving production of transuranium nuclei was done by Hahn et al.[15] This remains one of the few studies in which kinematic measurements were attempted. Hahn et al. studied the excitation functions, recoil range distributions and angular distributions of the heavy transuranium recoil products. In particular, they studied the characteristics of the production of ^{245}Cf and ^{244}Cf via the transfer reactions ^{239}Pu (^{12}C, α2n) and ^{239}Pu (^{12}C α3n) and via the complete fusion reactions ^{238}U (^{12}C, 5n) and ^{238}U(^{12}C, 6n). As expected, the complete fusion reaction products are strongly forward focused with their angular distribution peaked at 0° and show Gaussian range distributions with mean ranges that increase with increasing projectile energy and whose values agree with the assumption of complete fusion. The same $^{244,\,245}$Cf products when produced in the transfer reaction show angular distributions which peak near the complement of the grazing angle and show asymmetric range distributions whose mean value decreases with increasing projectile energy. The yields of $^{244,\,245}$Cf are much larger in the transfer reactions compared to the complete fusion reactions. The yields of the transfer products are described by Hahn et al. with modest success using a modification[16] of the semi-empirical Sikkeland systematics of product yields in heavy fusion reactions.[17,18] These calculations indicate that the reason for the higher product yields in the transfer reaction is the relatively cold residual nucleus produced in this reaction compared to the complete fusion reaction.

Demin et al.[19] used multi-nucleon transfer reactions to produce ^{246}Cf, $^{251,\,253}$Es, $^{250,\,254}$Fm, and ^{256}Md from ^{249}Cf using ^{22}Ne projectiles. Perhaps the most significant of the recent "transfer" reaction studies as far as creating interest in these reactions as useful tools for transuranium nuclide synthesis is the work of Lee et al.[20] Lee et al. measured the yields of heavy actinides formed in the interaction of near barrier energy ^{16}O, ^{18}O, ^{20}Ne and ^{22}Ne with

^{248}Cm. In a follow-up to this work, Lee et al.[21] measured the excitation functions for the production of isotopes of berkelium through fermium in bombardments of ^{248}Cm with ^{18}O ions and of isotopes of berkelium through nobelium in bombardments of ^{249}Cf with ^{18}O ions.

Schädel et al.[22] measured the distributions of heavy actinide products from reactions of ^{18}O and ^{22}Ne with ^{254}Es and found greatly enhanced yields, by many orders of magnitude, especially for neutron-rich products, of mendelevium and nobelium isotopes as compared with those produced by the same projectiles with ^{248}Cm or ^{249}Cf targets. For example, the yields of $\Delta Z = 2$ products - californium isotopes from ^{248}Cm and mendelevium from ^{254}Es - were approximately equal, indicating the tremendous advantage of using a ^{254}Es target for the production of the heaviest actinide isotopes.

Apparently, in one reaction mode, at the higher energies, for these transfer reactions the projectile breaks up elastically in the nuclear field with the breakup probability having a maximum for the grazing angle (the angle of deviation from the original direction for a projectile nucleus making a peripheral collision with a target nucleus). A fragment of the projectile fuses with the target nucleus, while the remainder of the projectile carries away a large amount of the available energy as kinetic energy, thus reducing the excitation energy of the target plus the absorbed fragment and producing a cold nucleus. The excitation functions appear to be consistent with calculations[23] based on simple energy balance considerations using the masses of the projectile, target nucleus, and products and assuming the energy of the projectile in excess of the Coulomb barrier is apportioned to the target nucleus according to the fraction of the projectile mass transferred. At energies close to the reaction barrier the quasielastic transfer mechanism apparently prevails.

Extrapolations of the yield curves suggest that higher energy transfer reactions may provide a means of producing new neutron-rich isotopes of known elements. In this process, at least formally, such transfer reactions provide a source of exotic projectiles. For example, ^{22}Ne could give rise to ^{21}F capture, and ^{18}O to ^{17}N capture. This mechanism, with heavier projectiles such as ^{48}Ca, might offer another route to superheavy elements.

Somerville _et al._[24] have produced a number of interesting isotopes that decay via spontaneous fission, by bombarding heavy transplutonium nuclei with light heavy ions. These include an isotope with a half-life of about 100 milliseconds, produced with the unexpectedly large cross section of a microbarn by the bombardment of ^{254}Es with ^{18}O ions. Another interesting isotope, presumably ^{260}Rf (element 104), produced by the reaction of ^{15}N ions with ^{249}Bk nuclei and by other reactions, has been shown by Hulet _et al._[25] (when produced by the reaction of ^{15}N ions with ^{249}Bk nuclei) to decay with an unusual symmetric distribution of fission products. This may indicate that the reactions and decay of nuclei in this region may be governed by a single fission barrier, in contrast to the doubly humped fission barrier characteristic of lighter heavy transplutonium nuclei.

Deep Inelastic Transfer Reactions. For heavy targets and heavy ions with $A \leqslant 40$, it has been observed that the complete fusion cross section is a very important part of the reaction cross section. By extrapolation, it was felt that this situation would continue with projectiles as heavy as krypton. Thus, the reaction of ^{209}Bi with ^{84}Kr was thought to be a possible avenue for producing transuranium nuclei. However, it was discovered in the course of this attempt to make new transuranium nuclei that the complete fusion cross section was negligibly small and that a new type of reaction, deep inelastic scattering, was occurring.[26] This failure of heavy nuclei to fuse is due to the fact that th Coulomb repulsive forces between the touching nuclei exceed the nuclear attractiv forces leading to fusion, resulting in the inability of the nuclei to interpenetrate inside the fission saddle point.[27] However, it was soon realized that this new reaction with its characteristic extensive exchange of nucleons between projectile and target nuclei during the reaction could lead to significant production of trans-target species. The reaction product mass distributions are bimodal with centroids near the target and projectile masses[28] and with distribution widths larger for high mass target and projectiles. Also the emission directions of the products are more complicated than for the other reaction mechanisms. Thus, deep inelastic transfer reactions involving uranium or heavier targets with heavy projectiles would be expected to lead to the production of transuranium nuclei with atomic numbers ranging well above that of the target nuclei.

The most significant use and understanding of deep enelastic transfer reactions to produce transuranium nuclei has been in the studies of the ^{238}U + ^{238}U reaction at the Universal Linear Accelerator (UNILAC) at GSI. The first realization of the unusual potential of this reaction for transuranium nuclide synthesis was in the work of Hildenbrand, Freiseslebén and co-workers,[29,30] who found, from reconstructed primary Z and Q value distributions, more particle transfer at a given energy loss than in other systems, i.e., the diffusion process seems to proceed colder in this system. Cold transfer is, of course, just what is needed to make the fragile transuranium species. Radiochemical studies by Schädel et al.[31] confirmed the coldness of the products from the ^{238}U + ^{238}U reaction and its implications. A somewhat expanded version of these studies has been reported by Gäggeler et al.[32] The distribution of target-like fragments from the deep inelastic reaction peaks at Z = 91 rather than Z = 85 (as found in the Xe + U reaction[33]) or Z = 79 (as found in the Kr + U reaction[34]). Thus, the "goldfinger" (as this feature was dubbed in Reference 34) had become the "Protactinium finger". This upward shift of Z of the peak of the survivor distribution and its broadening are further indications of the colder diffusion occurring in this system. Reconstruction of the primary target-like fragment distribution led to an estimation of the production cross section of Z = 70 fragments, in this reaction of 10^{-28} cm^2 which, under the assumption of a binary process, must also be the estimate of the primary fragment yield of the superheavy element 114 in this reaction.

The fact that the transuranium element distributions have the same general shape in the U + U and Xe + U reactions and the fact that the centroids and widths of the distributions change little with projectile energy[35] can be understood in terms of the fact that despite changes in the primary distributions with projectile Z, A and E, only those few nuclei in the low excitation energy, low J angular momentum tails of the primary distributions will survive fission. The principal advantage of the U + U reaction is that because of the generally broader primary product distributions, the number of nuclei in the tails of the distributions increases enormously.

As a logical follow-up to the work with the ^{238}U + ^{238}U reaction, Gäggeler et al.[32] and Schädel et al.[36] have reported the results of attempts to produce transuranium nuclei in the reaction of 7.4 MeV/u ^{238}U with ^{248}Cm. The shapes and centroids of the isotopic distributions are similar to those observed in the ^{238}U + ^{238}U reaction, but the magnitudes of the yields are much greater in the ^{238}U + ^{248}Cm reaction. For example, the ^{238}U + ^{248}Cm reaction gives $\sim 10^4$ times more Cf, and 10^3 times more Fm than the ^{238}U + ^{238}U reaction. Gäggeler et al.[32] extrapolate to a 10^2-fold enhancement in the Md and No yields in the ^{238}U + ^{254}Es reaction and a $\sim 10^3$-fold enhancement in the Lr yields.

Unfortunately, however, no products beyond Z = 101 were observed even in the ^{238}U + ^{248}Cm reaction, indicating that the deep inelastic transfer will not provide a route to new transuranium elements, although it should provide a route to new transuranium isotopes.

TECHNIQUES FOR IDENTIFICATION OF TRANSURANIUM REACTION PRODUCTS

General. In the study of heavy ion reactions resulting in transuranium products, it is of paramount importance to be able to isolate and uniquely identify the products as to their atomic number (Z), mass number (A) and formation cross section. Indeed the claim to discovery[2] of a new element must involve identification of Z, while the claim of discovery of a new nuclide must involve measurement (and/or deduction) of both Z and A. Nitschke[37] has classified the commonly used techniques of isolating transuranium reaction products by the half-life ($t_{\frac{1}{2}}$) of the products and the minimum detectable cross section. His classification scheme is shown in Figure 1. Some of the isolation techniques shown in Figure 1 such as chemistry, magnetic spectrometers, etc., can also serve as methods of establishing the Z and/or A of the species involved.

Chemical Methods. For reaction products with the longest half-lives, chemical separation techniques offer a convenient method of isolating individual reaction products and establishing their atomic numbers. These techniques offer the greatest sensitivity of all methods because of the large amounts of target material that can be used.

A typical example of the use of chemical techniques to study heavy ion reactions is the effort of Kratz, Herrmann and their co-workers at GSI[38,39] to study the production of trans-target actinides and possible superheavy elements formed in the reaction of ^{238}U with ^{238}U. The chemical problems involved in these studies are formidable. Because of the large cross sections for deep inelastic scattering and the high fissionabilities of the transuranium nuclei, the sought after actinide (Fm, Md) production cross sections are approximately 10^7 less than those of interfering Ra, Ac and Th activities. The separation scheme used is illustrated in Figure 2 and involved the use of four linked chromatographic columns, three of which involved high performance liquid chromatography techniques. A chemical yield of 80-90% with a separation factor of greater than

10^7 was achieved. Similar chromatographic techniques were used by Unik et al.[40] to study actinide production in proton-irridated U targets while ion exchange procedures devised by Kratz, Liljenzin and Seaborg[41] and Lee et al.[20] have been widely used in heavy ion reaction studies at Berkeley.

The Helium Jet, Drums, Tapes and Wheels. For species with half-lives in the range from $0.1 \leqslant t_{\frac{1}{2}} \leqslant 10$ sec, the helium jet is a superior method of isolating reaction products, as witnessed by its use in the discovery of new elements.[7] In this method, first developed by Ghiorso et al.,[42] Friedman and Mohr,[43] and McFarlane and Griffoen,[44] reaction products recoiling from the target are thermalized in helium gas at approximately one atmosphere pressure which leaves the target chamber via a connection to a low pressure area, creating a "jet" or stream of helium[45] (Figure 3). The helium gas stream impinges upon a collection device such as a tape or wheel or drum which moves the activities to the detectors. The selectivity of the jet system may be improved by performing a gas phase chemical separation in the jet during transport of the stopped recoils.[46]

Identification of the collected reaction products can be made with a variety of techniques. Perhaps the most important of these techniques is the "mother-daughter" or "double-recoil" method which establishes a genetic link between the unknown reaction product and known daughter and/or granddaughter activities. In this technique (see Figure 3), the recoil heavy atom produced by the alpha-decay of the collected initial reaction product strikes and imbeds itself in a "mother crystal". The mother crystal is then moved in front of a "daughter crystal" which can detect the alpha-decay of the imbedded atom in the mother crystal. The procedure can be extended to detect additional descendents in the alpha-decay chain. If the alpha particle decay characteristics of the daughter, granddaughter, etc., nuclei are known, then a genetic link is established and the (Z, A) of the parent are established. This technique was used in the discovery of several elements and isotopes.[47,48,7,49]

A newer technique of exceptional power to identify the Z of collected reaction products is the X-ray method.[50] In this technique the coincidences between the alpha particles emitted by the decay of the collected recoils and the K X-rays of the daughter nuclei (produced as a result of internal conversion decay in the daughter) are observed. The energies and relative intensities of the X-ray lines [50,51] serve to identify the Z of the daughter, and therefore the parent nucleus.

For species whose half-lives are in the range 1 ms $\leq t_{\frac{1}{2}} \leq$ 100 ms, the product collection device is placed in close proximity to the irradiated target and catches the recoils emerging from the target directly. In such systems, the heavy ion beam after passing through the target will strike the collection surface (drum, tape, etc.). Schematic diagrams of two such collection devices, are shown in Figures 4 and 5.[52] Unfortunately, such devices offer no selectivity as to which reaction products are collected, the recoils are usually implanted so deeply that alpha spectra are those obtained from a very thick source, and it is difficult to detect the radioactive decay of the reaction products amidst a high beta particle background. Therefore these devices are used frequently to detect new spontaneously fissioning nuclides. Since spontaneous fission cannot, in general, be used to identify the Z and A of the fissioning system, experimenters frequently resort to arguments based upon nuclear reaction energetics, systematics and excitation functions to identify the collected products. Such identifications are generally considered unreliable and make up the bulk of those identifications classified as E, F and G by the Table of Isotopes compilers.[53]

Magnetic Spectrometers, Velocity Filters. The principal problem with the isolation devices discussed above (tapes, jets, etc.) is that the reaction product must be stopped and mechanically transported to radiation detectors before product identification can occur. This restricts their use to studies of nuclei whose $t_{\frac{1}{2}} \geqslant 1$ ms. For detection and identification of species whose $t_{\frac{1}{2}} \geqslant 1$ μs, an instrument based upon magnetic and/or electrostatic deflection of target recoils can be employed. One of the most successful of these devices in recent years is the velocity filter SHIP located at the UNILAC at GSI.[54,11] A schematic diagram of this separator is shown in Figure 6. Evaporation residues produced in a nuclear reaction emerge in the forward direction from the target and pass through a thin carbon foil which has the effect of equilibrating the ionic charge distribution of the residues. The ions then pass through two filter stages consisting of electric deflections, dipole magnets and a quadrupole triplet for focusing. The solid angle of acceptance of the separator is 2.7 msr with a separation time for the reaction products of approximately 2 μs. Since complete fusion evaporation residues have very different velocities than target-like transfer and deep inelastic products, the separator with its ± 5% velocity acceptance range effectively separates the evaporation residues from other reaction products. Following separation, the residues pass through a large area time of flight detector and are stopped in an array of seven position-sensitive detectors. From their time of flight and their energy deposit in the position-sensitive detectors, a rough estimate of their mass may be obtained. The final genetic identification of the residues is made by recording the correlations between the recoil position in the detector and subsequent decay signals from alpha or spontaneous fission decay or even signals from ~~gamma~~ or X-Ray detectors placed next to the position-sensitive detector. This device has been used in the discovery of element 107[11] and element 109[13] and the identification of the new nuclides ^{247}Md, ^{243}Fm and ^{239}Cf.[12]

Separators like SHIP are quite expensive and represent major instrumentation projects. A less sophisticated spectrometer which costs considerably less and provides the capability to measure the formation cross sections, recoil range distributions and angular distributions of short-lived ($t_{\frac{1}{2}} \geq 1$ ms) alpha emitters formed in heavy ion reactions has been described by Dufour et al.[55]

Another type of device used to isolate and identify transuranium nuclei ($t_{\frac{1}{2}} > 1$ μs) is the gas-filled mass separator, typified by the separator SASSY (Small Angle Separator System) in use at the Lawrence Berkeley Laboratory.[56] In this system (Figure 7) the heavy product recoils from a nuclear reaction enter a helium-filled (1 torr pressure) magnetic spectrometer. The time of flight and energy of the recoil nuclei are measured, giving a rough determination of the product mass number. The recoil nuclei which are imbedded in the focal plane detectors are identified by their alpha-particle decay and the decay of their daughters. SASSY has been used to discover a new $_{86}$Rn isotope produced in the bombardment of $_{50}$Sn nuclei with $_{86}$Kr projectiles,[57] and its efficacy in the transplutonium region has been demonstrated by its use to observe the production of ^{254}No from the ^{208}Pb (^{48}Ca, 2n) reaction.[58]

Time of Flight, Decay in Flight and Blocking Techniques. To detect species whose lifetimes are substantially less than 1 μs, special techniques must be employed. They include time of flight (TOF) techniques which when combined with a measurement of the product energy will give information about the product mass number. For suitable mass resolution, the time of flight must be approximately 10-100 ns. When searching for rare events, some selection process (like SHIP or SASSY) must be employed to reduce the "background" levels in the apparatus. The decay in flight (DIF) technique whose use is described in Reference 59, and the crystal blocking technique[60] ($10^{-18} < t_{\frac{1}{2}} < 10^{-14}$ sec.) give very little information about the identity of a reaction product other than its existence and its approximate lifetime.

FUTURE DIRECTIONS

New Technical Developments. Of the chemical isolation and identification techniques to be used in the future, those capable of being used for short half-lives are likely to find the most use. The aqueous chemistry and volatility separation techniques[61] that have been used in off-line experiments will need to be further adapted to on-line operations to make it possible to detect short-lived products. The use of volatility separation techniques is of particular interest because some of the superheavy elements have been predicted to be very volatile (number 112) or quite volatile (number 114) in the elemental (metallic) form.[62] In addition, chemical isolation and identification techniques will probably use the more modern physical chemical techniques. An example of these techniques is the use of lasers[63] to do single atom detection as in the work of Bemis et al.[64] to measure the optical isomer shift for the 1 ms spontaneously fissioning isomer ^{240}Am. The other traditional identification techniques involving genetic identification via observations of decay chains or direct measurement of product Z by X-ray or photoelectron detection appear to be quite applicable to short half-life species, especially with improvements in detector efficiency. Clearly the fast isolation techniques such as the magnetic spectrometers or velocity separators will have special importance particularly if adapted to study transuranium nuclide production by a variety of different reaction mechanisms. For a number of the transuranium production methods of the future, new target technologies, similar to those currently used at the ISOLDE facility for p-nucleus reactions,[65] to allow the use of higher intensity, heavy ion beams, will have to be developed.

Light Heavy Ion Transfer and Deep Inelastic Transfer Reactions. As indicated above, current research in the use of light heavy ion transfer[20,21,22] and deep inelastic transfer[32,36] reactions has progressed far enough to indicate that transfer reactions involving heavier targets such as ^{249}Cf or ^{254}Es could lead to the production of more neutron-rich heavy actinides. It should be possible to produce and identify important new isotopes of transactinide elements. In addition to the near transactinide elements, the possibility might extend as far up as the superheavy elements. Hoffman[66] has speculated that in the ^{48}Ca + ^{248}Cm reaction, one might be able to produce $^{288}112$ or $^{291}113$ in a relatively "cold" manner.

Cold Fusion Reactions. The success in synthesizing elements 107 and 109 using cold fusion reactions has revived interest in the use of the ^{48}Ca and ^{248}Cm reaction to make superheavy elements. Current attempts,[67] still in progress, to synthesize superheavy nuclei with the ^{48}Ca + ^{248}Cm cold fusion reaction, are using bombarding energies closer to the interaction barrier. These collaborative experiments are using off-line chemical, including volatility, procedures and the on-line detection devices SASSY at LBL and SHIP at GSI. Previous experiments[68,69] that give negative results had been carried out at approximately 20 MeV above the barrier because theoretical estimates indicated that beyond a certain critical size of projectile and target, an extra energy above the interaction barrier would be required to fuse the nuclei.[70-72] The critical nuclear sizes, above which this "extra push" phenomenon would set in, were not known at the time. If the ^{48}Ca + ^{248}Cm system turned out to be beyond the critical size, then an extra bombarding energy would be needed for fusion, but whether this would do more harm than good was an open question. Experimental confirmation of the extra push phenomenon is accumulating in recent studies,[73-78] and estimates of the critical nuclear reaction sizes are becoming available. They indicate that the ^{48}Ca + ^{248}Cm reaction is, indeed, close to the critical condition, but the qualitative description of the extra push phenomenon and of the subsequent fission vs. neutron emission competition is not sufficiently precise to enable one, even now, to decide whether an extra bombarding energy would or would not be advantageous as regards the final probability of making a superheavy nucleus. It is still necessary to make a careful experimental study of the relevant cross sections as a function of energy, in a range from somewhat below to somewhat above the interaction barrier.

Secondary Beams. One interesting idea for using heavy ion reactions to synthesize transuranium nuclei has been put forth by Dufour, Fleury and Bimbot.[79] The basic idea is to use a heavy ion reaction to create an "exotic" secondary beam with which to do the actual synthesis reaction. The principal difficulty is that such processes involve the product of the probabilities of two events, the initial beam generation reaction and the synthesis reaction. However, as Dufour, Fleury and Bimbot show, there are some particularly attractive secondary beam possibilities. For example, with the use of projectile fragmentation reaction in the intense 10^{12} part/sec 86 MeV/n heavy ion beams at the Synchro-Cyclotron (SC) at European Organization for Nuclear Research (CERN), one might expect to produce ^{16}C beams with an intensity of approximately 10^9 part/sec. The use of such neutron-rich secondary bemas in complete fusion reactions might lead to the production of 10-100 atoms/hr of ^{260,261}No. Similar studies with proton-rich secondary beams are estimated to produce 10^1-10^2 atoms/hr of ^{237,238,239}Bk. These examples are only illustrative of the many possibilities.

Exotic Targets. Because of its large number of neutrons (155) the isotope ^{254}Es may be the best route to the synthesis and identification of the superheavy elements. This is the case if nuclear species containing 184 neutrons or very close to 184 neutrons must be produced in order to have a half-life sufficiently long to be detectable. To reach this goal ^{48}Ca would have to be used as the projectile. This combination might produce a nuclear species containing 182 neutrons by a reaction utilizing the one neutron channel (cold nucleus intermediate) as follows:

$$^{254}_{99}\mathrm{Es} + ^{48}_{20}\mathrm{Ca} \rightarrow ^{301}119 + n$$

The isotope ^{254}Es is difficult to produce even in microgram quantities, but it is probably the best available target material. Other possibilities are more difficult to realize. The isotope ^{255}Es as target material could lead to an odd-odd nuclear species with 183 neutrons (even more desirable), but it would be very difficult to produce more than nanogram quantities reasonably free of its intensely radioactive precursor (^{253}Es) in the chain of neutron capture reactions required for its production; the 40-day half-life of ^{255}Es is more difficult to deal with than the 275-day half-life of ^{254}Es.

Another desirable material is ^{250}Cm, with 154 neutrons, but this could be made available only by recovering it from the debris of underground nuclear explosions, an expensive undertaking. Here the one neutron channel with the reaction:

$$^{250}_{96}\mathrm{Cm} + ^{48}_{20}\mathrm{Ca} \rightarrow ^{297}116 + n$$

would produce a product of smaller atomic number (presumably an advantage) with 181 neutrons.

IMPORTANCE OF TRANSPLUTONIUM RESEARCH

There is much to be learned about nuclear reactions and their products by continuing and extending the study of the reactions of heavy ions with transplutonium target nuclei. Especially through the use of the heaviest available target nuclei, such as ^{248}Cm, ^{249}Cf, and ^{254}Es, and possibly ^{250}Cm and ^{255}Es, it will be possible to produce interesting new high Z actinide and transactinide isotopes. The determination of their decay properties will make it possible to determine the role of the 152 neutron shell in this region.

With the competing fission reaction playing a role as a monitor of nuclear temperature it should be possible to reach a better understanding of the puzzling mechanism of transfer reactions initiated by light heavy ions. Similarly, the competing fission reaction should provide an additional dimension in helping to measure the distribution of excitation energy as a function of the number of nucleons transferred in the deep inelastic transfer reaction initiated by the heaviest heavy ions, and in studying the degree of coldness of heavy nuclei produced in fusion reactions. Such information should also throw light on the behavior of nuclei as a function of angular momentum.

If it should prove possible to produce and identify superheavy elements, we will learn much about fission barriers and the nature of closed shells in a region of proton and neutron numbers well beyond where we now have an understanding of these quantities. The nuclear decay properties of superheavy elements are impossible to predict with any degree of accuracy and thus an experimental knowledge of these properties, and the decay sequences of genetically related nuclei, would provide information to put our understanding of the nuclear structure of the very heaviest nuclei on a sounder basis.

The chemical properties of the superheavy elements will be of extraordinary interest because of the importance of relativistic effects in determining their electron configuration.[62] For example, the six 7p electrons are predicted to be split into two groups, four $7p_{3/2}$ and two $7p_{1/2}$ electrons, with the splitting between their energies being such that the filled $7p_{1/2}^2$ subshell will act as a closed shell and additional $7p_{3/2}$ electrons will act as electrons outside a closed shell. As an example of this effect, element 115 (ekabismuth) is predicted to have its valence electrons in the configuration $7p_{1/2}^2\ 7p_{3/2}$ with a stable +1 oxidation state, in contrast to the stable +3 oxidation state of its homologue bismuth. Thus chemists are excited about this possibility of studying "relativity in a test tube". The chemical properties of the near transactinide elements which have not been studied so far (105, 106, etc.)

should be compared with those of their homologues (tantalum, tungsten, etc.).

Research concerned with the limits of the periodic table of elements has been growing more and more demanding as the lifetimes of the isotopes in question decrease into the millisecond range or less, and the cross sections for producing them plunge into and below the nanobarn regime. Past progress in this field has already relied heavily on having available the right targets and projectiles. There are many examples where the substitution of one combination for another can improve the cross sections for making the desired isotope by orders of magnitude. This situation will become ever more drastic in the future, when it will be more and more common that a new element or isotope can only be made in a single, highly specific reaction, involving a unique combination of target and projectile. In particular, it is clear that reaching the predicted island of superheavy elements will not be easy, and if this quest is eventually crowned with success, it will most likely involve exotic transplutonium targets such as ^{248}Cm, ^{250}Cm, ^{254}Es or ^{255}Es. A whole area of research at the extreme limits of the periodic table may then hinge on the availability of some such exotic target material: only the laboratory fortunate enough to have access to such a target will be able to explore this field of research. If on an expedition you come to a crevasse 20 feet wide and want to explore the land beyond, you either have a 20+ foot plank available or you don't reach that land. A 19 foot plank will not do.

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FIGURE CAPTIONS

Figure 1. Classification of techniques used to isolate transuranium reaction products by minimum detectable $t_{\frac{1}{2}}$ and production cross section. See text for a discussion of these techniques. (From Reference 37.)

Figure 2. Schematic diagram of chemical procedures used by Schädel *et al.*[36] to isolate actinide elements from heavy ion irradiated U targets.

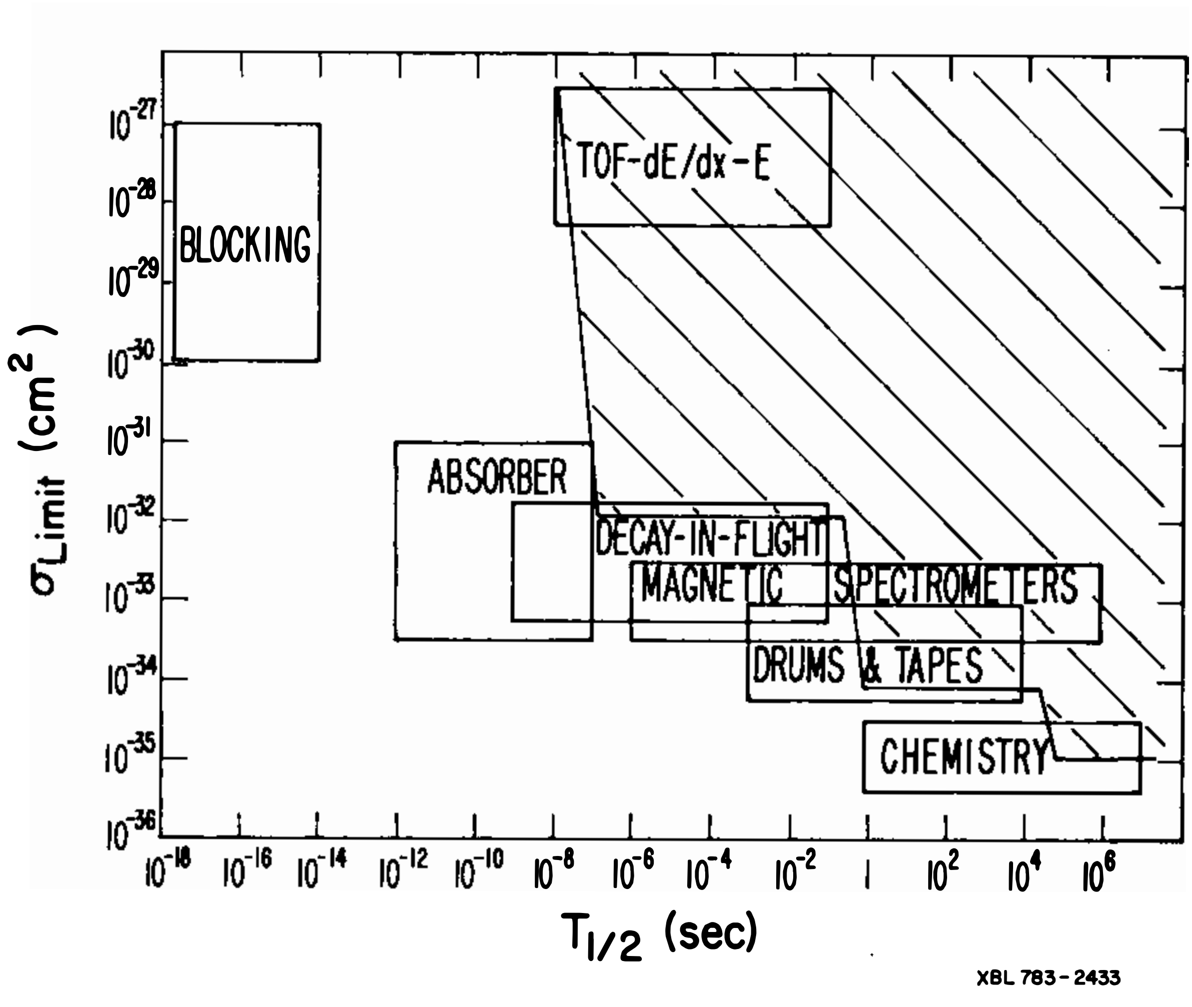
Figure 3. Schematic representation of a "gas-jet" recoil transport assembly. Thermalized product atoms are transported in the He gas stream and collected on the periphery of a wheel or other suitable collection device. Periodically, the wheel is moved to position the spot in front of the detectors. A "mother-daughter" detector assembly is illustrated in the lower portion of the figure and is used to establish a genetic link. From Bemis (Reference 45).

Figure 4. Rotating and scanning drum system for the detection of short-lived spontaneously fissioning nuclei. (From Reference 52.)

Figure 5. Details of a tape system for the collection and detection of short-lived spontaneously fissioning nuclei. (From Reference 52.)

Figure 6. A schematic diagram of the velocity filter SHIP at GSI.

Figure 7. A schematic diagram of SASSY at LBL.



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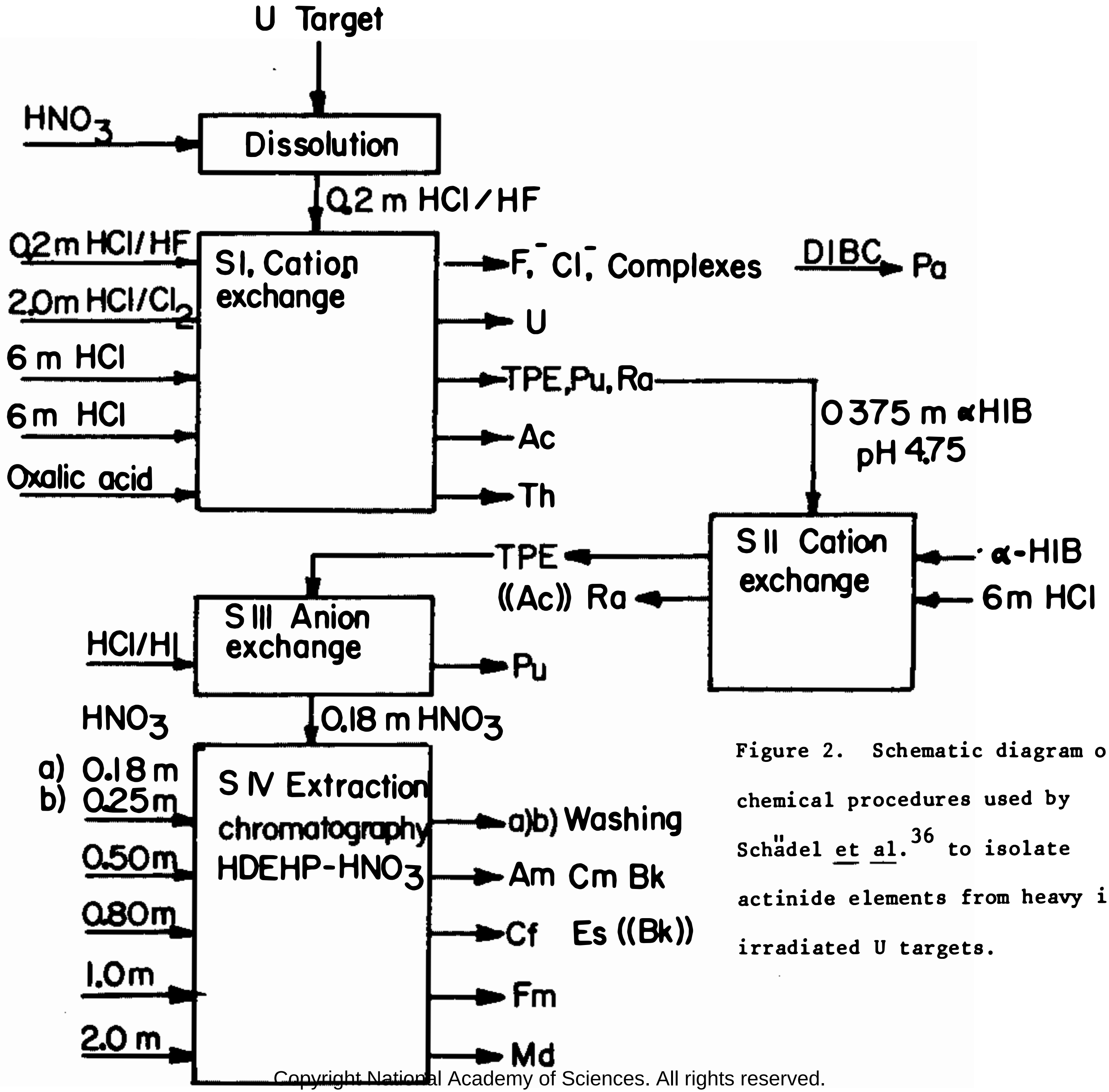

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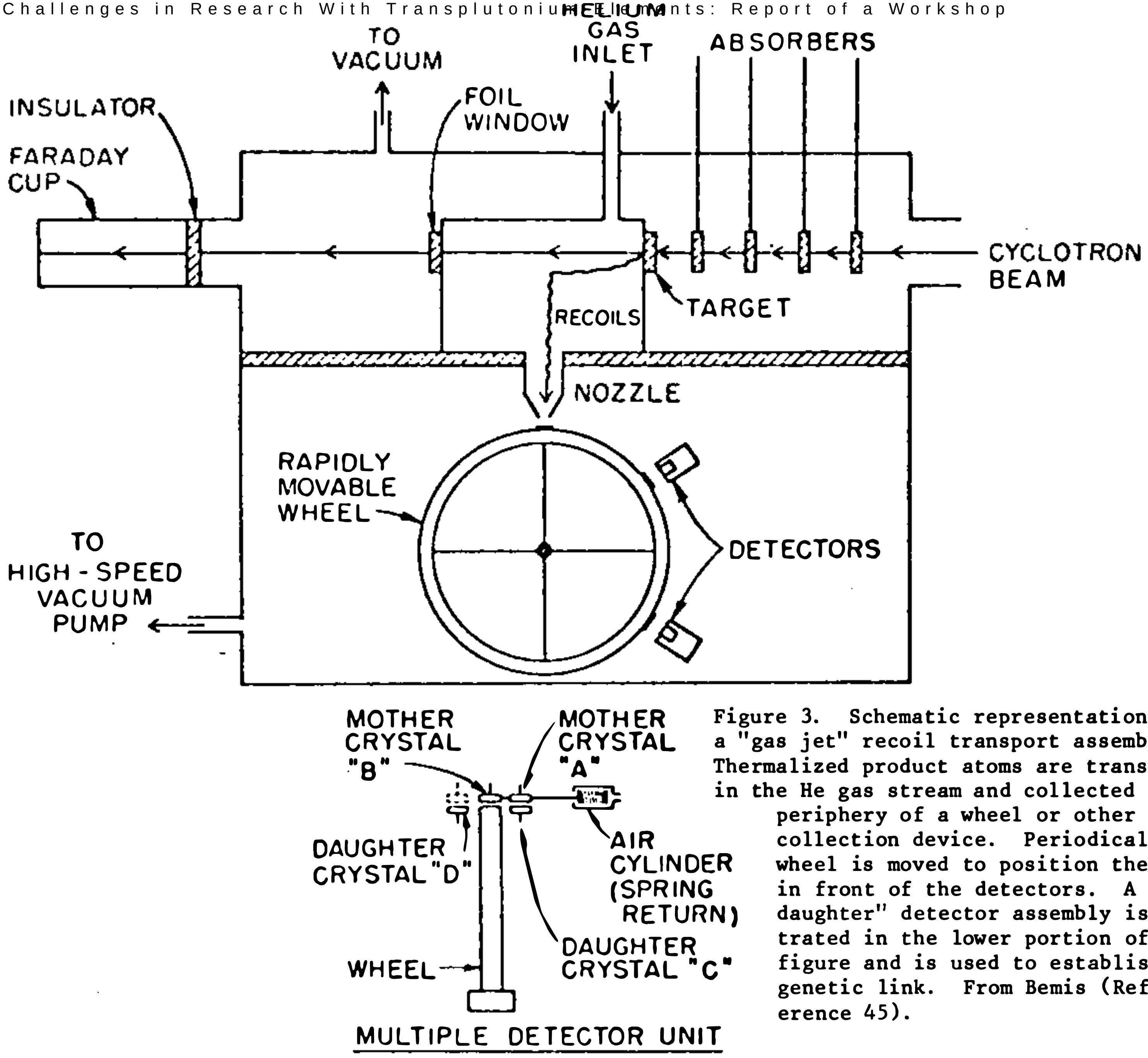

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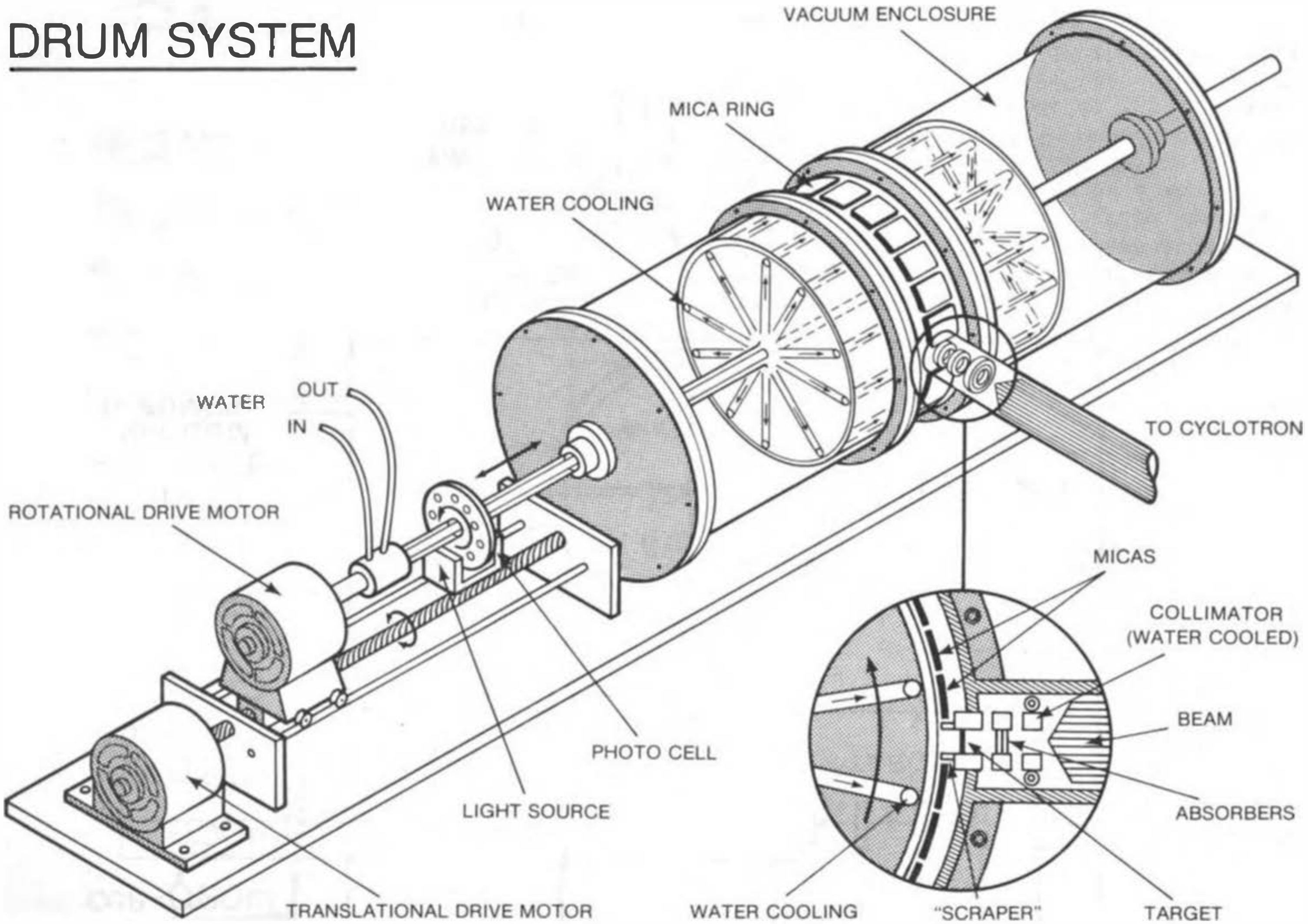
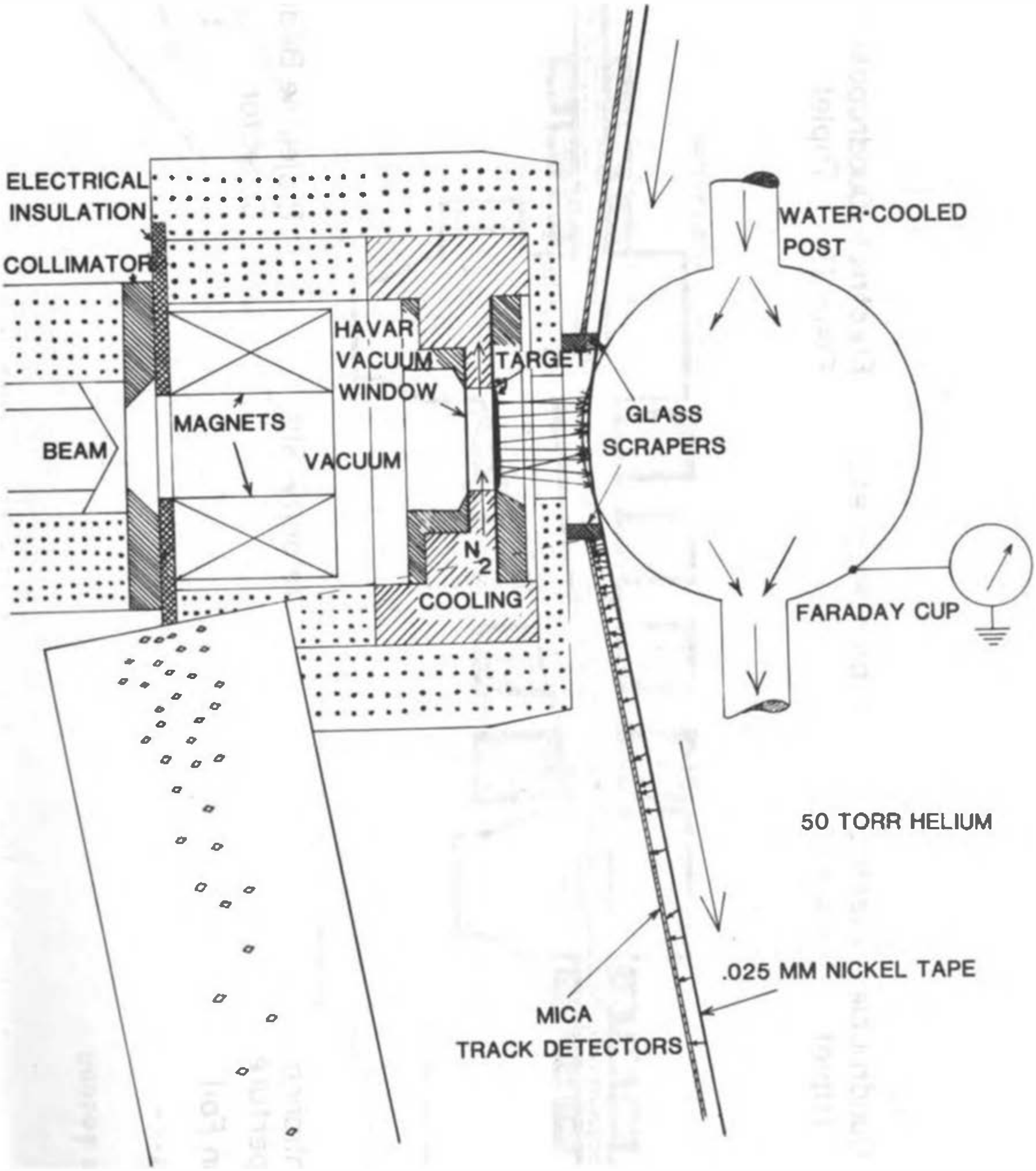


XBL 7912-13728

Figure 4. Rotating and scanning drum system for the detection of short-lived spontaneously fissioning nuclei. (From Reference 52.)



XBL 799-11395

Figure 5. Details of a tape system for the collection and detection of short-lived spontaneously fissioning nuclei. (From Reference 52.)

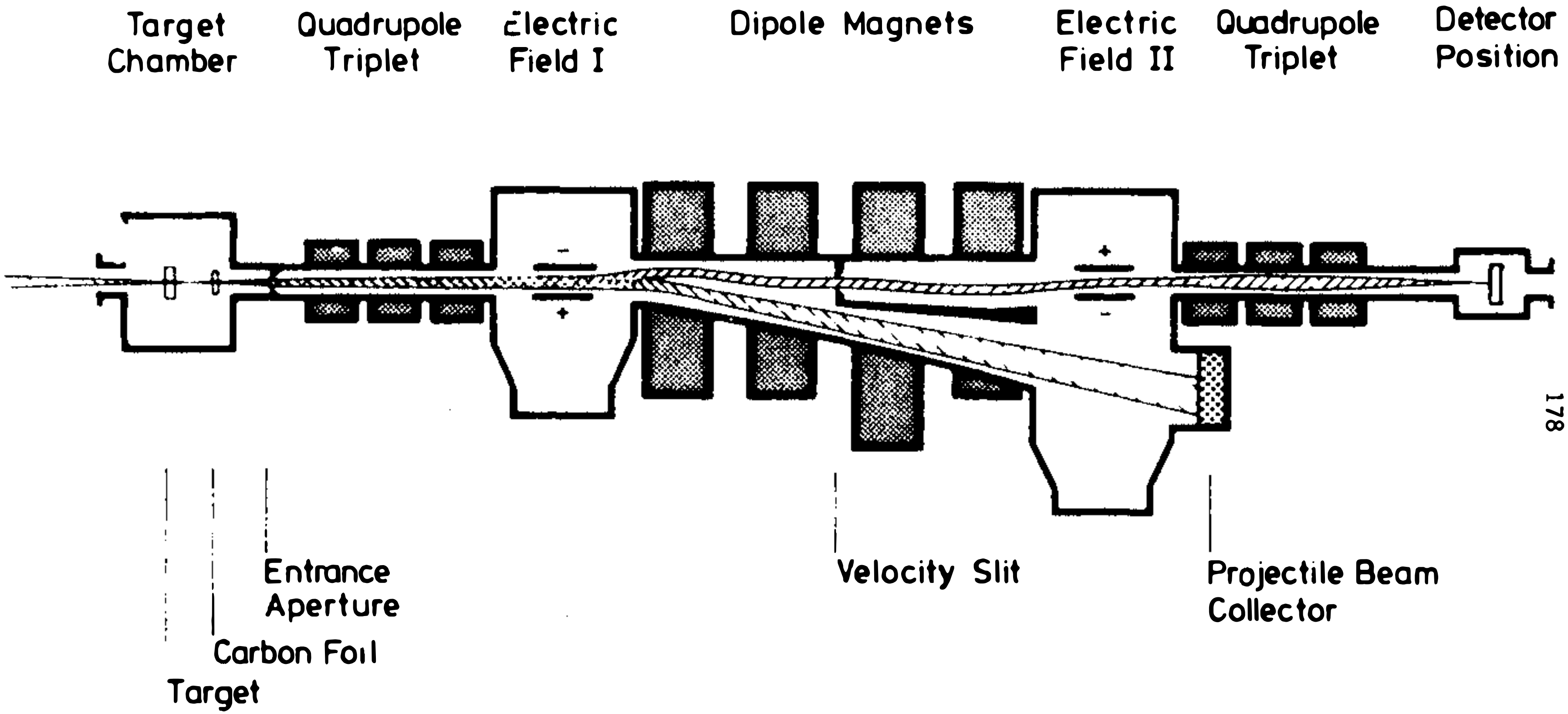
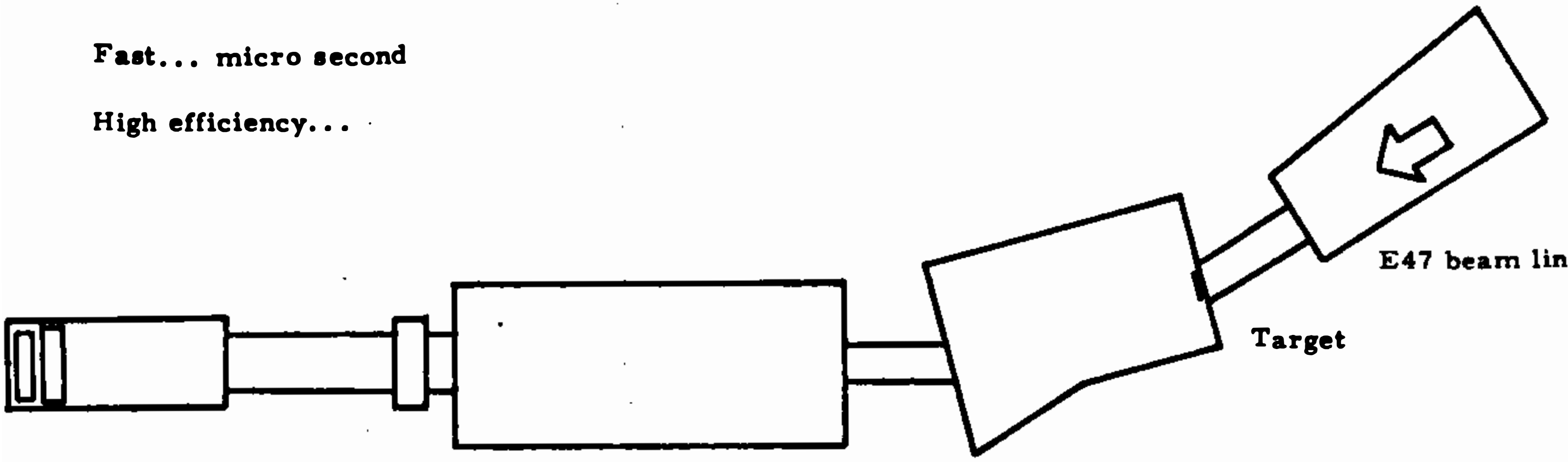


Figure 6. A schematic diagram of the velocity filter SHIP at GSI

SASSY (Small Angle Separator SYstem)

Fast... micro second

High efficiency...



Detector Array

a. 2 position sensitive proportional counters

b. 10 Si crystal array

Recoil energy

α, S.F

Quadrupole Magnet

Time of flight

Bending Magnet

a. Suppression of beam.

b. Mass separation.

14 feet from target to focal plane

Operating in 1 torr He

Figure 7. A schematic diagram of SASSY at LBL

APPENDIX E

DIRECTIONS FOR NUCLEAR RESEARCH IN THE TRANSPLUTONIUM ELEMENTS

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INTRODUCTION

The heavy element region has long constituted, and continues to constitute, one of the frontiers of nuclear research. If the study of nuclides with mass greater than 230 were restricted to nuclides found in nature, research in this area would be limited to the study of the properties of ^{232}Th, ^{234}U, ^{235}U, ^{238}U, and trace amounts of ^{244}Pu. In fact, 200 nuclides with $A > 230$ have been identified$^{1)}$ and studied. This represents one of the major achievements of physical research in the twentieth century, and it is made possible by the availability of reactor produced Transuranic elements.

The study of the heavy nuclides has played a vital role in our understanding of the alpha decay process, nuclear fission, nuclear binding energies and the limits of nuclear stability. This study has led to the understanding of novel shape degrees of freedom, such as the very large quadrupole deformations associated with the fission isomer$^{2)}$ process, and the very recently discovered octupole$^{3)}$ deformation. The existence of these unique phenomena in the heavy element region is not accidental. Fission isomerism is due to the delicate balance between nuclear forces holding the nucleus together and Coulomb forces causing nuclear fission. Octupole deformation arises from the increasing strength of matrix elements with increasing oscillator shell. Both illustrate the unique features of the heavy element region. Fission studies have given us information about large collective aspects in nuclei and the importance that nuclear structural effects can play in altering these macro properties. A new class of atomic studies has become possible with the availability of heavy elements. With these isotopes, we are now able to produce electric fields of such magnitude that it becomes possible to spontaneously create positron-electron pairs in the vacuum.

Much has been gained in our knowledge of physical properties from the study of the heavy elements and much is still unknown, awaiting future developments. Success in these studies will be proportional to the support provided for the continued production of the required heavy element isotopes as well as that provided for the scientific studies which will use these products. Without support for both, the possibilities of understanding the properties of the heavy elements and the fundamental limits of nuclear stability will be greatly restricted.

We have organized this presentation into three major sections: nuclear structure, fission studies and atomic studies of supercritical systems. In each we will try to emphasize the new directions which can benefit from the continued availability of isotopes supplied by the Transplutonium Production Program.

NUCLEAR STRUCTURE OF THE HEAVY ELEMENTS

In this section we present information on the nuclear structure properties of the heavy elements and the important role played by the Transplutonium Production Program in supplying these isotopes. However, we feel that a restriction of the discussion to only Transplutonium elements makes an artificial demarcation in the heavy element region. It makes much more sense to discuss heavy elements in their entirety. Only in this context, is it clear what is the role of Transplutonium elements in answering the important scientific questions in the heavy element region.

Our understanding of the important nuclear properties in this mass region is intimately related to our understanding of the nuclear single-particle potential, and the orbits of nucleons in this potential. Through an appropriate choice of the nuclear single-particle potential, many aspects of nuclear structure can be simply understood and many residual interaction effects can be taken into account in a simple way. We organize this section around the quadrupole deformed single-particle potential and the valence orbitals of this potential in the heavy element region. We then discuss the residual interactions that are important for an understanding of nuclear structure in this region. We combine this with a discussion of areas of active research and point out the value of Transplutonium isotopes in this context.

Review of Known Features

We consider a schematic Hamiltonian$^{4)}$

H = H single particle + H pairing

$$- \sum_{\lambda} V_{\lambda} \sum_{\mu} (-1)^{\mu} \sum_{i,j} < i | r^{\lambda} Y_{\lambda}^{-\mu} | j > a_i^{\dagger} a_j \sum_{k,l} < k | r^{\lambda} Y_{\lambda}^{\mu} | l > a_k^{\dagger} a_l \qquad (1)$$

where the single-particle potential might be thought of as a spherical hamonic oscillator, or more realistically, as a Woods-Saxon potential with a spin-orbit interaction. The pairing interaction plays an important role in the nuclear structure of the heavy elements, as it does in other mass regions. In this region, however, there appear to be some unique aspects of this interaction. The final term in our schematic interaction is a sum over particle-hole multipole-multipole terms. Noting the low-lying 2^+ rotational state in the even-even heavy elements, it is clear that the quadrupole-quadrupole term is most important. We consider this term in some detail as a paradigm for other residual interaction modes. The octupole (P_3) and hexadecapole (P_4) modes also play an essential role in determining the structure of the actinides. The P_6 mode may also play some role for the elements with $Z \simeq 100$.

In many instances, the total energy of a nuclide is minimized by going to a state of lower than spherical symmetry. This is a nuclear equivalent of the well known Jahn-Teller effect in molecules. In the heavy elements, the state of lower symmetry is one of cylindrical symmetry. Accordingly, we concentrate on the cylindrically symmetric components of the multipole-multipole interaction. In the state of cylindrical symmetry, the quadrupole moment operator has a non-zero expectation value. This implies a non-spherical potential for the individual nucleons. The quadrupole correlations may be treated in one of two ways. The first is to handle the full two-body quadrupole-quadrupole interaction. The second is to introduce the non-zero quadrupole moment directly into the single-particle potential by setting

$$\beta_2 = V_2 \sum_{i,j} \langle i | r^2 Y_2^0 | j \rangle a_i^\dagger a_j \qquad (2)$$

and diagonalizing this modified single-particle Hamiltonian as a function of the quadrupole deformation parameter, β_2. States of good angular momentum are then projected from the deformed intrinsic state. This second procedure incorporates most of the effects of the quadrupole correlations into our description directly and rather simply. Carrying out this procedure leads to a Nilsson diagram[4)] description of nuclear orbitals. In these diagrams, energy levels are plotted as a function of the deformation parameter. In figs. 1 and 2, we display Nilsson like diagrams for heavy element orbitals. Actually, we have used[5)] a more physically realistic deformed Woods-Saxon potential with a spin-orbit interaction.

The regions denoted A and B on these figures are those where the single-particle levels are well studied. The small area on the lower left marked B on both figures denotes the well known spherical levels near Pb. The region marked A is the deformed actinide region. Many single-particle levels in this region have been identified experimentally through a combination of decay scheme studies and of single-nucleon transfer reactions. The single-nucleon transfer reaction[6)] is often definitive, as there is a characteristic signature associated with each deformed orbital.

Apart from the deformation inducing quadrupole interaction, the most important interaction is the pairing force.[7-9)] The effect of the pairing force is to compress the level spectrum in odd mass nuclides and to produce a gap in the spectrum of even-even nuclides. In most regions of the periodic table, it has been found that a model with constant pairing force matrix elements gives an adequate description of the nuclear structure. Such is not the case in the heavy elements. Because of the large differences in radial and angular densities of orbitals near the Fermi level in the heavy elements, the deficiencies of such a simple description become apparent. One finds that a density-dependent delta interaction[10)] does give pairing force matrix elements that describe the mid-actinide region rather well. This should be regarded as a prototype of the knowledge that can be obtained by studying the heaviest elements. The large differences in radial and angular densities between orbitals such as the $j_{15/2}$,N = 7 state and the $p_{1/2}$,N = 5 state make apparent the breakdowns of simple prescriptions for residual matrix elements and point the way to more accurate ones. Using these pairing matrix elements, and experimental data, one can extract a set of single-particle level spacings for nuclei in the mid-actinide region. These level spacings vary fairly smoothly between neighboring nuclides, and the variations can be fairly well understood in terms of changes in the deformation.

In relating the extracted single-particle spacings to the magnitude of deformation parameters in this region, permanent hexadecapole deformations must also be taken into account. Here, we set

$$\beta_4 = V_4 \sum_{i,j} \langle i | r^4 Y_4^* | j \rangle a_i^\dagger a_j \tag{3}$$

and we characterize the nuclides in terms of β_2 and β_4 deformations. These deformations can be measured, in a model-dependent way, by measuring E2 and E4 transition probabilities11) in even-even nuclides. Rather than comparing extracted single-particle spectra with Nilsson diagrams, we can calculate the total nuclear energy as a function of the deformation energy. The values of β_2 and β_4 for which the energy is minimized are the equilibrium values. Such a minimization procedure is quite difficult and would involve a self consistent Hartree-Fock calculation using a fairly realistic nuclear two-body interaction. Calculations of this sort using a Skyrme interaction12) have been carried out with some success. A much faster way to determine the equilibrium values of the deformation parameters is to exploit the fact that a deformable liquid drop model13,14) gives a good overall description of nuclear binding energies. The deviations of nuclear binding energies from the smooth liquid drop trends can be quantitatively correlated with fluctuations in nuclear single-particle level densities using the Strutinsky prescription.15,16) The various calculations and experimental results for β_2 and β_4 are all in good agreement with each other.

For many multipole modes, the interaction is not sufficiently strong to lead to deformation. Yet the correlations induced by the mode may play a significant role in the description of excited states. In the actinides, these effects become important at ~800 keV. Because these vibrational states (or phonons) are so low in energy, in the actinides, one is able to study the interactions of single-particle degrees of freedom with the phonons in the actinides. The experimental observation of these particle-phonon excitations helps to determine the role of specific particle configurations (i.e., the microscopic structure) of the collective phonon. Calculationally, these configurations have been treated using refined particle phonon interaction17,18) techniques. These calculations account well for many states and transition probabilities observed in the actinide region.

The shapes and nuclear structure near ground are well understood in the mass range $230 < A < 250$.

High Spin States

There are some caveats in our claim that nuclear structure is well understood in the mid-actinide region. In the past few years, heavy ion reaction studies have been carried out on heavy element targets. One of the motivations for these studies is to explore the yrast line (this is the line connecting the lowest energy states for each value of the angular momentum, in an energy vs. angular momentum plot) of heavy elements. In the deformed rare earth region, one observes the phenomena of backbending or upbending19,20) along the yrast line. Backbending and upbending indicate two different forms of a decrease in the inertial parameter A_i along the yrast line. This parameter relates energy to angular momentum through the rotational spectrum relation

$$E_i = A_i \, [I(I + 1)] \qquad (4)$$

This sudden decrease at some critical angular momentum is thought to be due to the alignment of single-particle angular momenta along the nuclear rotation axis. The orbitals that are most important for this phenomenon are those with large values of J and small values of J_z. J_z is the projection of J, the angular momentum on the nuclear symmetry axis. Calculations invoking this rotational alignment process are fairly successful in explaining yrast lines, including backbending, in the deformed rare earths.

When similar calculations[21)] are made for actinide nuclide, one finds that sharp decreases are predicted for the inertial parameters for $10 < I < 20$. However, the experimental studies[22)] of the nuclides ^{234}U, ^{236}U, ^{238}U show no sharp decreases through $I = 28$. In ^{248}Cm[23)] there is somewhat better agreement between the calculations and the observed yrast line. There are some very recent studies of ^{244}Pu that indicate backbending. It would be most worthwhile to study the yrast lines in other heavy nuclides in order to understand the casues for the breakdown in the high spin calculations. One relevant observation is that the calculations predicting rotational alignment were made using the constant pairing force matrix elements, which we have already noted to be inadequate for the states near ground. It was found that the $j_{15/2}$ orbitals, in particular, have much larger than average pairing force matrix elements. It is just the $j_{15/2}$ neutron orbitals and the $i_{13/2}$ proton orbitals that are most important for rotational alignment. Preliminary calculations, using larger pairing force matrix elements for these orbitals, indicate[24)] a delay in the calculated onset of backbending.

We emphasize the need for measurements of the yrast line in the Transplutonium elements, to develop a better understanding of nuclides at high angular momentum.

Transition Regions: The Light Actinides and the Transplutonium Elements

The light actinide region is one of theoretical and experimental ferment at present. By the light actinides, we mean the mass region $215 < A < 230$. This is a region with few long-lived isotopes, a transition region between the spherical Pb region and the long-lived actinides with $A > 230$. The heavy Transplutonium region ($A > 260?$) forms a complementary transition region between the long-lived deformed actinides and the hypothesized/hypothetical long-lived spherical superheavy elements. Many of the phenomena being studied in the light actinides should also be searched for and studied in the Transplutonium region.

The nuclides in the light actinides are difficult to study because there are only a few long-lived isotopes. The region is equally challenging theoretically because it is one with several simultaneous (or almost simultaneous) deformation transitions. Apart from the well known onset of quadrupole deformation, one has the onset of hexadecapole deformation here. It now appears that octupole deformation[3,25,26) plays an important role in the description of some states in this region, and strong octupole correlations[25) are important for a correct description of many other states. In such a transition region, the notion of deformation parameters such as β_2 and β_4 is of rather limited value. In such cases, one must use more complicated techniques for a theoretical description; techniques that deal in some way with the full two-body interaction. One such technique, used for the study of octupole deformation, is a direct treatment of the cylindrically symmetric components of the residual interaction. Another approach that is now being applied in this region is the Interacting Boson Approximation (IBA).[27) In this approach, nucleon pairs are replaced by Bosons that carry angular momentum and the nucleon-nucleon interaction is replaced by a Boson-Boson interaction. In the simplest form of this approximation, there are S and D Bosons carrying 0 and 2 units of angular momentum, respectively. From the observations of strong octupole and hexadecapole matrix elements in this region, it is clear that the IBA will have to be extended to include large numbers of F and G Bosons. Recently observed fast E1 transitions[28,29) in this region indicate that there may be a need for P Bosons[30) as well. As there are several parameters associated with each type of Boson, it is necessary to obtain large amounts of information on spins and transition probabilities of the nuclides in this mass region to provide an adequate test of such an extended IBA. One important technique for studying a nuclide, in this detail, is the (n,γ) reaction that populates many levels[31) in a rather non-selective way (apart from spin selection rules). Gamma ray spectroscopy utilizing this reaction[32) will be valuable.

The experimental observation of octupole deformation in the light actinides should be followed up in this region by measurement of B(E3) transition probabilities and of the energy splittings of the parity doublets characteristic of octupole deformations in odd mass nuclides. These parity doublets should also be considered as a means of studying parity mixing interactions in nuclei. The single-particle orbitals that contribute most importantly to the onset of octupole deformation are the neutron orbitals $j_{15/2}$ and $g_{9/2}$; these orbitals are connected by a large E3 matrix element.

In the superheavy element region, the $j_{15/2}$ and $g_{9/2}$ orbitals also are near the Fermi level, now as proton orbitals. Somewhat more accessible are the proton orbitals $f_{7/2}$ and $i_{13/2}$ which are just below the gap at $Z = 114$ in fig. 2. The components of these orbitals with low J_z contribute to the octupole correlations in the light actinides. Just above the gap at $N = 184$ in fig. 1, we see the $h_{11/2}$ and $k_{17/2}$ orbitals. These two orbitals are also connected by a large E3 matrix element. If ever we are able to study the superheavy elements, it seems likely that we will observe many instances of octupole deformation effects. The large E3 matrix elements connecting the $d_{5/2}$ and $h_{11/2}$ neutron orbitals might lead to octupole deformations at somewhat lower neutron number. This is a strong motivation for studies of nuclear structure in the Transplutonium region.

In the transition region, just beyond Pb, there are two unique phenomena. One is that alpha decay to the $I^{\pi} = 1^{-}$ excited state is almost completely unhindered1) relative to the ground state transition. The second is the occurrence of very strong E1 transitions.28,29) One model that has been introduced to explain both of these phenomena is an alpha clustering model. Experimental measurements of E1 transition probabilities will provide a test of this model when they are compared with the detailed theoretical predictions. It would seem worthwhile to look for these phenomena in the Transplutonium region.

We also feel that the production of intensely radioactive materials and their fabrication as targets, e.g., ^{227}Ac should be encouraged in the light actinides as well as in the Transplutonium elements.

Very Heavy and Superheavy Elements

The subject of the stability of the superheavy elements is a controversial one. Estimates of superheavy element lifetimes vary over many orders of magnitude. Here, we sidestep the issue by focusing on what we can learn about superheavy element stability from studies of the heavy elements.

Theoretical predictions$^{13,14)}$ have been made about equilibrium deformations and nuclear binding energies in this transition region. Nuclear spectroscopic studies are needed to test this picture of the heavy Transplutonium transition region. Such tests will refine the predictions of superheavy lifetimes.

In order to estimate superheavy element lifetimes, one uses the same combination of the liquid drop model and the Strutinsky prescription discussed above in determining equilibrium values of deformations. This necessitates a very precise knowledge of the single-particle energy level spacings, as the estimates of fission lifetime vary by ~2 orders of magnitude with a 1 Mev change in the shell correction. This uncertainty in level spacings is one of the main reasons for the uncertainty in superheavy element lifetimes. The neutron levels beyond N = 184 and the proton levels beyond Z = 114 contribute significantly to the shell corrections. Through spectroscopic studies of the Transplutonium elements, it may be possible to learn something about the positions of these levels. The proton orbital 1/2 - [521] has already been identified$^{33)}$ in the isotopes ^{247}Bk and ^{251}Es, thereby furnishing direct information on the position of the $f_{5/2}$ proton orbital which determines the gap at Z = 114; similar studies might identify the proton orbitals 1/2 - [770] and 1/2 + [651], thereby furnishing information on the positions of the proton $j_{15/2}$ and $g_{9/2}$ orbitals. Similarly by finding the neutron orbitals 1/2 - [750] and 1/2 + [880], we would reduce the uncertainties in the magnitude of the neutron shell correction substantially.

Possibility of Long-Lived Isomers

In nuclei near the upper end of the heavy elements (region C in figs. 1 and 2) whose neutron number approaches 184 and whose proton number approaches 114, there are a large number of single-particle states of high angular momentum whose excitation energy will be at or close to that of the ground state. Near the line of stability, nuclei with Z < 112 are predicted to be deformed. For higher values of Z, they are expected to be spherical. For the spherical nuclei of region C these states inlcude the neutron hole states $g_{7/2}$ and $d_{5/2}$ and the proton states $f_{7/2}$ and $i_{13/2}$. For the deformed nuclei of this region, these states include the 11/2

(606), 9/2 (604), 15/2 (707), and 13/2 (716) neutron levels as well as the 11/2 (615), 9/2 (624), and 5/2 (512) proton levels.

If the unpaired proton and unpaired neutron in an odd-odd nucleus are trapped in these states at low excitation energies, the resulting nucleus will have a pair of isomers. The isomeric states will have values of $k = k_n \pm k_p$ with an energy separation between rotational bands of the order of 100 keV. The relative excitation energies of the bands are given by the Gallagher-Moszkowski selection rules.34)

The beta decay of odd-odd nuclei takes place to even-even nuclei which have no high spin states at low excitation energies. For nuclides lying near the line of beta stability there will be little decay energy and the transitions will thus be forced to take place to states of low angular momentum. The beta decay of these high spin states will thus be hindered due to large changes in angular momentum. Alpha decay will be inhibited since transitions to favored states in the daughter nuclei will be at a cost in decay energy; either one, or both, of the single-particle states of the parent configuration will be an excited state in the daughter nucleus. Transitions to states in the daughter nucleus involving the change of one single-particle orbital are generally hindered by 1 to 2 orders of magnitude; transitions which involve the change of both single-particle orbitals are never observed.

Past studies of Transplutonium elements have indicated1) that spontaneous fission is inhibited by about 5 orders of magnitude in odd-odd nuclei relative to even even nuclides. Therefore, for odd-odd nuclei whose ground states are the higher angular momentum isomer, we can expect extraordinarily long half-lives. In addition, if the neutron and proton angular momenta are about equal, we can also expect low-lying isomeric states with greatly hindered gamma ray transition rates.

The exact position of the occurrence of these long-lived nuclei will depend on the order of filling the single-particle orbitals, which is strongly dependent on the nuclear deformation. For nuclides in region C having between 109 and 114 protons, the protons will be in either spherical shell model states of high spin or deformed states of high spin and there will be a high probability of isomer formation with concomittently long half-lives.

There are two potential benefits which could be obtained if these long-lived odd-odd nuclei exist and are detected. First, they would provide a test of nuclear structure at the heaviest region including measurements of the n-p interaction. Anantaramam and Schiffer35) have inspected a large number of doublets of this type for nuclei which are only two nucleons from closed shells and have determined a unique set of range and potential energy parameters. Katori, Friedman, and Erskine36) have examined doublets in the deformed nuclei and have found that the same set of parameters can be used to calculate their energy splittings. It would be important to determine the universality of the potential energy and range parameters.

Second, the half-lives of the high-spin isomers should be long enough to allow an accumulation of enough atoms to study the chemistry of these transactinide elements at the tracer level. Simple tracer experiments can readily yield information on oxidation state, solubilities, and volatility which can be used to deduce the probable electronic structure of these elements.

Nuclear Structure at Large Deformations

The existence of fission isomers37) provides an opportunity to obtain nuclear structure information at large deformations. The region marked E in figs. 1 and 2 corresponds roughly to the deformations of actinide nuclides in the second minimum. This region is, however, extremely difficult to study experimentally, and the amount of nuclear structure information is limited.

Inertial parameters of 3.3 keV have been experimentally measured38,39) for rotational bands of the fission isomers in ^{236}U, ^{238}U and ^{240}Pu. These inertial parameters are ~1/2 the values found for normally deformed actinides. The equilibrium deformations deduced from these inertial parameters are β_2 of ~0.6, which corresponds to a major/minor axis ratio of 2. A measurement of the optical isomer shift by Bemis et al.40) gives a similar value for the deformation. The calculation of inertial parameters is rather sensitive to the strength of the pairing interaction, and it appears that a pairing interaction strength that varies proportionately to the nuclear surface41) provides a slightly better explanation of these inertial parameters than does a constant pairing force.

There have been tentative identifications of single-particle states in ^{237}Pu and ^{239}Pu, and a spin assignment of 5/2 has been made[42)] in ^{239}Pu. The magnetic moment of this state[42)] indicates that the unpaired neutron is in an orbital whose spin projection, s_z, is down. When conventional single-particle potential parameters are used, there are no such orbitals near the Fermi level for $N = 144$. Hamamoto and Ogle have noted[43)] the possibility of getting such an orbital near the Fermi level by increasing the strength of the spin-orbit term in the single-particle potential. The identification of additional levels in the region of large deformation would be extremely valuable for testing this hypothesis.

FISSION STUDIES

Fission properties have been centrally linked to the Transplutonium Production Program since its inception. Fission is the process which limits the production of heavy elements, but it is just from the study of this heavy element fission that we are able to learn the most about this interesting decay mode. The purpose of this presentation is not to review[44)] the many significant accomplishments in fission studies which have benefited from using isotopes supplied by the Transplutonium Production Program, but to preview the areas which will benefit from the continuation of the program. We believe that future fission studies will be most productive by investigating the region of unstable nuclei having $Z \geq 100$. The fission properties in this region are rapidly changing and provide the greatest challenge to emerging theories. Access to such a region will be possible only with a strong commitment to the production of heavy element isotopes.

In this section we will discuss many aspects of transplutonium fission. The possibility of fission studies is, of course, directly linked to production mechanisms, which are discussed in the paper in this workshop on "Nuclear Reactions and Synthesis of New Transuranium Species" by Glenn T. Seaborg.[45)] Production mechanisms include transfer reactions, compound studies, heavy-ion probes, light-particle reactions, and elementary particle investigations. Physical fission questions cover fission barriers, direct decay observables of mass and kinetic energy distributions, isomeric fission production and decay, Coulomb fission properties, giant resonance studies, fission product properties, elementary particle coupling effects to fission, and fission statics and dynamics from muonic attachment. The broad base future success of these and other unthought of areas will depend on collaborative efforts which combine the unique materials offered by the Transplutonium program with the unique capabilities in equipment and accelerator facilities on a world-wide basis. Efforts will truly have to be international since no one laboratory, or country, can afford to have comprehensive capabilities in all the exciting new areas.

Light-Particle Reactions

Historically light-particle reactions, along with spontaneous fission, have provided the most complete information for our understanding of the detailed properties of fission. They are generally characterized by specific well known conditions. The isotope produced is unambiguously identified and we usually have, as well, a good knowledge of the excitation energy and angular momentum brought into the system. Fission barrier properties have been extensively studied in the actinide nuclei and the current status is reviewed by Britt.46) Fairly complete measurements of barrier properties have been obtained using light-ion direct reactions on most long-lived actinide targets up to as heavy as ^{250}Cf. The most significant result from these systematic studies has been to establish the importance of enhancements to the fission decay width caused by collective bands. These bands are built on the non-symmetric shapes which occur at the fission barriers. However, there are two important areas which have not, to date, been investigated with regard to fission barriers. The most dramatic changes in fission decay observables have been for the neutron excess isotopes in the Fm region. No systematic fission barrier properties are known in this region. Theory47) predicts that the outer fission barrier for these heavy isotopes should be substantially decreased (even to below the ground state energy in some cases) while the inner barrier48) remains at a fairly high level. This condition should result in a very penetrable fission barrier whose properties could be investigated by suitable direct reaction studies. The effects of barrier properties on fission decay observables49) are not well established, and the striking effects observed in the Fm region are most usually attributed to shell stabilization near scission.50,51) However, since theory is predicting a rapid change of barrier properties in just this exciting region, it is important to investigate this area. For these studies, suitable targets of ^{254}Es (possibly ^{255}Es) and ^{257}Fm would be required. Only one previous barrier study with ^{254}Es[52)] has been performed. The target in these studies contained only ~0.1 μg of ^{254}Es on a C foil backing. The contaminants in the target, along with the poor target/backing atom ratio, limited the results to estimates of the inner barrier heights for ^{255,256}Es and ^{255}Fm. No information was extracted on the important question of barrier curvature. An adequate target containing some 3-5 μg of material on a 0.1 cm^2 spot on a thin C backing would be ideal for these investigations. This seems feasible under current transuranium processing plant/high flux isotope reactor (TRU-HFIR) production capabilities. Of more intrinsic interest would be the use of ^{257}Fm as a target material. This would permit direct probes into the most interesting neutron excess regions. Of course, microgram quantities of this species are not going to be available. However, there has been tremendous advancement over the last few years in the field of large position-sensitive gas counters. It is now at least conceivable that some studies could be done using a ^{257}Fm target of ~10^{12} atoms/cm^2 on a 2 mm diameter spot. The gas counters detecting fission fragments can be made insensitive to the high fluence of light ions required for the measurements while still providing high geometric efficiency for position-sensitive heavy ion detection. Though this would be, at best, a difficult experimental program, one thing is certain: it cannot even be attemped without a supply of the ^{257}Fm target material.

The other significant area for future fission barrier studies involves the effects of excitation energy and angular momentum on the collective degrees of freedom. To date, the detailed studies have been performed using direct reaction techniques which populate actinides from fission threshold to ~10 MeV of excitation energy. As stated above, these experiments have led to the significant conclusion that the quantitative fission decay competition is governed by strong collective effects associated with transition states at the fission barrier.[53)] The open physical question is what happens to these collective effects as the nuclear excitation energy and angular momentum are increased. If the collective degrees of freedom come from a closed basis of single-particle structural states, which for certain configurations result in a superposition of strength and a projection to low excitation energies, will such strength be able to continue indefinitely with excitation energy or will the collective enhancements saturate? This important question can be addressed through studies which probe the fission/neutron decay competition at well defined conditions of excitation energy and angular momentum. Direct reaction techniques such as (^{7}Li α)[54)] and (^{12}C,^{8}Be)[55)] offer the possibility of reaching well defined excitation energy conditions of up to ~20 MeV and are an important next step for the studies. However, this field has only had the barest amount done to date and will benefit from increased activity and the continued availability of the wide spectrum of actinide materials required for targets.

In addition to its obvious very practical applications, neutron induced fission has provided information on detailed properties of the fission barrier. Resonance studies have provided us with the most precise knowledge of fission transition states.[56)] Future studies of more exotic actinide species will continue since improvements in experimental capabilities will continue. The high-fluence neutron facilities such as the Intense Pulsed Neutron Source (IPNS) at Argonne, Oak Ridge Electron Linear Accelerator (ORELA) and now the Weapons Neutron Research Facility (WNR) at the Los Alamos Meson Physic Facility (LAMPF) provide the required intensities for precise time of flight measurements. These capabilities will be augmented with the operation of the proton storage ring at the WNR facility in 1985 which will provide a burst of neutrons in a pulse period as short as 1 nsec.

High-resolution fission product spectrometers such as HIAWATHA[57)] at Illinois and LOHENGRIN[58)] at Grenoble are contributing to our detailed knowledge of fission distributions and energetics. Low-energy fission still provides the best technique for probing dynamical effects and pairing correlations in complex systems. The ability to select the highest kinetic energy release events[59)] has resulted in information on pairing associated with cold fragmentation and the variation of even-odd effects with proton number. Such fine structure effects cannot be selected in heavy ion nuclear reactions. The strong variation of observable properties as a function of selectable mass and kinetic energy release can best be studied using the high-yield (n,f) reaction at a reactor. The structural effects are strongly dependent on the fissioning system and point to the need for heavy element isotopes from the Transplutonium program to permit systematic investigation of the decays. Material requirements are on the order of 1 mg for these studies and will have a future need for all sufficiently fissile isotopes (^{241}Pu, $^{245-248}$Cm, ^{249}Cf). In sufficiently high fluence regions the (2n,f) reaction can be potentially studied using ^{241,243}Am, ^{249}Bk and ^{253}Es. Using an external neutron beam port, studies with microgram quantities of exotic isotopes are feasible. In this case adequate fission product resolution is obtained using time of flight techniques. Rare Cm isotopes and ^{254}Es seem to be potential targets for this type of study.

It should be noted that the neutron and light-ion direct reaction techniques have given, and will continue to give, information of fission decay probabilities and properties which are important to emerging requirements in reactor design as well as defense applications. Techniques using direct reactions to simulate60) neutron induced fission cross sections can provide data for isotopes not readily studied (due to short half-life and/or unavailability) in the laboratory but of possible importance in high-neutron fluence environments such as present in certain reactors and weapon systems.

Probably the most dramatic experimental finding in fission since the discovery of isomeric fission has been the observed rapid change in the fission mass and kinetic energy distributions associated with the heavy Fm isotopes61,62) (see fig. 3). The $N \geq 158$ Fm isotopes show a rapid change to symmetric fission accompanied with high kinetic energy release which is totally outside the established fission phenomenology.63,64) What is equally striking is that this appears to be a very isolated region. The $N = 158$ Cf isotope does not show an anomalous behavior62) while the $N = 158$ Md65) seems to have a symmetric mass division but a kinetic energy release which is relatively consistent with established systematics. The frustrating part experimentally is that this most interesting region is extremely difficult to reach. Light-ion probes were used to study ^{258,259}Fm, and advancements in target quality will enable these studies to be extended. One very interesting physical question is what happens to the highly symmetric fission as the excitation energy is increased. Direct reaction techniques to produce isotopes in the Fm region could be used to establish known excitation energies. If these are done in coincidence with fission, they would provide the required information. Again the most heavy element targets such as ^{248}Cm, ^{254}Es (^{255}Es?) and ^{257}Fm would be required. Promising direct reactions are (d,p) on ^{257}Fm targets, (^{7}Li,^{4}He) or (^{7}Li,^{3}He) on Es targets and (^{18}O,^{8}Be) on ^{248}Cm targets. In addition to the properties of fission from excited states, much more information is required on the decay by spontaneous fission. Of particular importance are the neutron excess isotopes above Z = 100. The production of these will certainly require the heaviest most neutron rich targets available.

Heavier Ions

Heavy ion beams and heavy element targets offer real possibilities for the production of interesting isotopes for fission decay studies. The breaking point between light- and heavy-ion reactions is, of course, not well defined. We will concentrate on three, also not clearly distinguishable, types of reaction studies: compound formation, transfer reactions and heavy-ion deep inelastic effects.

Compound studies are the traditional method of producing new isotopes. They make the highest Z combination between target and projectile and thus provide the limit to the maximum region of interest. Also, importantly, this reaction results in complete momentum transfer and thus a relatively high-energy composite system which is strongly forward focused. Both of these characteristics enable the construction of efficient spectrometers66,67) for the detection of rare events. The most striking recent successes of this approach have been the production of elements 107$^{68)}$ and 109$^{69)}$. Current experiments are underway to attempt to observe cold fusion between ^{48}Ca and ^{248}Cm at both Berkeley and Gesellschaft für Shwerionenforschung (GSI) Darmstadt. With sub-nanobarn sensitivities these methods should be viable for both the production of selected isotopes of interest and for the continuation of efforts to identify new heavier elements. The production cross section is almost always maximized by choosing the heaviest target and lightest projectile to reach a desired area. Because of this, substantial quantities of heavy isotopic targets will continue to be in demand. For most studies ^{254}Es will be the heaviest practicle target isotope. Currently there is an emphasis on production of new elements but it appears likely that the future emphasis will be in producing highly unstable isotopes with Z > 100. Understanding the nuclear structure effects and the fission decay properties of this limit of stability will surely be a challenge for future theoretical efforts. Very little is now known about the fission of isotopes having Z > 100. The Fm and Md results show that dramatic effects are possible and this should be a most interesting region to explore.

One further aspect of studies involving the formation of a compound nucleus using heavy actinides should be emphasized. The understanding of the limits of fusion in heavy ion reactions is of theoretical and experimental interest. The importance of the entrance channel mass ratio in determining the fusion probability can be tested by attempting to produce the same heavy-element composite system using both light-heavy ions on Transuranic targets and heavier ions on lighter element targets. The investigation of the stability of these systems against fission induced by excitation energy and/or angular momentum considerations can help establish the important parameters in the fusion process. The new heavy-ion facilities such as Holifield, Argonne Tandem Laboratory Accelerator System (ATLAS) and Michigan State University (MSU) will be involved in questions of fusion/fission competition. For these studies the availability of heavy-element targets will be important.

In many respects transfer reactions offer the best hope to produce the interesting neutron rich high-Z actinide isotopes. These reactions proceed with relatively high cross sections when compared with the compound reactions required to reach the same isotope. This is presumably due to the lower residual excitation energy imparted in the transfer process. In general, the small region of phase space available in the transfer process is more than compensated for by the colder formation. This then avoids the disastrous fission/neutron decay competition which must occur in most compound reaction formation processes. Even in cases where the compound processes have sufficient surviving probability, they are moved to the neutron deficient side by the neutron evaporation process. Thus, the desirable neutron rich isotopes are often not reachable by existing target/projectile combinations. The transfer process is not bound by this constraint and has been shown to have a product distribution with a substantial enough width to extend well into the neutron rich side. Of equal importance, the transfer probability appears to be, for the same cluster transfer, nearly independent of the target. Figure 4, from Schadel et al.70), shows their results for 2p,xn transfer from ^{18}O and ^{22}Ne on ^{254}Es

near the interaction barrier along with the cross sections for the same transfer clusters observed by Lee et al.71) for ^{18}O and ^{22}Ne on ^{248}Cm. The peak magnitudes, centroids and widths are similar. This clearly emphasizes the importance of using the heaviest target for obtaining the maximum yield of heavy isotopic products. The production of Md isotopes with ^{18}O projectiles near the interaction barrier are some 4 orders of magnitude greater with a ^{254}Es target compared to a ^{248}Cm target.

The disadvantages of the transfer process are (1) it is not a full momentum transfer process and (2) it is not very selective. Both of these make it hard to establish the identity of new species produced in the reaction. The existing mass separators and velocity filters such as Small Angle Scattering System (SASSY)66) and Separator for Heaty Ion Reaction Products (SHIP)67) are primarily designed for compound reaction formation and take advantage of the foreward focusing of these reactions. The transfer products will have a much broader angular and kinetic energy distribution. The non-selectivity of the reaction when applied to heavy targets results in the possible production of several unknown heavy isotopes which are expected to be short lived and decay by spontaneous fission. To fully realize the potential of using the transfer reaction mechanism to study these new regions, substantial development efforts will be necessary. It would be prudent to characterize the transfer reaction mechanism in more controlled areas than are available with heavy-target studies. The excitation functions to maximize specific transfers should be investigated. To complement these reaction studies, detection techniques will have to be developed which are capable of identifying the primary fissioning species by measurement of the prompt fission fragments. High-efficiency, fast fission detection systems such as the Lawrence Livermore National Laboratory Spinning Wheel Analyzer of Millisecond Isotopes (SWAMI)72) are important initial steps in the study of fission properties for transfer produced fission activities. Development of gas counter techniques to directly identify the transfer reaction produced activity by its subsequent fission decay seems on the verge of feasibility and with sufficient encouragement could be brought to more rapid fruition.

Heavy-ion reactions also have a role in the production of possible interesting fissile isotopes. Studies of mass transfers in the reactions $^{238}U + {}^{238}U$73) and $^{238}U + {}^{248}Cm$74) have shown broad distributions for the production of isotopes. Unfortunately, the residual excitation energy left in the heavy isotope is usually sufficient to cause it to undergo prompt fission. However, these studies have been done at relatively low bombarding energies near the interaction barrier. These reaction conditions tend to maximize diffusion and statistical processes. The new direction in heavy-ion accelerators is toward higher energies. What role heavy actinides will play in these new facilities is uncertain at this time. Certainly non-equilibrium processes will come into play and there will be a transition in the reaction mechanism from one which is dominated by diffusion-deep inelastic processes toward one that is dominated by nucleon-nucleon interactions at the highest relativistic energies. The Holifield accelerator at Oak Ridge, the Michigan State University cyclotron, the Schwerionen Syncrotron (SIS) project at GSI, the heavy ion Syncro-cyclotron capabilities of the European Nuclear Research Center (CERN) and the Grand Accelerateur National d'Ions Lourds (GANIL) facility in France are all going to be active in the near future. Unique facilities tend to attract unique target capabilities as well, so it seems only a matter of time until the heavy targets are used at these installations. What role they will have in elucidating the fission mechanism is not clear at this time.

Elementary Particle Probes

Elementary particle probes provide us with fundamental information on how elementary interaction can be propagated into the collective processes required for fission. Negative muons interact with nuclei through the electromagnetic and weak interaction. This provides interesting possibilities of changing the Coulombic part of the potential energy surface without disturbing the nuclear part. On the other hand, strong interacting particles like pions provide information on how intrinsic nucleon interactions can propagate into the collective degrees of freedom. Future studies with the more exotic elementary particles will permit the concentration of substantial excitation energy into localized regions of the nucleus. The propagation of these hot spots in fissile isotopes will provide interesting data on the time evolution of fission. In all of these areas the available beam intensities are usually quite low, by nuclear charged particle accelerator standards, and therefore require significant amounts of target material for the reactions to be studied. Heavy-actinide targets have a future role in all areas of elementary particle interaction studies. However, on the short term, they will not be used with the most exotic elementary particle beams.

In many respects, negative muonic experiments have high physical interest as well as the greatest need for heavy-element targets. The negative muon, having a mass that is 207 times the mass of an electron, behaves like a heavy electron. Sufficiently slowed muons are captured in outer atomic orbitals and cascade, through the ejection of Auger electrons, and muonic x-rays, until they reach the 1s orbital. They remain in this orbital which, due to the heavy muonic mass, has a small radius that strongly overlaps with the nuclear volume. They can decay either by the free muon decay channel or via a weak interaction with the nucleus. The lifetime varies from the 2.2 μsec free muonic lifetime to ~80 nsec for the heaviest elements where the decay is dominated by the weak interaction. For heavy fissile nuclei this normal decay mechanism can be altered in a most interesting way. During the muonic capture cascade process an atomic transition can be absorbed into the nucleus via a virtual photon interaction resulting in a "radiationless" excitation of the nucleus. If this absorbed energy is comparable to the fission barrier, then the nucleus can undergo fission decay. Therefore, following atomic muonic capture there are two mechanisms which can result in actinide nuclei fissioning. One is the "delayed" fission which results from the weak interaction decay of the muon and has a characteristic half-life of ~80 nsec. The second is the "prompt" fission which occurs from the virtual photon absorption of a radiationless transition during the atomic cascade.

The prompt process is the one of high interest. Under these conditions the fissioning system has a muon in its 1s orbital. This causes a distortion of the fission barrier (fig. 5) due to the readjustment of the Coulombic part of the potential energy surface in the region of overlap between the muon and nucleus.75) Geometric effects of the muonic orbital cause the largest change to be made in the outer fission barrier. This opens the possibility of producing new regions of fission isomerism along with an improvement in our understanding of the process. However, to date, searches for isomeric effects in muon induced fission on U isotopes76) have not given conclusive results. This may be due to the rapid rise in the outer barrier (fig. 5) which may cause the decay to preferentially tunnel into the first well and thus be non-detectable. The hope then would be to use heavier actinide targets (^{244}Pu and ^{248}Cm would be logical initial choices since they are relatively abundant and long lived) which do not, under normal conditions, form fission isomers since presumably their outer fission barriers are too low. With the attached muon the outer barrier should be preferentially increased and could result in the formation of detectable new regions of fission isomerism.

Heavy actinides will also play a role in measuring the prompt/delayed fission ratio following muon capture. This quantity is dependent on the height of the fission barrier and has been only measured for isotopes up to ^{242}Pu77,78). In ^{238}U the Γ_n/Γ_f decay competition for prompt muonic systems was measured to be ~40 79) which is an order of magnitude greater than that observed in photo induced fission of ^{238}U to the same excitation energy region. This again points to the advantage of using heavy-element targets. For heavy systems the fission probability is dominated by the inner barrier and this will undergo a smaller increase than the outer barrier. Therefore, these cases should have significantly higher prompt fission decay branches. Also recent experiments80) have shown the importance of muon induced quadrupole photofission in the ^{238}U system. The quadrupole 3d → 1s transition was shown to be a significant contributor to the prompt fission yield in muonic capture on a ^{238}U target. It would be very interesting to study quadrupole induced fission in heavier systems to see if changing barrier properties and ground state quadrupole moments influence the yield.

Another interesting area of study would be to look at the dynamics of fission using the prompt muonic fission as a probe. One aspect of this would be to measure the change in kinetic energy release when the muon is attached to the fissioning system. This attachment could alter the path toward scission and result in significant perturbation to the fission observables. Again a wide range of heavy-element targets would be desirable for these studies. Since the initial starting conditions for the prompt muonic fission cannot be altered for any specific target, the only method for obtaining systematic information will be to perform the measurements on a wide variety of targets. The other advantage of the heavy elements is that they should have, as explained above, a much higher fission probability. This should help overcome the greater intrinsic difficulties associated with both the handling of these exotic materials and their limited availability.

One exciting new area of muonic fission studies centers on the fate of the muon following prompt fission. If the path toward scission is slow compared with the muonic orbital velocity, then the muon will follow the minimum potential energy path and stay with the heavy fission fragment. The extent to which the muon is bound to the light fragment or ejected into the continuum will tell us of the breakdown of this adiabatic assumption. Current theories[81-83)] show that this process provides a clock for the important question of fission dynamics. Experimental studies[84,85)] have implied that the heavy fragment retains the muon the majority of the time. However, definitive experiments which directly measure the precise ratio of the light/heavy muonic attachment have not been performed. Heavier element targets should again be useful by increasing the yield of prompt fission.

A very interesting corollary to the muon attachment problem is the question of muon conversion yields from excited fission fragments. Prompt muonic induced fission may be the only mechanism by which we can have a muon bound in its 1s orbital to a nucleus with sufficient excitation energy to eject it into the continuum through the internal conversion process. Muonic binding energies for light- and heavy-fission fragments are on the order of 3.3 MeV and 5.8 MeV, respectively. This would imply that the light-fission fragments have a much higher probability for muonic conversion than their heavy complementary fragments. Experimental emulsion track studies[86,87)] have seen evidence for this interesting decay mode. Accurate determinations of this process will be of high theoretical interest in testing electromagnetic predictions of the decay yields as well as a probe for high-spin isomeric states of fission fragments.

Pions offer a different type of elementary particle probe to study fission. These strong interacting particles capture on nucleon pairs, resulting in a prompt cascade process which, for heavy systems, can terminate in fission decay of the excited nucleus. This process offers a time scale for studying fission. The cascade should be prompt with respect to fission, and current experimental results[88)] imply this is true. However, it is known that following stopped pion capture the fission probability is 90% for ^{238}U targets. The Γ_n/Γ_f competition throughout the process is not well established. Pion studies offer a method which starts with a nucleon-nucleon interaction process and evolves into one with sufficient collective excitation to decay by fission. A substantial fraction of the pionic rest mass of 140 MeV can be imparted into the fissioning nucleus while not introducing large amounts of angular momentum. This is contrary to most nuclear reaction techniques which can only reach excitation energies with the introduction of substantial amounts of angular momentum. A central question in pionic interactions with nuclei is the possible capture on clusters of nuclei as opposed to simple pair capture. One method of looking at this question might be to measure momentum transfer to the fissioning nucleus. Cluster capture would presumably favor higher initial particle-hole state population and better absorb the full beam momentum. Studies of momentum transfer to fissile systems near the 3,3 resonance might provide insight into the reaction mechanism. These measurements are, of course, difficult due to the low incident momentum of the pion and the angular dispersion of the fission fragments introduced through the neutron evaporation process. If such studies are undertaken, the systematics that can be gained by using a variety of heavy element targets will be valuable.

The use of more exotic elementary particle probes to study fission is only at a very speculative stage. The new capabilities which will be associated with the high anti proton beam intensities at CERN as well as the possibilities at proposed new kaon factories will challenge the experimental community to use exotic targets. These special probes will interact in small regions of nuclear matter resulting in localized "hot spot" excitation. The propagation of these hot spots toward collective excitation will be of interest. Hypernuclei studies of heavy-fissile systems may serve as a probe of how simple intrinsic excitation can be transformed into a fission decay. As has proved to be true in the past, the exotic accelerator capabilities will attract the exotic target materials and help push us toward the limits of understanding.

Fission Topics

Other areas of fission which will benefit from heavy-element materials include fission product studies, isomeric fission properties, giant resonance excitations, and Coulomb fission. Fission product studies have provided us with much of our primary understanding of nuclear structure effects associated with isotopes removed from the line of stability. It is still a very viable method to produce medium weight neutron rich isotopes. The use of heavier actinides as fissile sources will increase the yield of the high-mass fragments in the light-element peak and broaden the heavy-element peak. Both of these effects open up new isotopes for study. Increasing the number of neutrons in the fissioning system directly moves the centroids of the fission mass chain yields toward the neutron excess side. The neutron rich isotopes in the Tc-Pd region have high interest from a nuclear structure standpoint. Large ground state quadrupole moments have been established for these isotopes89) and recent studies90) have implied that they are soft toward triaxial deformations as well. Great strides have been made in rapid automated chemical separations91) which enable detailed spectroscopic studies to be made on very short-lived products. Reactor induced fission product studies using ^{249}Cf and, if available, ^{251}Cf will be increasingly important in future studies. Preliminary physical measurements of prompt fission product radiations have been made for the spontaneous fission of systems as heavy as ^{254}Cf92). This spontaneous fission gives very neutron rich fragments and thus helps extend the study of nuclear structure systematics to the otherwise inaccessible neutron excess region. Fission studies using Es, and possibly Fm, will result in increased yields of isotopes near the ^{132}Sn doubly magic nuclear core. Since so much of our nucleon structure understanding is based on single-particle effects in closed shell regions, any new information on this important class of nulei will be valuable.

It can be argued that fission isomers were the primary driving force which has lead to the modern emphasis of heavy-element and heavy-ion physics. The theoretical development which resulted in coupling oscillating microscopic nuclear structure effects with smoothly varying macro potential energy surfaces was directly motivated by the desire to explain the occurrence of fission isomers. This evolved into the predictions of long-lived superheavy elements which spurred a new generation of heavy-ion accelerators to be constructed and thus ushered in the strong commitment that we now have in heavy-ion physics. Fission isomers occur in the Z = 92-97 region and are thus directly in the heavy-element region supplied by the Transplutonium Production Program. The efficient method of making these isomers involves light-ion reactions and thus requires heavy-element target materials. Modern studies have evolved past measuring the isomer occurrence and now emphasize exotic decay channels and the nuclear structure aspects of the isomeric shape. The decay branch back to the first well has been reported to be observed 93) but to be considered firmly established, corroborating future experiments will be required. Recent studies 94) have observed the alpha decay branch from the ^{242m}Am isomer back to the ^{238}Np ground state. The high hindrance factor for this transition is consistent with a large nuclear structure change being required to go from the isomeric to the ground state shape.

Probably the most dramatic recent fission isomer study has been the measurement of the quadrupole moment through optical isomer shift measurements using laser induced optical pumping of atomic levels. 40) This measurement provides direct information that the fission isomers are indeed associated with shape distortions. Another area of recent success in isomeric fission studies has been the development of techniques which permit the detailed spectroscopic study of nuclear structure in the isomeric second well. 95) This type of information, as discussed in the previous section, provides very stringent constraints on theoretical nuclear structural studies. The challenge is to have models that predict correct structure sequences from spherical ground state configurations through fission isomeric shapes. Only such broad based capabilities can help ensure confidence in the extrapolative power of theory to venture into uncharted off-stability regions.

A new generation of high-efficiency gamma ray detection systems such as the Crystal Ball at Heidelberg and the Spin Spectrometer at Oak Ridge is coming on line. If a continuing supply of target materials is available, these new facilities offer the hope of extending the study of the spectroscopy of fission isomers to even greater precision than has been reached. Also, laser optical pumping techniques are still in a preliminary phase. More experiments using this technique are called for and will provide important structural information on the fission isomers in the future.

Giant resonances, especially the giant quadrupole resonance, offer a method of determining the collective coupling that leads toward fission. The magnitude of the fission probability in giant quadrupole studies has not been consistently determined. Some experiments have found it to be low[96,97) with respect to expected actinide fission values, while others[98-101) report a value comparable to normal actinide decay. Improved experimental data are needed. Of special interest would be efficient angular distribution studies to address the question of K state conservation in the giant resonance induced fission. By extending these studies to heavy-actinide targets, one can measure the effect of changing barrier properties and ground state quadrupole moment on the fission decay probabilities and angular distributions. Also of interest is to determine if direct fission couplings through the giant resonance affect the fission mass and kinetic energy distributions. A thorough understanding of the relative importance of dynamical and potential energy effects on the fission observables is not presently available. To this end, giant resonance induced fission studies could be very beneficial.

Another emerging area of studies involves Coulomb induced fission. This process, which is done with heavy-ion beams and heavy-element targets, uses non-nuclear interactions to excite heavy isotopes to sufficient energies to undergo fission decay. Since the Coulomb excitation process favors collective excitations, these experiments enable us to determine fission decay properties without the complication of particle-hole excitations introduced in nuclear reaction studies. Recent experiments[102,103) have, for the first time, been able to unambiguously identify this process, and this has lead to a revived theoretical interest. Current models[104,105) which use a vibrational-rotational coupling combination are reasonably able to explain the magnitude of the Coulomb induced fission cross sections. However, more detailed aspects of the decay process have not been fully determined. Predictions of Coulomb-nuclear interference effects have not been observed, and existing angular distribution studies have not shown the strong structural effects predicted by some models. Future investigations of this process will rely on heavy-element target materials. The Coulomb excitation probability is directly dependent on the target charge. Since Coulomb induced fission is a multistep process, the charge dependence is raised to a power which has been experimentally determined to be on the order of 6-7.[103) Clearly, heavy element studies will enhance the yield of this process.

ATOMIC STUDIES OF SUPERCRITICAL SYSTEMS

One of the most exciting areas of research with heavy-element materials has been the search for spontaneous positron emission from quasimolecular systems formed in heavy-ion/heavy-target collisions. Theory predicts[106)] that for finite sized nuclei the 1s atomic binding energy will become greater than twice the electron rest mass when combined target and projectile charge become $\geq$173. Under these conditions the binding energy enters the negative energy continuum or "Dirac Sea". If an electron hole would be created in the static atomic field of such a supercritically bound system, then a spontaneous positron-electron pair would be created in this vacuum, resulting in the electron's filling the atomic vacancy and the positron's being ejected into the positive energy continuum. This important test of quantum electrodynamics has attracted a substantial amount of experimental and theoretical effort in the past several years. The major impediment to those studies is that, unfortunately, stable atomic systems with charge > 173 do not exist. However, with modern heavy-ion accelerators and suitable heavy-element targets, transient quasimolecular systems having the required charge can be produced in the laboratory. It would seem at first glance, and initial experiments were fired with this optimism, all that would be necessary would be to bring sufficiently heavy systems near enough together to create the required supercritical field and then detect the emitted positrons. Unfortunately, the dynamical aspect of the required collision process results in induced positron emission caused by the rapidly varying electric field.[107)] These dynamical effects can induce positron emission in subcritical systems. In fact, calculations[108)] show for an unperturbed Rutherford collision trajectory, only a smooth dependence in the positron yield with increasing atomic charge and no discontinuous changes are predicted in the yield or spectrum when supercritical field conditions are reached. If the colliding system followed such a trajectory, then the onset of spontaneous positron-electron pair creation could only be inferred from a detailed stripping of the observed spectrum using theoretical production estimates for the various components. If, however, the trajectory is perturbed through nuclear interactions, then some observable effects of the spontaneous creation process may become more readily identifiable. Experiments to study the properties of these very heavy quasimolecular systems have centered in three areas: characteristic x-ray measurements, delta electron studies, and direct positron detection. In all cases the very strong dependence of the atomic effects on the combined atomic charge for these relativistic systems makes the use of the very heaviest target materials extremely desirable.

During the collision process there is a reasonably high probability that an inner shell electron of the interacting particles can be ejected into the continuum. Under bombarding conditions near the nuclear interaction barrier the projectile velocity is on the order of 0.1 c, and since the bound electron velocity is ~c, this permits near adiabatic adjustment of the electron to the changing atomic field. In asymmetric collisions the 1s electron orbital in the heavy positron becomes the 1sσ orbital for the combined quasimolecular system. If a hole is created in the heavy partner 1s orbital, then it will most probably survive the collision process and be detected subsequently as a characteristic K x-ray of this element. This is caused by the fact that even for supercritical field conditions the time for spontaneous positron creation for reachable systems is, from the calculated resonance widths[109,110)] inferred to be on the order of 10^{-19} sec. This is approximately 2 orders of magnitude longer than the time the Couloumb trajectory system spends within the critical field region. The probability for ejecting electrons in the collision is dependent on the binding energies during the process. Thus the measured yield of characteristic K x-rays of the heavy partner following the collision provides information on the binding energy of the forming quasimolecular species.[111)] These results, though model dependent, provide important quantitative information on the binding energies of extremely heavy systems. A difficulty of this approach is that only asymmetric collisions can be directly studied. For near symmetric collisions the 1sσ orbital of the quasimolecular system can no longer uniquely be attributed to the 1s orbital of a particular interaction partner. Due to the near degeneracy of the atomic orbitals in the separating system, a hole which was created initially in the N = 2 shell of the quasimolecular system (a condition which, from simple geometry and binding energy cosiderations, is much more probable than N = 1 hole production) can undergo a "vacancy sharing" exchange which results in a 1s hole in the separated products. Under these conditions the characteristic K x-ray yield will no longer provide unambiguous information on the quasimolecular 1sσ orbital. In practice, the vacancy sharing problem can be minimized by having a projectile-target charge difference of ~10. Due to a lack of suitable targets and projectiles, this requirement has limited the heaviest of these studies to Pb beams on actinide targets. The heaviest system studied has been ^{208}Pb + ^{248}Cm, giving a combined Z of 178. The availability of even heavier target material (such as ^{249}Cf and possibly ^{254}Es) would make it potentially feasible to use a Th beam and still not have too severe vacancy sharing effects. Thus by increasing the Z of the target by 2 or 3 units, a gain of 10 or 11 charges could be obtained. Since the binding energies of the quasimolecular system depend on the distance of closest approach of the colliding ions, the measurement of the K x-ray yield as a function of scattering angle provides, in a single experiment, substantial information with which to check theory. The spontaneous positron creation is predicated on the binding energies' becoming greater than 1.02 MeV. The measurement of characteristic K x-ray production provides a viable method for obtaining quantitative information on this important binding energy question. Future experiments will rely on the availability of heavy-element targets to address these problems. Improved information may be possible by performing coincidence measurements between characteristic K x-rays and ejected delta electrons. A more distant future proposal might be the use of heavy-element beams to obtain the ultimate total combined charge. Atomic x-ray production has reasonably large cross sections, and minute beams of ^{244}Pu and possibly ^{248}Cm impinging on ^{254}Es targets would enable the study of the heaviest systems if vacancy sharing problems can be overcome.

A complementary area to the x-ray studies is that of production of delta electrons. High-energy delta electrons ejected in the collision of heavy ions can only be caused by the strong binding associated with the quasimolecular system.112,113) Therefore, recording these spectra for heavy-element interactions as a function of projectile scattering angle provides direct information on the atomic binding. As mentioned above, a combination of these measurements with coincident x-ray measurements should quantitatively improve our understanding of the atomic binding energy of quasimolecular systems at, or near, supercritical field conditions. As always, the ultimate push in these studies is to use the heaviest target material available.

Certainly the most important aspect of the atomic studies with supercritical fields is the observation of spontaneously created positrons. The degree of sophistication in experiments has undergone tremendous growth in the last several years. A review of the current experimental status can be found in the "Proceedings of the NATO Advanced Study Institute Conference on the Quantum Electrodynamics of Strong Fields"114). In general, the detection systems use a solenoid magnetic spectrometer with suitable baffle systems to suppress the copious electron yields, since they have the opposite helicity from the desired positrons. Positron energy spectra are recorded in solid state detectors, and positive identification assignments are made by observing their annihilation radiation. In addition, information can be obtained on the primary scattered projectile and target ions by using suitable counters. This permits correlation of the positron spectra with primary reaction parameters.

In addition to the sought-for spontaneous positron creation process, other methods, even for subcritical field conditions, can produce positrons. If the projectile has sufficient energy to be above the nuclear interaction barrier, then nuclear reactions can occur. Under these conditions, transitions having energies above 1.022 MeV can decay through a positron-electron pair creation process. It is therefore necessary to be able to estimate the yields of this process and make suitable corrections to the positron spectrum to remove this contamination. Fortunately, this can be done rather accurately by calibration techniques using lighter target systems where supercritical fields are not possible. A more severe background is associated with the so called "induced" positrons. These are created through the dynamics of the reaction107) by the high-frequency Fourier components in the rapidly changing electric field of the colliding system. For a non-perturbed Coulombic trajectory these induced positrons have a yield which monotonically increases with total charge, and their energy spectrum shows a smooth exponential falling behavior. No dramatic changes are predicted for the onset of supercritical field conditions. If, however, a perturbation is introduced into the ion velocities through a nuclear interaction time, then an interference effect will be generated and the positron spectrum will show an oscillatory structural behavior. Observation of such patterns can then provide a check for the nuclear interactions. Deviations from the Coulombic predictions have been observed in recent experiments115) with U + U at 7.5 MeV/u. The positron yield is observed to fall off more rapidly than predicted by theory. Delta electrons recorded at the same time also show deviations between elastic scattered events and those associated with fission. Analysis of this with coupled channel calculations imply a time delay on the order of 10^{-21} sec. Such a value would be too small to result in substantial spontaneous positron creation.

However, a very significant new development has been observed in recent116) results obtained for $^{238}U + ^{248}Cm$ experiments done at 5.8 MeV/u. The preliminary results from these experiments for the positron spectrum observed with kinematic selection conditions which maximize (a) backward and (b) foreward projectile scattering are shown in fig. 6. These spectra have not been corrected for the solenoidol transport efficiency, for Doppler line broadening, for the line shape of the positron Si(Li) detector, or for the nuclear background. Nevertheless the strong peak structure at a positron energy of ~320 keV for backward scattered projectiles appears inconsistent with any background or anomalous detector effects. Of special importance is the narrowness of the peak. The observed width of ~80 keV is consistent with the expected Doppler broadening from a system moving with the quasimolecular velocity. The intrinsic width of the line might be substantially narrower than the observed value. The narrow width implies a lifetime of $>10^{-20}$ sec. If the supercritical atomic field exists for such a long time, then the static decay conditions of the vacuum become important and a peak in the positron spectrum would be predicted. In fact, the calculated binding energy for the supercritical field for the U + Cm quasimolecule is predicted to give a resonant positron decay energy117) consistent with the observed value. The physically exciting aspect of the observation is that some mechanism must be present to cause a sticking of the quasimolecular U + Cm system for a time $\geq 10^{-20}$ sec. This is over an order of magnitude larger than such dinuclear systems are expected to exist. The conditions for production of this long-lived system are apparently quite specific, since such phenomena are not generally observed. Clearly these exciting results demand expanded experimental efforts to systematize the effects. The need for transplutonium target isotopes to address these questions is crucial.

CONCLUSION

We have tried to demonstrate the importance of continued efforts in the study of heavy elements. Experimental and theoretical programs in this area are vital if we are to probe the limits of stability. This region encompasses the isotopes for which there is a delicate balance between nuclear attractive forces and Coulombic repulsion. New structural information is emerging regarding the importance of symmetry breaking degrees of freedom for the heaviest systems. The existence of octupole deformations has been established in the light-actinide region and they are likely to occur in the very heavy actinides as well. The large quadrupole deformations associated with fission isomers have been experimentally confirmed and provide fundamental information on the pairing interaction. The emerging spectroscopy in the second well is hinting at problems associated with the conventional spin-orbit term in the single-particle potential. The spectroscopy of the heavy-actinide region is beginning to provide detailed information about level assignments which are relevant to the determination of the stability of superheavy elements. Studies of back-bending and upbending at high spins provide fundamental information on the nature of residual interactions in the heavy elements. Similar information may be obtained from studies of the properties of the high-spin two quasi-particle states predicted to cause isomerism in the very heavy elements.

The Transplutonium Production Program will be of vital importance in future fission studies. The fission barriers of the Transcalifornium isotopes are essentially unstudied even though this is a region where theory predicts rapid changes in the barrier properties. Another area of barrier properties requiring a broad systematic study is the effect of excitation energy and angular momentum on the collective enhancements which have been established for fission transition states at low excitation energies. The thermally fissile heavy actinides through studies of the cold fragmentation process will provide information on the dynamic pairing correlations in fission. They will also serve as a source of the very interesting neutron rich light-fission fragments which have large static deformations. The mass distribution and kinetic energy release associated with the spontaneous fission of the heavy Fm isotopes having $N \geq 158$ are very anomalous. A systematic study of the decay properties in this region for both spontaneous and excited state fission would be illuminating. Production mechanisms to provide access to this region will use all types of nuclear reactions, but the most promising avenue appears to be transfer reactions using the heaviest actinide target materials and neutron rich light-heavy-ion projectiles. Elementary particle probes, especially negative muons, offer new directions in fission studies. Coulombic alterations of the nuclear potential energy surface due to the large overlap of the bound muon with the nuclear Coulomb field are of high interest. Fission studies with muonic probes may also provide fundamental information on fission dynamics as well as on the theoretically interesting muonic internal conversion process.

Atomic studies of systems having supercritical field conditions cover one of the most fundamental areas of investigations with heavy elements. The atomic binding energies for transient colliding systems having $Z \geq 173$ are such that the spontaneous vacuum creation of electron-positron pairs should be possible. This test of quantum electrodynamics can be best performed with the heaviest systems using isotopes provided by the Transplutonium Production Program. Preliminary results imply that this much sought-after spontaneous positron emission process may have been observed in the $^{238}U + {}^{248}Cm$ collision. The narrowness of the observed positron peak may imply that nuclear interaction times are over an order of magnitude longer than previously estimated and that a long-lived quasimolecule may be formed under very special bombarding conditions. This area demands expanded efforts to verify and systematize these results.

Clearly, there is much activity in research using the products of the Transplutonium Production Program. The past has been bright and the future seems equally as promising.

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FIGURE CAPTIONS

Fig. 1. Actinide neutron single-particle levels obtained from momentum-dependent Woods-Saxon potential as a function of quadrupole deformation.

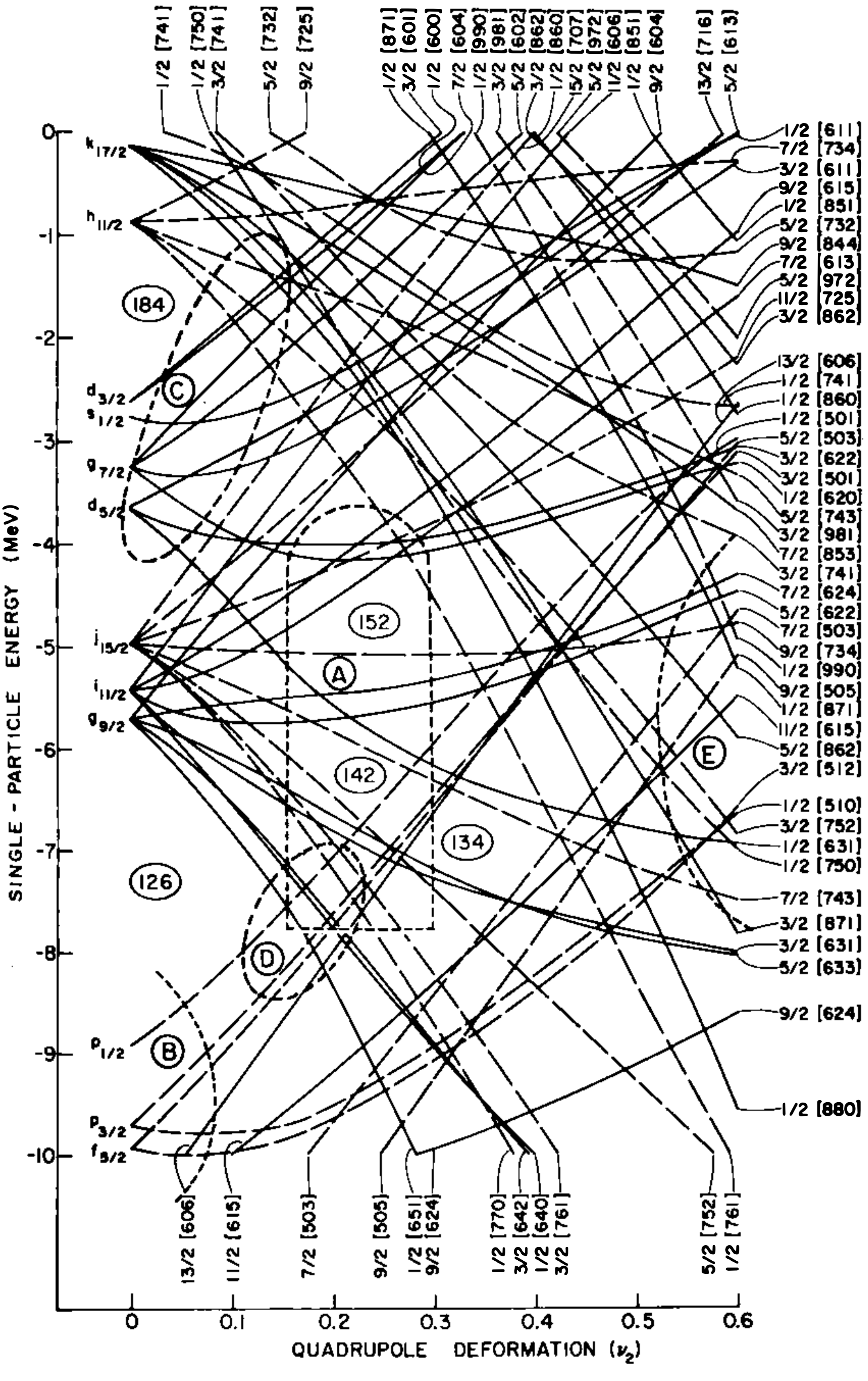
Fig. 2. Actinide proton single-particle levels obtained from momentum-dependent Woods-Saxon potential as a function of quadrupole deformation.

Fig. 3. Mass yield curves for the spontaneous fission of $^{254,256-259}Fm$ (from Ref. 62).

Fig. 4. Comparison of 2p,xn transfer cross sections for the reactions ^{18}O with ^{248}Cm and ^{254}Es (left) and ^{22}Ne with ^{248}Cm and ^{254}Es (right). Curves are Gaussians with $\sigma = 0.977u$ (from Ref. 70).

Fig. 5. Fission barriers for ^{236}U and ^{248}Cm with and without a negative muon bound in the atomic 1s orbital (adapted from Ref. 75).

Fig. 6. Positron energy spectra from 5.8 MeV/u $^{238}U + ^{248}Cm$ collisions selected in coincidence with kinematic conditions to emphasize (a) backward and (b) forward scattering of projectiles. The spectra are not corrected for the solenoidal transport efficiency, for Doppler broadening, for the Si(Li) detector line shape and for the nuclear background (preliminary results from Ref. 116).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1/2 [600]
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1/2 [860]
15/2 [707]
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1/2 [851]
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9/2 [624]
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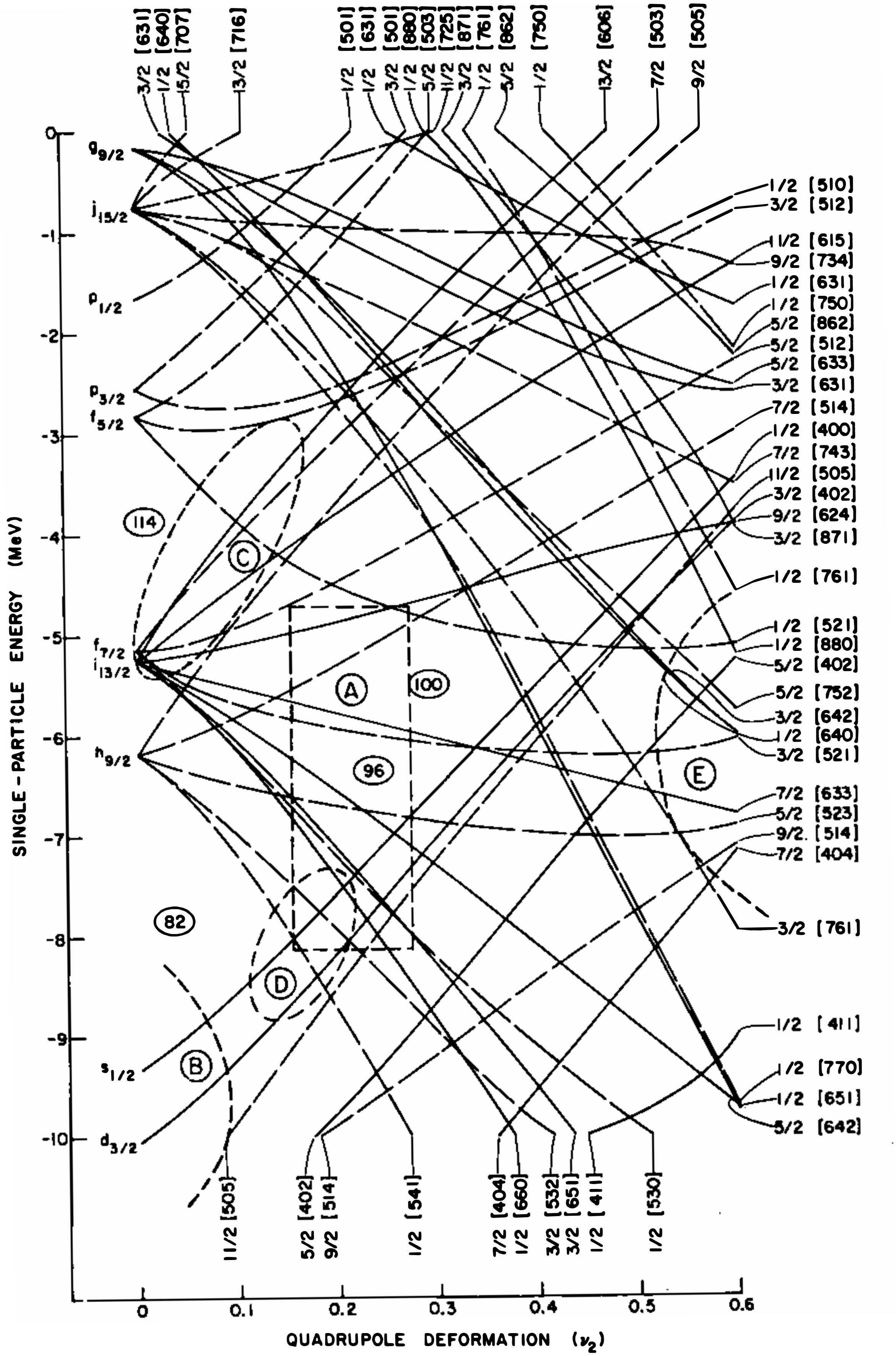
3/2 [642]
1/2 [640]
3/2 [761]
5/2 [752]
1/2 [761]
$k_{17/2}$
$h_{11/2}$
$d_{3/2}$
$s_{1/2}$
$g_{7/2}$
$d_{5/2}$
$j_{15/2}$
$i_{11/2}$
$g_{9/2}$
$p_{1/2}$
$p_{3/2}$
$f_{5/2}$
184
C
152
A
142
134
126
D
B
E
SINGLE - PARTICLE ENERGY (MeV)
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
0
0.1
0.2
0.3
0.4
0.5
0.6
QUADRUPOLE DEFORMATION (ν_2)

Figure 1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7/2 [404]
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3/2 [651]
1/2 [411]
1/2 [530]
$g_{9/2}$
$j_{15/2}$
$p_{1/2}$
$p_{3/2}$
$f_{5/2}$
$f_{7/2}$
$i_{13/2}$
$h_{9/2}$
$s_{1/2}$
$d_{3/2}$
114
100
96
82
A
B
C
D
E
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
SINGLE-PARTICLE ENERGY (MeV)
0
0.1
0.2
0.3
0.4
0.5
0.6
QUADRUPOLE DEFORMATION (ν_2)

Figure 2

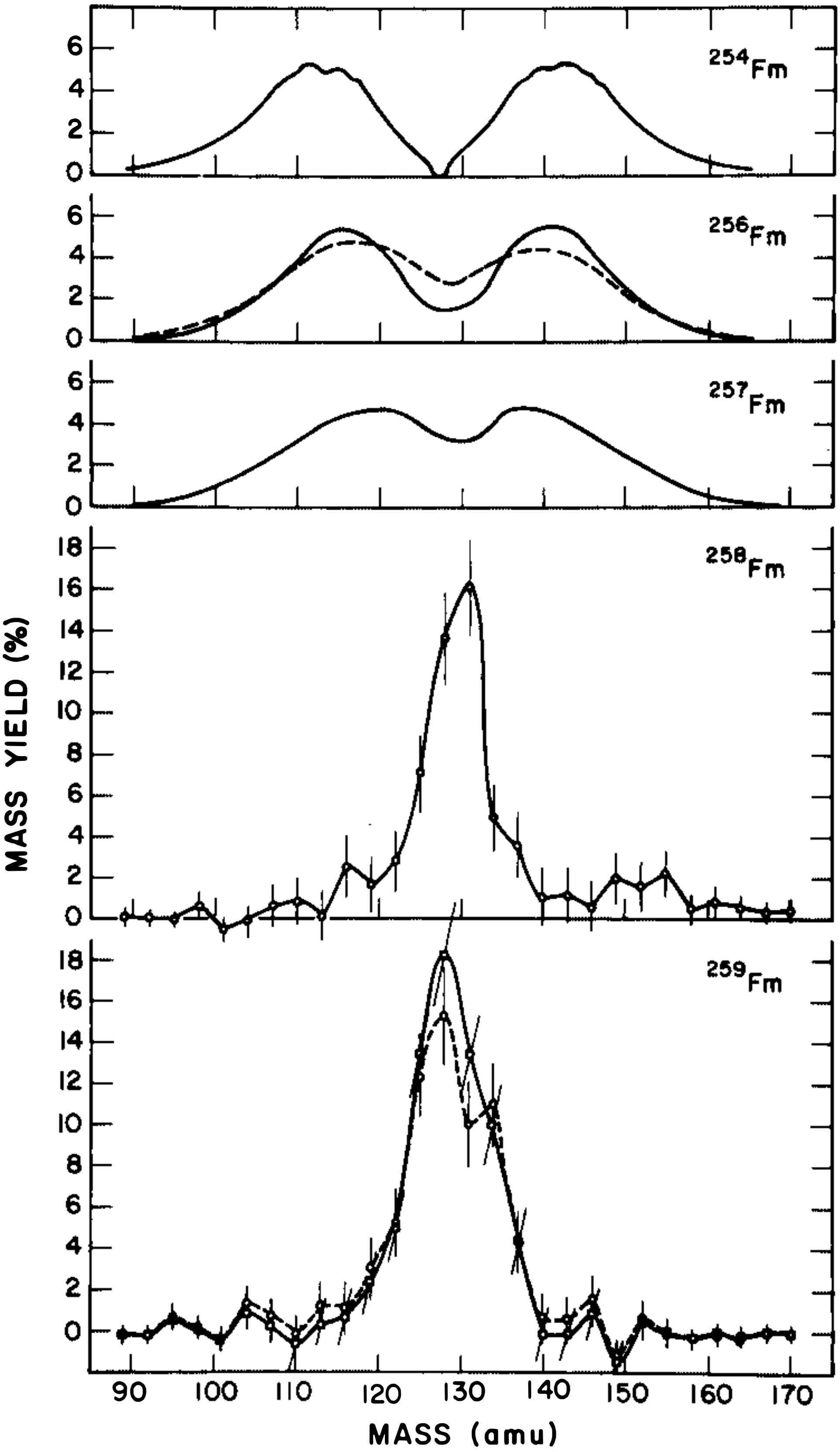
^{254}Fm
^{256}Fm
^{257}Fm
^{258}Fm
^{259}Fm
MASS YIELD (%)
MASS (amu)
0
2
4
6
8
10
12
14
16
18
90
100
110
120
130
140
150
160
170

Figure 3

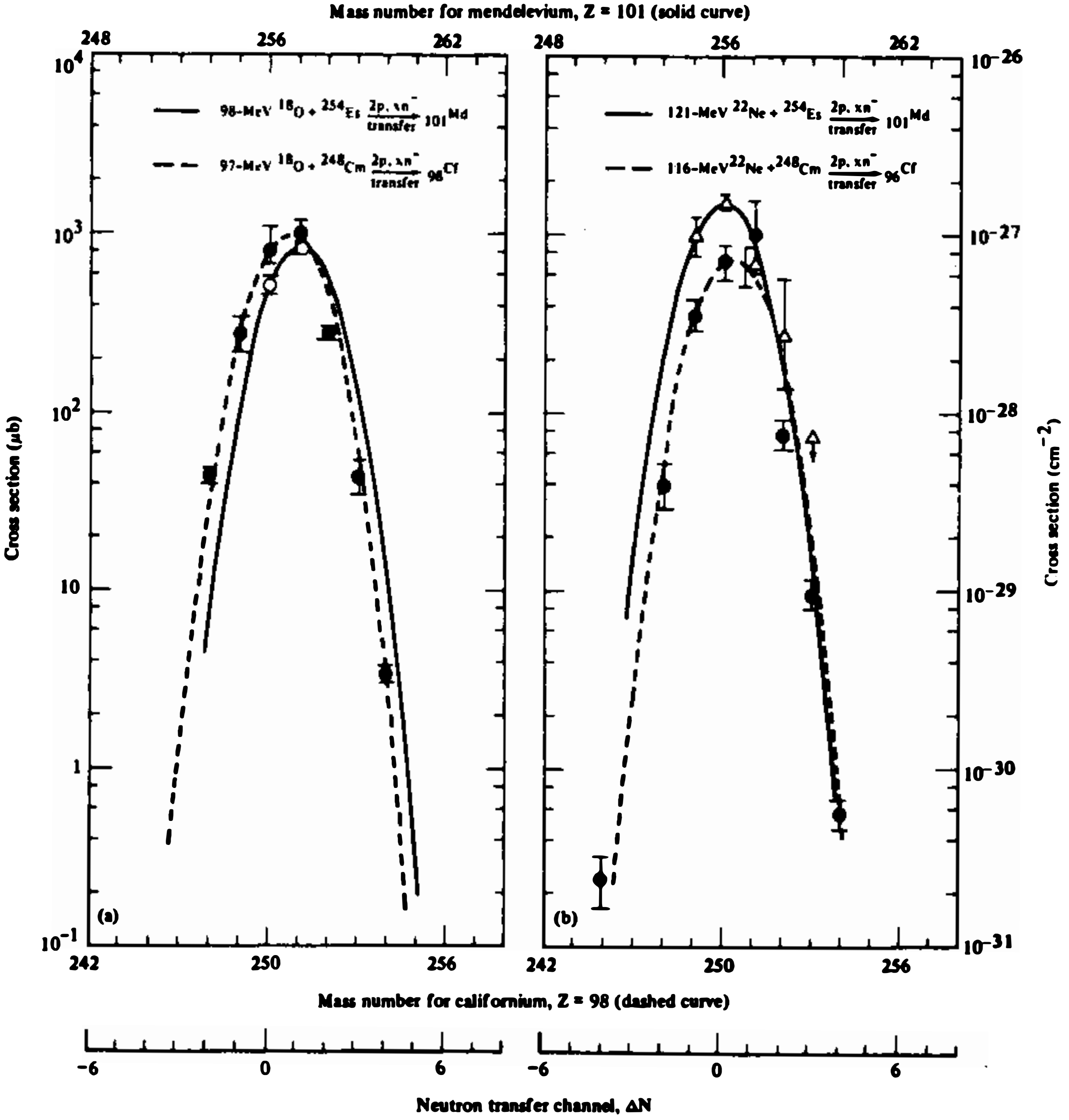
Mass number for mendelevium, Z = 101 (solid curve)
248
256
262
248
256
262
98-MeV $^{18}O + ^{254}Es \xrightarrow[transfer]{2p, xn^-} {}_{101}Md$
97-MeV $^{18}O + ^{248}Cm \xrightarrow[transfer]{2p, xn^-} {}_{98}Cf$
121-MeV $^{22}Ne + ^{254}Es \xrightarrow[transfer]{2p, xn^-} {}_{101}Md$
116-MeV $^{22}Ne + ^{248}Cm \xrightarrow[transfer]{2p, xn^-} {}_{96}Cf$
Cross section (μb)
10^4
10^3
10^2
10
1
10^{-1}
Cross section (cm^{-2})
10^{-26}
10^{-27}
10^{-28}
10^{-29}
10^{-30}
10^{-31}
(a)
(b)
242
250
256
242
250
256
Mass number for californium, Z = 98 (dashed curve)
-6
0
6
-6
0
6
Neutron transfer channel, ΔN

Figure 4

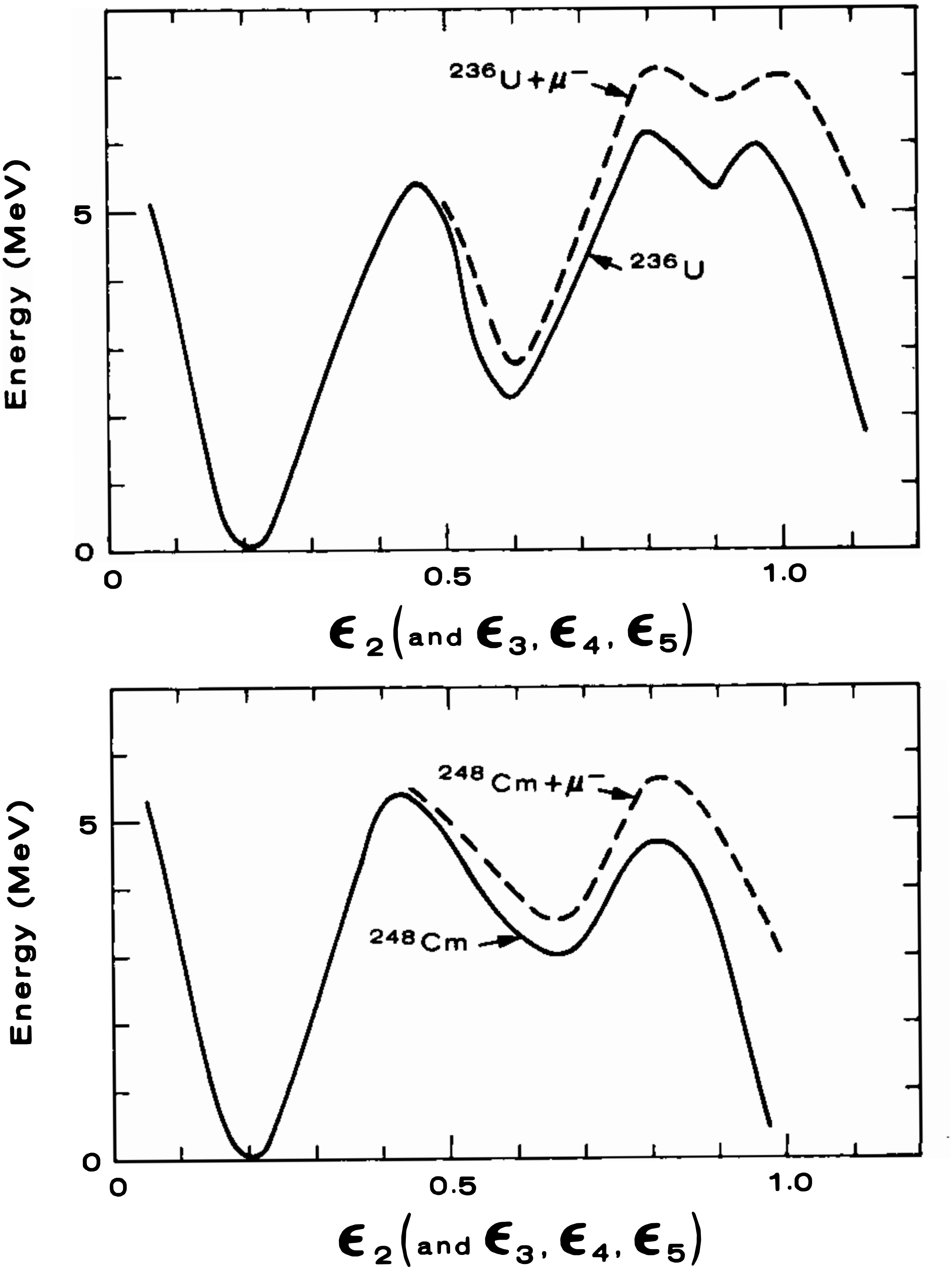
$^{236}U+\mu^-$
^{236}U
Energy (MeV)
5
0
0
0.5
1.0
ϵ_2 (and $\epsilon_3, \epsilon_4, \epsilon_5$)
$^{248}Cm+\mu^-$
^{248}Cm
Energy (MeV)
5
0
0
0.5
1.0
ϵ_2 (and $\epsilon_3, \epsilon_4, \epsilon_5$)

Figure 5

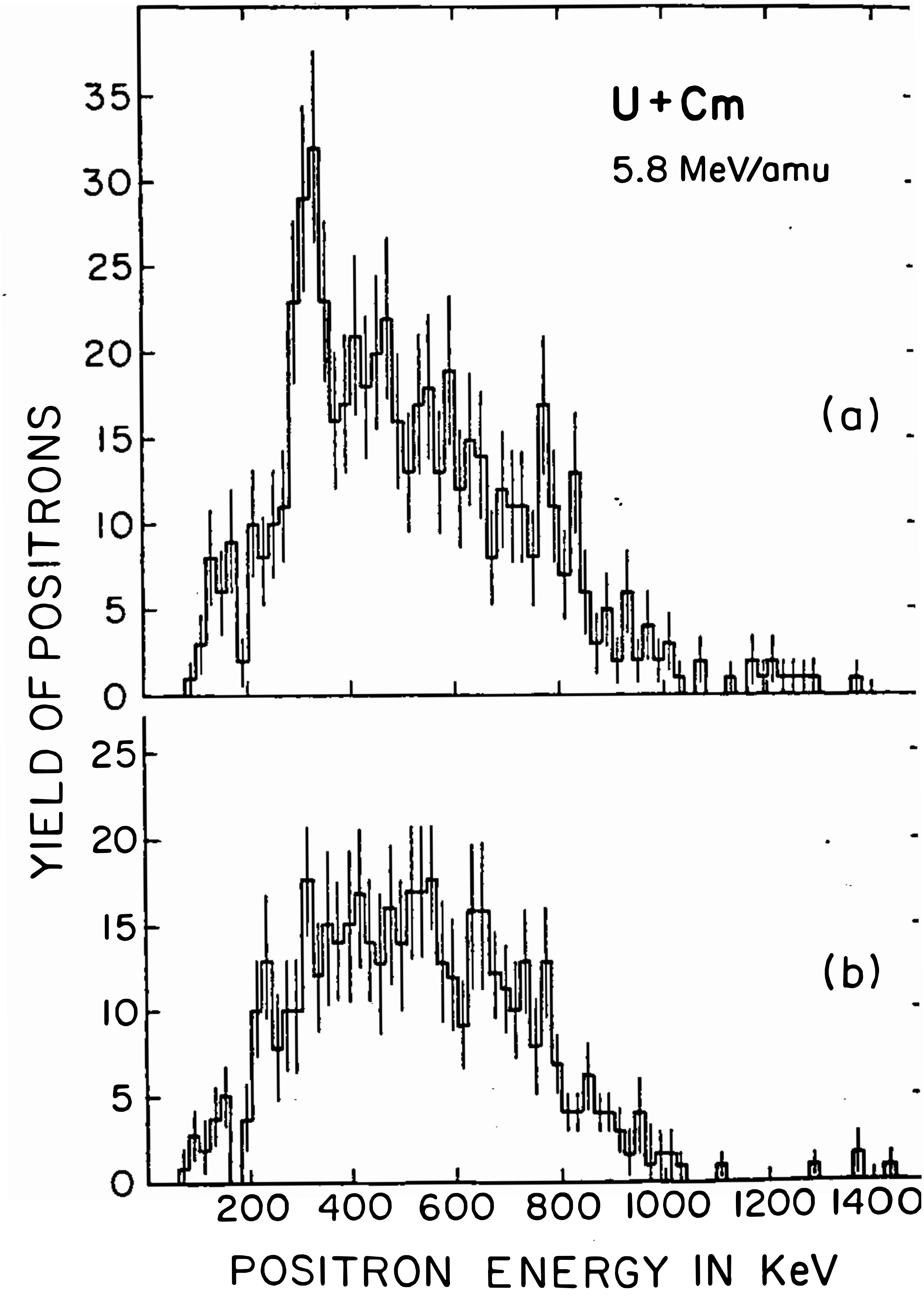
U+Cm
5.8 MeV/amu
(a)
(b)
YIELD OF POSITRONS
0
5
10
15
20
25
30
35
200
400
600
800
1000
1200
1400
POSITRON ENERGY IN KeV

Figure 6

APPENDIX F

THE CHEMISTRY OF THE TRANSPLUTONIUM ELEMENTS

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INTRODUCTION

One of the major scientific advances in the past half century involved the addition of some sixteen new elements heavier than uranium to the periodic table of elements, long considered terminated at uranium, element 92. Furthermore, the heaviest naturally occurring elements, actinium through uranium, were established as members of a second inner transition series whose true beginning had been obscure.[1-6]

This latter fact, now universally accepted, was born in controversy. Its recognition was complicated by the multiplicity of neptunium and plutonium valence states and the ease of their interconversion. In the first half of the actinide series, the promotion energy (5f-6d) is less than that (4f-5d) for the lanthanides, while the reverse is true for the actinide elements heavier than curium.[7] Only in the transplutonium elements does the trivalent aqueous state become dominant. Also, metals of the series have lanthanide-like characteristics only from americium on, while by contrast, plutonium has the most complicated structures of any known metal.

Based on his x-ray diffraction data on the four dioxides ThO_2, UO_2, NpO_2 and PuO_2, the first quantitative recognition of these elements as part of a 5f series was made in mid-1944 by

W. H. Zachariasen. He called the new "rare earth type series" thorides because of the persistence of the dioxide structure from thorium through plutonium (and, as we know now, well beyond).[8] G. T. Seaborg had a deeper chemical understanding and named them the actinides,[9] placing curium, element 96, as the series midmember. He predicted a dipositive state for element 102 analogous to Yb(II), adjacent to the final trivalent member, element 103. Actually element 102 was found to be normally divalent in solution.[5,6] The existence of the divalent state was expected but its great stability versus the trivalent state was a surprise.

Relativistic effects become important with the very heavy elements, involving mainly increased binding of s electrons (and $p_{1/2}$ electrons). This effect is apparently responsible for the unexpectedly small radius found for metallic actinium. As a result, actinium and lanthanum have nearly the same metallic radii, even though their tripositive ionic radii differ, with Ac(III) being substantially larger than La(III) in similar compounds.[10] The increased binding energy of s electrons due to such relativistic effects in the region of Z = 100 is estimated to be ca. 20 KeV higher than values given by the simpler Hartree-Foch treatment.[11a]

There are two major phenomena that have been discovered in the high Z elements beyond Bk, element 97. Both of these phenomena are important on their own merits and because they are suggestive of further research that can tell us about the thermodynamic, kinetic, and general chemical influences of the strong relativistic effects on the electronic configurations in this high Z region. The first of these phenomena discovered was the unexpectedly strong stability of the divalent state relative to the trivalent one in the elements Cf through No. This effect first shows itself in the anhydrous californium dihalides and culminates in the aqueous No^{2+} ion being substantially more stable than the aqueous No^{3+} ion. This behavior of nobelium is in marked contrast to the behavior of its lanthanide homolog, ytterbium, whose 2+ aqueous ion is unstable relative to the 3+ ion. Since the electronic configuration of Yb is $4f^{14}6s^2$ and that of nobelium is $5f^{14}7s^2$, the clear implication is that 5f electrons are more tightly bound than 4f electrons at the ends of their respective series. The magnitude of this increase in 5f binding energy, particularly as it may influence the formation of $5f^{14}$ closed shells, merits considerable experimental and theoretical investigation. One possibility would involve further attempts to discover Md^{+1}, perhaps using non-aqueous solvents. (The electronic configuration of Md is $5f^{13}6s^2$.)

The second phenomenon of importance is the establishment of the transactinide series beginning with element 104.[6,11b] This series is presumed to be a new d electron series analogous to the known 5d series beginning with hafnium. There is no doubt, however, that relativistic influences on chemistry in this region will be apparent. Deviations from Mendeleev type periodicity are predicted for the elements as Z increases much past 100. The first ionization of elements 103-112 is predicted to involve removal of 6d electrons.[11a] Up until now, the only members of this series whose chemistry has been studied are elements 104 and 105.[11b] An important result of these chemical studies is the demonstration of the validity of the prediction that lawrencium is the last member of the actinide series; element 104 has a completely different chemistry from that of 102 (No) and 103 (Lr).

The trends of chemical properties in the new transactinide series will be difficult to determine because the isotopes of these elements have such short half-lives and their production rates are exceedingly low. Nonetheless, this chemistry is so important to our understanding of the periodic table and the influence of relativistic effects that it is well worth doing. Fortunately the use of ^{254}Es targets and of new nuclear reactions promises larger yields of the heavy actinides and possibly of 104 and 105 for chemical studies.

For a heavier alkaline earth metal such as Z = 120, substantially increased ionization potentials are predicted;

the small experimentally observed reversal in ionization potentials of Ba and Ra will be continued and magnified.[11a] Increased binding of $p_{1/2}$ electrons will be observed. Eka-thallium and eka-lead (113, 114) will show substantially increased ionization potentials. An indication of the radically new chemistry expected in this region is indicated by the argument of Penneman and Mann that decreased binding of $p_{3/2}$ electrons for element eka-francium (119) should provide chemists with an alkali metal displaying valences greater than unity.[11a]

The application of modern theory to electronic structure and predicted behavior of still heavier elements has led to increased understanding of the complexities of the inorganic chemistry and solid state properties of the early actinides. For plutonium chemistry we extrapolate from a much broader data base today than 40 years ago when its macrochemistry was just developing. Even so, there are surprises. This is exemplified by a recent report of the dramatic difference in properties of $U(BH_4)_4$ and $Pu(BH_4)_4$. Whereas $U(BH_4)_4$ is a compound of low volatility, $Pu(BH_4)_4$ is quite volatile; this startling difference can be rationalized but was not anticipated.[12]

TRANSPLUTONIUM CHEMISTRY REQUIRES SPECIALIZED FACILITIES[1-6]

The above-mentioned surprises reinforce our argument that actinide chemistry remains an experimental science and the chemistry of the transplutonium elements and its understanding is still evolving. As experimental techniques mature, measurements unattainable a few years ago become possible and new ones appear. It should be emphasized that work with these elements requires specialized equipment to minimize hazards of handling and ingesting these highly radioactive species. Except at trace concentrations, which can be handled safely in properly equipped university laboratories, work with the transplutonium elements continues to be centered at national laboratories in the United States and similarly equipped laboratories in the rest of the world.

THE HEAVY ACTINIDES AND THE U.S. ROLE IN INTERNATIONAL SCIENCE

Whereas in the two decades following World War II the U.S. role in transplutonium chemistry was preeminent, this is no longer true. European and Russian publications reflect their strong contributions to this field, in some areas of which they are the leaders. It is worthy of mention that the number of U.S. investigators in this important area has declined, and that their replacement is not at all assured. Only in the United States and the USSR are the transcurium elements produced, making these countries centers for study of these precious materials. International collaboration involving U.S. and European scientists is relatively common, especially since, as is now so often the case, the European laboratories have the advanced equipment and experimental teams needed for such efforts. The availability of the transplutonium elements to U.S. investigators is the sine qua non of such collaboration.

THE FIRST OF THE TRANSPLUTONIUM ELEMENTS

Americium and curium are of major concern in nuclear waste storage since both are produced in irradiated plutonium fuel. After about 600 years, americium isotopes become the chief offenders for the next ten thousand years.[13] The total production of these transplutonium elements in the nuclear power program through 1978 has been estimated to be 1000 kgs of americium and 250 kgs of curium.[14]

The study of americium has been greatly aided by the availability of the ^{243}Am isotope ($t_{1/2}(\alpha) = 7400$ yr), since the shorter-lived isotope, ^{241}Am ($t_{1/2}(\alpha) = 432$ yr), causes self reduction in solution at a rate of ca. 4%/hr for americium valence states higher than III. In the case of curium, nature was not so kind to chemists since even the longer-lived of the more readily available isotopes, ^{244}Cm, has a half-life of only 18 years, while ^{242}Cm has a half-life of ~ 1/2 year. The high specific activities of these isotopes release sufficient energy in solid lattices that every bond to curium can be broken many times a day. It is obvious that only the most stable solids can be studied and, e.g., organometallic compounds cannot be isolated and studied.[15] Largely because of such problems, the chemistry of curium has been studied relatively little.

For all studies of the transplutonium elements other than americium and curium, U.S. chemists are entirely dependent on the high flux isotope reactor/transuranium production plant (HFIR/TRU complex). From there come the milligram amounts of 1-year ^{249}Bk, 350-year ^{249}Cf, and 10^7-year ^{248}Cm (produced via alpha decay of ^{252}Cf), as well as the microgram amounts of einsteinium, and the even smaller quantities of fermium. Still heavier elements have been produced by bombardment of targets of these heavy isotopes.[5,6]

COMPARISON WITH THE LANTHANIDES

Since the actinide and the lanthanide elements have in common the filling of electronic f-orbitals, comparison of the chemistry of the two series has been a basis of much of the chemical research. A significant difference is the multiplicity of oxidation states in the actinides compared to the prominent stability of the 3+ state in the lanthanides. For all of the actinide elements after plutonium the oxidation barrier between the 3+ and higher states becomes sufficiently large to restrict their aqueous chemistries under normal conditions to that of the trivalent state. In some transplutonium elements, higher oxidation states can be formed in aqueous solution by strong oxidizing conditions aided, usually, by the formation of strong complexes. Stabilization effects in solids permit a wide range of valences to be observed (II, III, IV, V, and VI in the case of americium).[1] Tetravalent curium is its highest valence with oxygen or fluorine as oxidants,[2] although it has been claimed that CmO_2^{++} results after the beta decay of AmO_2^+.[16] The divalent state is observed first with the americium halides, and again with californium. Only at the end of the series with Md and No is the divalent state important in solution chemistry; in the case of nobelium the divalent state is dominant.[5,6]

TRIVALENT ACTINIDES AND LANTHANIDES

The trivalent actinide elements strongly resemble the trivalent lanthanides in some of their chemical behavior: they form insoluble salts such as the hydroxides, fluorides, oxalates, phosphates and double sulfates, and they form soluble complex ions of the same types with organic ligands. Like the lanthanides the transplutonium elements have "hard acid" cations -- that is, their bonding is rather well described by an electrostatic model and they show strong preference for oxygen and fluorine as donor atoms. There is evidence for some greater degree of covalency in actinide-ligand bonds than in analogous lanthanide-ligand bonds, but for both groups, the ionic character of the bonding is predominant. This is true for the metal-oxygen and metal-nitrogen donor bonds prevalent in complexes in aqueous solution[17] as well as for the metal-carbon bonds in organometallic compounds.[18]

As a result of the ionic nature of the bonding, actinide cations coordinated to various ligands do not display the restricted stereochemistry typical of the d-transition elements. The coordination number and the geometry of the coordination sphere in the d elements are strongly influenced by the overlap and symmetry of the metal and ligand orbitals. By contrast, in the ionic interactions of actinide complexes, the number and arrangement of the ligands are determined primarily by steric and electrostatic factors. This leads to a range of coordination numbers from 6 to 12 observed for complexes with simple actinide cations. Even in polydentate complexes such as $\mathrm{CmEDTA}^{-1}_{(aq)}$, the coordination sphere probably includes water molecules.

Separation and Purification (Trivalent States)

Although much of the chemistry of the trivalent lanthanides and actinides is quite similar, significant differences are present in some systems and form the basis of separations of the two groups. A successful class separation of the actinides from the lanthanides uses a cation exchange resin and 13 M hydrochloric acid; an anion exchange process with concentrated lithium chloride is also effective.[19] In aqueous thiocyanate solution, trivalent actinides are sorbed onto an anion exchange resin much more strongly than lanthanides[20] and this process has been used for large-scale americium/lanthanum separation.[21] Solvent extraction with tertiary amine hydrochlorides and concentrated lithium chloride solution is used to separate transplutonium elements from lanthanides efficiently.[22] A useful technique borrowed from biochemistry, that of pressurized chromatography, utilizes micron sized resins and high flow rates under pressure to achieve excellent separations in spite of radiation effects.[23]

TRANSPLUTONIUM ELEMENT PRODUCTION

It should be appreciated that in order to reach ^{242}Pu via neutron irradiation of 239, great losses (~90%) due to fission of ^{239}Pu and ^{241}Pu must be endured. To arrive at ^{242}Pu containing <1% ^{241}Pu requires a major investment. Once at this composition, irradiation to produce ^{243}Am and ^{244}Cm is efficient. These latter nuclides are the springboards for production of the still heavier elements.

It is appropriate at this point to mention briefly the HFIR/TRU facilities at Oak Ridge which are the keystone of the transplutonium production program in the United States. The transuranium processing plant and the neighboring high flux isotope reactor produce transuranium nuclides for use in a variety of research. The most desirable for chemical studies are Z = 96, curium-248; Z = 97, berkelium-249; Z = 98, californium-249, 252; Z = 99, einsteinium-253, 254; and Z = 100, fermium-257. Since 1966 TRU has been the main center of production for transcurium elements in the United States,[24] and has produced 500 mg of ^{249}Bk-^{249}Cf, 4 g of ^{252}Cf, 18 mg of ^{253}Es, and 10 pg of ^{257}Fm. Elements past fermium can be made only by the use of accelerators.

In addition, and of special importance for curium chemistry studies, ~100 mg/yr of ^{248}Cm is presently obtained from the α decay of purified ^{252}Cf. We emphasize that there is no other source for long-lived ^{248}Cm and that a supply of the parent itself, ^{252}Cf, must be maintained because of its own short half-life (~ 2-1/2 years). Since ^{249}Bk has a short half-life (325 days), its supply also has to be replenished frequently. The daughter ^{249}Cf is of moderately long half-life (351 yr), making possible longer term chemical studies.

FEW-ATOM CHEMISTRY

Beginning with fermium, element 100, for which samples containing about ~10^9 atoms are available, studies of the heavier elements are carried out with increasing difficulty, e.g. with mendelevium ca. 10^6 atoms, nobelium <10^3 atoms, and lawrencium a few atoms/experiment.[5,6,11b] Extraordinary demands are placed on techniques and ingenuity of the investigators in the regime of "few atom chemistry". Nonetheless, important chemical data have been accumulated from studies on these heaviest actinides, in spite of their limited availability and short half-lives.

Sequential elution of the actinides from cation resins using α-hydroxyisobutyric acid as the complexing agent has been used not only for purification but for element identification, since the relative elution positions of the trivalent actinides follow a precise pattern versus atomic number.[25] In the case of the transactinides especially, because of their shorter half-lives, faster chemistry involving rapid solvent extraction techniques and gas transport chromatography of volatile compounds have of necessity been developed.[5,6,11b] Such experiments are tedious and need to be repeated many times to obtain statistically significant results.

AMERICIUM, Element 95

The chemistry of the transplutonium elements begins with that of americium.[1,2]

Only two isotopes of americium are important: ^{241}Am has $t_{1/2}(\alpha)$ of 433 years, with associated emission of a 59 KeV gamma ray important to industrial users. ^{243}Am has $t_{1/2}(\alpha)$ of 7370 years, and decays to 2.3-day ^{239}Np, a strong β,γ emitter. Thus, both isotopes require careful handling to avoid excessive radiation exposure. The lower rate of α emission from ^{243}Am is a distinct advantage for many studies.

Americium was first isolated in 1944-1945 from a sample of plutonium which had been exposed to extensive neutron irradiation [^{241}Pu(β^-, 14 yr)^{241}Am].[3,4] Beginning in the 1950's extensive investigations, which elucidated much of americium chemistry on a macroscale, were undertaken at the Los Alamos Laboratory by Penneman, Asprey, Keenan and Coleman, who isolated the first grams of ^{241}Am. The work involved discovery of Am(VI), soluble Am(IV), disproportionation of Am(V), and other fundamental findings.[1]

In this case, as is usual with the actinide elements, the chemistry involved in element isolation also provides information concerning its fundamental chemistry. We cite development of the thiocyanate anion exchange process,[5] the homogeneous precipitation of La-Am oxalate which concentrates Am over La,[6] as well as the oxidation of Am(III) to either Am(V) or to Am(Vl) for purification from lanthanum as well as curium.[7,8] Details of a cation exchange process for large-scale separation are reported by Wheelwright et al.[9] and Hale et al.[10,11]

Present day plutonium metal is so pure that after removal of residual plutonium by anion exchange, the americium remaining can be precipitated as the oxalate and calcined to produce an AmO_2 product of 95 to 99% purity.[12] Filtrates from the peroxide precipitation of plutonium remain today the chief source for ^{241}Am, the production of which is 1 to 2 kg per year at Los Alamos.[12]

SEPARATION AND RECOVERY OF AMERICIUM BY SOLVENT EXTRACTION

Much of the following is applicable to the rest of the transplutonium elements and will not be repeated in their descriptions.

Solvent extraction processes with amine and organophosphorus extractants are extensively used for the initial recovery and separation of gram amounts of americium. See Weaver,[13] Myasoedov et al.[14] and Shoun and McDowell.[15]

Tri-n-butyl phosphate (TBP) is the extractant in widest use for nuclear fuel processing. Since TBP leaves Am(III) behind in the high level acid waste streams, a more effective extractant is needed to remove Am(III). Siddall found that neutral bifunctional organophosphorus extractants have this desirable property.[16] Schulz[17] and McIsaac[18] at the Hanford and Idaho Falls sites, respectively, have revived interest in plant-scale application of such compounds for extraction of <u>trivalent</u> actinides.

An excellent commercially available extractant for Am(III) (and the other trivalent actinides as well) is di-(2-ethylhexyl)phosphoric acid (HDEHP) which has been widely used for purification of americium.[19,20,21] For example, a countercurrent HDEHP extraction process was used at Hanford to recover 1 kg of Am and 50 g of Cm from irradiated Shippingport reactor fuel.[22]

THE METAL

Americium metal (m.p. = 1170°C) is appreciably more volatile than the metals of the neighboring elements plutonium or curium. Its volatility, utilized first at Los Alamos, has been exploited by workers at Karlsruhe in Germany[23-25] and in the United States at Rocky Flats.[26] As a consequence of the availability of very pure, redistilled americium metal, many properties have been examined in recent years by workers using a variety of techniques. This progression in purity and availability is a characteristic of studies in the whole actinide area. In double hexagonal, close-packed (dhcp) form, the metallic radius of americium is 1.73 Å in coordination number 12. Extremely interesting recent findings include the discovery of superconductivity[27] in dhcp americium metal at 0.79 K and the change from the dhcp form to the complicated α-uranium type of structure at high pressure.[28]

COMPOUNDS

Several hundred compounds of americium have been prepared and characterized. Since many reviews exist, the myriads of compounds will not be discussed here.

SOLUTION CHEMISTRY

There is evidence for all oxidation states II, III, IV, V, VI and VII with III through VI being well studied in acid solution. The lowest state, Am(II), reacts with water to yield Am(III). Indeed, oxidation states higher than III are powerful oxidants and are readily reduced to Am(III) by chemical reducing agents or self-irradiation effects. This latter effect amounts to several percent per hour for ^{241}Am.

As americium is the homolog of europium, it was originally anticipated that a divalent state for americium would be attainable in aqueous solution and that oxidation states higher than III would be difficult to attain. Despite many attempts to produce it, Am(II) was found only after the availability of americium metal made it possible to use it to reduce a mercury dihalide.[29] Am(II) in aqueous solution is unknown except as a transient species produced at low concentrations by pulsed radiolysis (Sullivan[30]).

Oxidation of $Am(OH)_3$ by hypochlorite or ozone results in formation of $Am(OH)_4$.[31] Soluble fluoride species, from which red $(NH_4)_4AmF_8$ can be crystallized, are obtained on dissolution of $Am(OH)_4$ in concentrated NH_4F solutions.[32] As reported by Soviet workers, tetravalent americium is also stabilized by phosphoric acid[33] or in heteropoly anions such as phosphotungstate.[34,35]

Pentavalent americium as the cation AmO_2^+ is formed as one of several insoluble carbonate compounds from K_2CO_3 solution when the solution is treated (hot) with oxidants such as ClO^-, O_3 or $S_2O_8^{2-}$. Dissolution of the trivalent hydroxides of americium and curium in strong K_2CO_3 solution followed by oxidation of Am(III) to the insoluble Am(V) double carbonate, affords a separation from curium.[8,36,37] Dissolution of this precipitate in dilute acids yields a solution of monomeric, linear AmO_2^+.[38] In concentrated acid, Am(V) disproportionates into Am(III) and Am(VI).[39] This disproportionation has been studied by Coleman, who used ^{243}Am(V) in his study to diminish radiation effects. He was able to elucidate a complex rate expression[39] that had been obscured in earlier studies with $^{241}Am(V)$.

Hexavalent americium, as the acid soluble, monomeric species AmO_2^{2+}, was first prepared by $S_2O_8^{2-}$ oxidation of Am^{3+}.[40] Ozone treatment of a slurry of $Am(OH)_3$ in $NaHCO_3$ yields a deep magenta colored complex of Am(VI).[41] There is recent evidence for the formation of unstable AmF_6 gas by the reaction of AmF_4 and KrF_2 in anhydrous HF.[42]

As mentioned previously, much of the solution chemistry of americium, as well as that of the other transplutonium elements, has been the result of development of separation and purification schemes. Complexation of trivalent americium has been studied with OH^-, SCN^-, Cl^-, NO_3^-, SO_4^{2-} and a variety of organic carboxylic acids. These confirm the ionic nature of the bonding and the general similarity to lanthanide behavior in the trivalent state.

The ions of americium and their preparation are listed in Table I.

TABLE I. IONS OF AMERICIUM

Oxidation State	Color	Preparation
III	pink-orange	AmO_2 + hot HCl or red'n agent; Am(>III) + I^-, SO_2, or radiation.
IV	rose, > 1 mM	$Am(OH)_3$ + OCl^-, O_3 or $S_2O_8^{2-}$; $Am(OH)_4$ + sat'd F^-, H_3PO_4, $P_2W_{17}O_{64}$ complex; electrochem. in $NaHCO_3/Na_2CO_3$.
V	yellow-tan	$Am(OH)_3$ in K_2CO_3 + O_3, OCl^-.
VI	light yellow; brown in SO_4^{2-}; magenta in CO_3^{2-}.	Am^{3+} + $S_2O_8^{2-}$, hot dil. H^+; electrochemistry; O_3 + Am(III) in $NaHCO_3$.
VII	green	Am(VI) + O_3 or γ irradiation in N_2O sat'd, cold NaOH.

CURIUM, Element 96

The isotope of curium which led to its discovery in 1944 is the short-lived, 164-day ^{242}Cm, which has been produced on a large-scale by neutron capture in ^{241}Am. The longer-lived isotope ^{244}Cm ($t_{1/2}(\alpha)$ = 18 yr) was made at Savannah River on the kilogram scale for use as a heat source material by irradiation of ^{242}Pu/^{243}Am targets.[1] Both ^{242}Cm and ^{244}Cm have been used in radionuclide batteries, but ^{238}Pu has largely supplanted the shorter-lived curium for this purpose. A cake of $^{242}Cm_2O_3$ weighing a few grams can be photographed by its own incandescence. The very features which are attractive for heat sources make these light curium isotopes difficult to work with in chemistry, except with the most radiation-stable solids or at tracer levels in solution. However, ^{248}Cm ($t_{1/2}(\alpha)$ = 3.8 x 10^5 yr) from HFIR/TRU is sufficiently long-lived to allow meaningful and extensive chemical research to be accomplished in the next decade.

THE METAL

Curium metal has been prepared and distilled after reduction of curium oxide with thorium metal. The malleable, silvery curium metal has a melting point (1340±40°C) which is higher than that for the immediately preceding actinide elements [U-Am (640-1200°C)], and similar to that of gadolinium (1312°C), its lanthanide analog.[2] Curium metal exists in a dhcp structure (α-lanthanum type) and a high temperature, cubic close-packed (fcc) structure. The dhcp form has lattice constants $\underline{a}$ = 3.496 and c = 11.221 Å with a metallic radius for Cm^0 of 1.74 Å.[2] There is disagreement concerning the reported high temperature fcc phases of curium metal.[3,4]

Curium has an entropy of vaporization similar to that of other lanthanide and actinide metals but its entropy of fusion is relatively high.[5] The vapor pressure of triply distilled ^{244}Cm metal has been measured;[5] the derived heat of fusion, entropy of fusion, and the average second-law entropy values are 3.31 kcal/mole, 1.19 cal/deg, and 25.86±0.72 cal/deg, respectively. The determination of low temperature, condensed phase thermodynamic parameters await further studies with the long-lived isotope ^{248}Cm.

CURIUM COMPOUNDS

$^{244}CmF_4$ has been prepared successfully from $^{244}CmF_3$ and fluorine.[6] With oxygen, however, the composition CmO_2 is not reached with ^{244}Cm; the stoichiometric dioxide occurs only with the long-lived ^{248}Cm. Compounds of Cm-containing organic ligands can be studied successfully only with ^{248}Cm. For example, the curium triscyclopentadienyl compound could not be made with ^{244}Cm, only with ^{248}Cm.[7] Radiation-induced interconversion of the solid sesquioxides has been reported. A number of solid halide and oxide compounds, mostly with ^{244}Cm, are known but most of this work should be repeated with ^{248}Cm. The chelate $CsCm(HFA)_4 \cdot H_2O$ (HFA = hexafluoroacetone) has spectroscopic properties which suggested laser properties; however, in the case of ^{244}Cm, this compound is decomposed by self radiation effects in a few hours.[8] The rapid darkening of the compound makes such studies impossible with ^{244}Cm.

SOLUTION CHEMISTRY

Trivalent curium is the only stable state in solution. There is evidence for the temporary existence of Cm(IV) in an alkali fluoride solution of CmF_4; the latter compound was previously prepared from fluorination of solid CmF_3.[9]

Transient divalent and tetravalent states have been observed in aqueous perchlorate media using pulse radiolysis techniques.[10] Recently, formation of a red Cm(IV) complex in phosphotungstate solution was reported using peroxydisulfate as the oxidant.[11] Kosyakov et al.[12] demonstrated that in such solutions the Cm(IV) is reduced much faster than can be accounted for solely by radiolytic effects. Recent successful generation of soluble carbonate solutions of tetravalent praseodymium suggests that Cm(IV) species may be prepared similarly.[13]

The aqueous absorption of Cm^{3+} and of Cm(IV) fluoride complex show narrow, line-rich spectra.[14,9] In the case of

^{244}Cm(IV), rapid radiation-induced reduction was found. It would be worthwhile to repeat this experiment using ^{248}Cm.

Curium(III) complexation in aqueous solution has been studied for the common inorganic and representative organic ligands.

The chemistry of curium thus far studied has often been circumscribed by radiation effects of the lighter curium isotopes. There is an obvious need to reexplore many of these experiments with ^{248}Cm and to develop new areas of curium chemistry using this long-lived isotope.

BERKELIUM, Element 97

Evidence for this element was obtained in 1949, but the first fraction of a microgram for a compound was not available until 1962.[1-3] Today ^{249}Bk is available in milligram amounts. Even so, studies of berkelium are complicated by the rapid ingrowth of the ^{249}Cf daughter (~1% each 5 days). Separation must be made frequently, or some means of compensation included in the experimental analysis. The latter can be accomplished by extrapolation from a pure californium phase. In aqueous solution, oxidation from Bk^{3+} to Bk^{4+} (e.g., with HNO_3/BrO_3^-) expedites separation from trivalent actinides.[4] Since tetravalent berkelium and cerium have similar oxidation potentials, a step specific for the isolation of berkelium must be included if cerium is also present.[5]

THE METAL

Berkelium metal (m.p. 986°C) has been reported in both dhcp and fcc crystallographic modifications.[6,7] Lattice constants are dhcp, $a_0 = 3.416$ and $c_0 = 11.069$ Å, yielding a metallic radius (in 12 coordination) of 1.7 Å. The fcc phase is reported as $a_0 = 4.997 \pm 0.004$ Å (note the lattice constant for BkN is 5.010 ± 0.004 Å).[8] The vapor pressure of the metal has been determined and is higher than that of curium at comparable temperatures.[9]

COMPOUNDS

The trivalent oxidation state is common for berkelium but the tetravalent state is exhibited in BkO_2 [10] and in BkF_4.[11] The chloride compound of tetravalent berkelium, Cs_2BkCl_6, can be precipitated from cold HCl/CsCl solution (n.b., this gives immediate reduction of Am(IV) to Am(III) when applied to americium). The Bk(III) compound $Cs_2NaBkCl_6$ can be obtained from similar HCl solutions.[12] Crystallographic data are known for some two dozen compounds, including berkelium oxides,[10,13] halides,[14-19] as well as the 1:1 pnictide series.[20] Some chalcogenides are also known.[10,12-14,21] The sole representative of the organometallic group are the cyclopentadienides of berkelium.[22]

Berkelium is the first actinide whose trifluoride exhibits the YF_3 type orthorhombic structure at room temperature.[15] The absorption spectrum of solid BkF_4 was obtained.[23] Mixed alkali metal (M)-Bk(IV) fluoride compounds of the types $MBkF_5$, M_2BkF_6, M_3BkF_7, and $M_7Bk_6F_{31}$ should be readily prepared.[24] The structure of $BkCl_3 \cdot 6H_2O$ is similar to that of $AmCl_3 \cdot 6H_2O$ and thus berkelium is likely present as eight coordinated $BkCl_2(OH_2)_6^+$ units.

SOLUTION CHEMISTRY

Complexation constants for Bk^{3+} with common inorganic and a dozen organic ligands are known. However, none have been reported for Bk(IV).

Carbonate ions form a very strong complex, with Bk(IV) altering the potential significantly.[25] In a manner similar to that first utilized to produce $Am(OH)_4$, oxidation of $Bk(OH)_3$ to yellow $Bk(OH)_4$ is accomplished by ozone.[26]

The absorption spectra of aqueous Bk(III) and Bk(IV) have been observed,[27,28] and interpreted.[29] Also, absorption bands of two organoberkelium compounds, $Bk(C_5H_5)_3$ and $[Bk(C_5H_5)_2Cl]_2$, have been published,[22,30] as well as spectral characterization of berkelium halides.[31] The fluorescence of Bk^{3+} in H_2O and D_2O solutions has been reported as part of a study for assessing the use of fluorescence detection for transuranic ions.[32]

CALIFORNIUM, Element 98

Californium-252 is such an intense source of fission neutrons that chemical studies done with it are limited to tracer level studies. The 249 isotope of 351-year half-life derives from the beta decay of ^{249}Bk. It is the isotope of choice for most chemical work as well as being used for target material for the preparation of still heavier elements. With the availability of multimilligram amounts of the ^{249}Cf isotope, it was possible to expand the thermochemistry of californium to include the heats of solution[1] and sublimation of the metal.[2] Californium is the element of highest atomic number that is (or expected to be) available in milligram amounts and that has a reasonable half-life (a few hundred years).

THE METAL

Californium is a rather low melting metal (900°C)[3] with a greater volatility than that of any earlier actinide,[2,4] again suggesting a tendency towards divalency. Its preparation is thus more difficult than that of Am, Cm or Bk.[5] Since californium metal "wets" tantalum, tungsten is the preferred container material for the metal. Several crystallographic studies indicate that the metal exists in both trivalent and divalent forms, although the temperature/pressure limits of such phases are still to be established with certainty.

COMPOUNDS

Californium is known in compounds with oxidation states of II, III, and IV. The tetravalent state is exhibited in CfO_2 and CfF_4, and the divalent state has been observed in $CfCl_2$, $CfBr_2$, and CfI_2.

The oxides of new elements are often among the first solids to be investigated. For californium oxides, three forms of the sesquioxide are known, plus rhombohedral Cf_7O_{12} (existing only over a narrow composition range), and an fcc phase, CfO_2.

The oxidation behavior of mixed (Bk,Cf) oxides was examined as a function of the californium content since ^{249}Cf grows into ^{249}Bk samples.[6] At ~25 mole % Cf, the californium-berkelium mixture could be readily oxidized in air to MO_2, similar to pure berkelium; when the californium content reached ~64 mole %, M_7O_{12} was the limiting composition.

The only binary Cf(IV) halide known is CfF_4, prepared by fluorinating either CfF_3 or Cf_2O_3 at 300-400°C.[7-9] The tetrafluoride has limited self-irradiation and thermal stability, decomposing to CfF_3. Mixed alkali metal fluoride complexes of the types $MCfF_5$, M_2CfF_6, M_3CfF_7, $M_7Cf_6F_{31}$ are unknown but are expected to exist.

Californium trifluoride is dimorphic (orthorhombic, YF_3 type; trigonal, LaF_3 type),[10-12] and the trichloride is dimorphic.[13,14] Californium tribromide is trimorphic, but only two of the three forms have been prepared directly. The third form, the $PuBr_3$ type orthorhombic structure, was formed via decay of an aged (after decay through several half-lives) orthorhombic $^{249}BkBr_3$ parent.[15]

All of the dihalides of californium have been prepared except the difluoride. The first compound of Cf(II) identified was $CfBr_2$ prepared by hydrogen reduction of $CfBr_3$.[16,17] Lime-green $CfBr_3$ undergoes thermal reduction (760°C) to amber-colored $CfBr_2$.[18] Two forms of CfI_2 are known.[19,20]

An organocalifornium compound, $Cf(C_5H_5)_3$, has been prepared and characterized crystallographically.[21] Both powder and single crystal x-ray data were obtained for this orthorhombic compound, which was prepared from $CfCl_3$ and molten $Be(C_5H_5)_2$ and isolated by vacuum sublimation (135-200°C).

SOLID STATE ABSORPTION SPECTRA

By use of absorption spectrophotometry the f-f and f-d transitions in californium spectra can be utilized to determine the oxidation state and coordination number of californium in compounds. Laser-induced fluorescence of Cf^{3+} in a $LaCl_3$ host has been reported.[22,23]

SOLUTION CHEMISTRY

Although californium exhibits oxidation states of II, III, and IV in the solid state, its solution chemistry is that of a trivalent ion. The tetravalent state in aqueous media is stabilized by complexation. It has been reported that Cf(IV) has been stabilized in phosphotungstate solutions.[24]

The calculated value for the IV/III couple of ~3.2 V [25] is consistent with the inability of Cf^{4+} to exist as a simple aquo ion. From a polarographic and voltammetric study[26] of californium, Musikas et al. concluded that californium is reduced via a two-step process as is samarium: (1) Cf(III) → Cf(II) and (2) Cf(II) → Cf(Hg). Potentials for these processes were given as -1.47 and -1.68 V, respectively. With corrections, these data yield a calculated value of -1.61 V for Cf(III)/(O).

Since Cf(II) can be prepared and maintained in the solid state, there still remains a possibility that Cf(II) can be stabilized in non-aqueous solvents or in molten salt media.

There are data dealing with californium complexation and the solvent extraction chemistry of Cf(III) using tracer techniques.[26-28] These data are consistent with its behavior as eka-dysprosium.[27]

EINSTEINIUM, Element 99

Based on the studies of the metal (m.p., 860±50°C) as determined by electron diffraction, einsteinium is likely divalent in the metallic lattice and has a higher volatility than "trivalent" metals.[1,2] Such studies have mostly used 20-day ^{253}Es. Radiation effects destroy the lattice before it can be defined by conventional x-ray diffraction. The annual production of ^{253}Es is about 2 mg/yr.[3] The chemical separation and isolation of einsteinium is a tour de force in separations technology since this highly radioactive materal is present in such small amounts. It is performed only in the United States and the USSR using sophisticated ion exchange techniques.[4,5]

Divalent einsteinium was identified by Mikheev and co-workers in the USSR by co-crystallization with $SmCl_2$.[6] They concluded that the Es(III)/(II) potential was close to that of the Sm(III)/(II) couple, -1.55±.06 V.[7] A few oxide, halide and oxyhalide compounds of einsteinium have been prepared.

Even fewer have been characterized structurally due to problems from radiation damage and film blackening from self irradiation in competition with the diffracted x rays. The divalent compounds EsI_2, $EsBr_2$ and $EsCl_2$ were characterized by their absorption spectra.[8] Divalent einsteinium has been identified as a guest ion in CaF_2 by the electron paramagnetic resonance (EPR) signal of Es^{2+}.[9]

The absorption spectrum of Es(III) has been measured.[10,11] Only a few stability constants for solution phase complexation have been determined.[12] Estimates have been given by David et al.[13-15] for the free energy, enthalpy, and entropy of formation of Es^{3+} in aqueous solution.

The possibility of increased ^{254}Es production is important with respect to improved chemical understanding of Es metal and compounds, especially since einsteinium is the last element expected to be available in "weighable" amounts, albeit at the microgram level.

FERMIUM, Element 100

The fermium isotopes ^{255}Fm and ^{257}Fm are available in amounts of 10^9-10^{11} atoms. Fermium-255 ($t_{1/2}(\alpha) = 20$ h) is obtained from ^{255}Es.

Since neither metallic nor compound forms of fermium have been prepared, investigators have had to rely on comparison methods to arrive at properties ordinarily associated with solids. An example of such a technique is the evaporation of Fm and Md tracers from molten lanthanum at 1150°C and the comparison with behavior of selected lanthanides and actinides. The order of volatilities was found to be Md, Fm > Cf > Am, with Cf ≅ Yb and Eu.[1]

The solution chemistry involves both Fm^{3+} and Fm^{2+}. Mikheev[2] about ten years ago was the first to reduce Fm^{3+} to Fm^{2+}, and found that the Fm(III)/(II) potential was essentially the same as the Yb(III)/(II) couple, ca. -1.15 V.[3,4] Samhoun and David,[5] after correcting empirically for the amalgamation potential,[6] propose a value for $Fm^{2+} \rightarrow Fm^0$ of -2.3_7 V. The migration rate in an electric field gradient was interpreted to indicate that the $Fm(H_2O)_8^{3+}$ ion was present in aqueous perchlorate solutions.[7]

The ground state electronic configuration of fermium has been established as $5f^{12}7s^2$ in an elegant atomic-beam measurement,[8] and other shells have been measured by electron spectroscopy[9,10] in the decay of ^{254m}Es to ^{254}Fm. These investigations illustrate the attainment of direct measurement of electronic properties in this region.

MENDELEVIUM, Element 101

The 77-min isotope ^{256}Md is made by accelerator bombardment of actinide targets (e.g., ^{254}Es).[1]

Separation of Md^{2+} from trivalent actinides was accomplished by Hulet et al. and involved passage of an impure Md^{3+} solution through a Jones Reductor onto an extraction column containing di-(2-ethylhexyl)phosphoric acid adsorbed on fluorocarbon powder.[1] Divalent Md^{2+} passed through while the trivalent actinides were retained. Separation of Md^{3+} is frequently accomplished using cation exchange with α-hydroxyisobutyric acid eluant.[2]

Its high volatility when present as a tracer in molten metals indicates that Md metal is divalent in metallic systems. Hulet cites Mály's conclusion that the Md(III)/(II) potential is close to -0.1 V in aqueous solution while the Md(II)/(O) couple has a value of -1.50 V.[3]

As noted for both fermium and mendelevium, Mikheev utilized co-crystallization with $SmCl_2$ to establish a divalent state of these actinide elements. Working similarly with CsCl and RbCl as carriers, Mikheev claimed evidence for Md^+.[4] However, Hulet and co-workers[5] precipitated Rb_2PtCl_6 from a solution containing Md^{3+} which had been reduced with Sm^{2+} and the precipitate did not carry Md, even though nearly all the Cs^+ present was carried. These workers concluded that Md^+ was not prepared using Sm^{2+} as reductant, and that the earlier claim for monovalent Md was thus not substantiated.

These studies have set limits on the stability of Md^+, and the divalent state can be estimated to be at least 1.3 V more stable. The possibility that the $5f^{13}7s$ state may be more stable than the $5f^{14}$ state is a tantalizing conclusion spurring the design of further studies combining theory and experiment.

NOBELIUM, Element 102

This element is found to have a divalent state in aqueous acid solution; it is more difficult to oxidize and to hold as No^{3+} than had been anticipated.[1] The specific identification of the prior actinides Am-Md could be established by their sequential order of elution from cation exchange columns with organic ligand eluants. This method of identification is not valid for nobelium because of its predominantly divalent nature. Rather, the atomic number and mass were established by observing characteristic K x rays from the known ^{251}Fm daughter in coincidence with the α decay of parent ^{255}No.[2]

Mály and, separately, Zvára et al. at Dubna have done important chemical research on transactinide elements; Mály collaborated with U.S. researchers to perform over 600 experiments which involved *in toto* ~50,000 atoms of ^{255}No.[3] Their studies at Berkeley and at Oak Ridge showed that No^{2+} behaves in a manner similar to the alkaline earths, with extraction behavior between Ca^{2+} and Sr^{2+}.[4] The reduction potential of the No(III)/(II) couple estimated to be -1.45 V.[5] The very few stability constants determined for No complexation have values between those of Ca^{2+} and Sr^{2+}, confirming the divalent nature of No.

Since a linear relation exists between the log of the distribution coefficients of the alkaline earths and their ionic radii, it was possible to estimate the ionic radius of No^{2+} as 1.1 Å.[4] This experimental value was confirmed by applying Pauling's correction to the radius of the outermost $6p_{3/2}$ shell calculated using a Hartree-Foch-Slater program. The polarizability of No^{2+} appears relatively low since it does not complex chloride ions as do Hg^{2+} and Cu^{2+}.

Future studies of nobelium chemistry should be aided in accuracy and complexity by the recent discovery of new nuclear synthetic methods, using ^{254}Es targets, of making 1-hour ^{259}No in 1,000 atom amounts. Studies to this time have been made using the 3.1-minute ^{255}No at levels of 20 to 200 atoms per experiment.

LAWRENCIUM, Element 103

Chemical identification of Lr was not made in the discovery experiments, but the atomic and mass numbers were established by nuclear generic relationships. The isotope ^{256}Lr ($t_{1/2}(\alpha)$ = 35 sec) is made by the reaction ^{249}Cf (^{11}B, 4n), to yield ~10 atoms per irradiation.[1]

Because of the 35-sec half-life, only one or two atoms are actually detected per chemical experiment, but Silva and co-workers at Berkeley could still use fast solvent extraction techniques to establish that Lr^{3+} was the stable state in solution. Soviet workers compared several actinide chlorides with that of $LrCl_3$ in a heated column and found its behavior to be consistent with that expected for eka-lutetium.[2]

Chemical studies of Lr are thus sparse indeed. It would be well worthwhile to investigate new nuclear synthetic procedures that use transfer reactions, perhaps based on ^{254}Es targets, to search for higher yield reactions for not only 35-sec ^{256}Lr but also ~3-min ^{260}Lr. Success in these nuclear experiments would open up new doors for the chemical studies.

Since the electronic configuration of Lr is strongly influenced by relativistic effects, there is some confusion as to whether the $7p_{1/2}$ orbital has been lowered in energy sufficiently to be filled rather than the 6d. Although the question of whether the electronic configuration of Lr is $5f^{14}6d7s^2$ or $5f^{14}7s^27p$ appears moot, it does suggest that an investigation of possible divalency in Lr might prove interesting in this highly relativistic region.

ELEMENT 104

Two short-lived isotopes of element 104 are available for study: 3-sec $^{259}104$, and 1-min $^{261}104$. Transport of gaseous chlorides through a heated column was used at Dubna by Zvára et al. to differentiate between MCl_4 (high v.p.) and MCl_3 (low v.p.).[1] The work established that the chloride of 104 compared in volatility with that of $HfCl_4$.

Solution work at Berkeley (Silva et al.) utilized 1-min $^{261}104$ in an ion exchange study to establish on the basis of ~10 events that element 104 had elution characteristics like Zr and Hf as expected for this first post-actinide element.[2] Hulet and co-workers found on the basis of 7 events that chloride complexation of 104 was clearly stronger than that for trivalent actinides and similar to that of hafnium.[3]

The architecture of the periodic table at the end of the actinide series and the beginning of the transactinide series has received considerable delineation in the difficult but critically important experiments on Md, Lr and 104. There is no question that the actinide series ends at Lr as required by the actinide concept. The next important question, the nature of the transactinide series, has received important though sparse illumination, in that 104 chemistry is clearly consistent with that of a typical group IVb element. The experiments of Silva, Hulet and Zvára are suggestive as to the avenues to be followed for establishing the oxidation states of 104 and its molecular and ionic species. Here again, new nuclear synthetic routes yielding larger numbers of $^{261}104$ atoms per experiment are needed for successful implementation of these experiments.

ELEMENT 105

Zvára et al. used 2-sec $^{261}105$ and thermochromatographic techniques to investigate the volatility of the chloride of element 105. Zvára's interpretation was that the chloride of 105 is more volatile than $HfCl_4$ and less volatile than $NbCl_5$.[1,2] The meaning of these results is unclear. Better defined conditions are needed to investigate possible new trends in the periodic table. One possibility, suggested by Zvara's results on 105, is that members of the transactinide series may behave more like the lighter members of the groups than the heavier.[3] It would be interesting, in this regard, to attempt to employ carbonyl chemistry for element 105 since Nb and Ta do not form carbonyls although $V(CO)_6$ is known, but has limited stability. The three elements mentioned do form anions of the type $M(CO)_6^-$.

ELEMENT 106

Although no chemical properties have yet been determined for element 106, the half-life of 1 sec for $^{263}106$ offers possibilities. Zvára has reported experiments with tungsten in preparation for such work.[1] Zvára finds with $SOCl_2$ as the chlorinating agent that the W deposition is well separated from Hf and Nb in his chromatographic column. Carbonyl chemistry might also be of interest for element 106 since volatile $W(CO)_6$ is well known.

ELEMENTS 107 AND 109

No chemical properties have been reported for these elements.

SUMMARY: SOME AVENUES FOR NEW RESEARCH

METALS, COMPOUNDS AND VALENCE STATES

Reactions of the Metals

With the increasing availability of milligram amounts of ^{248}Cm, ^{249}Bk, ^{249}Cf and micrograms of ^{253}Es, the properties of the metals and of solid compounds can be investigated with greater sensitivity and in more systems. New areas of study are suggested as well as further investigation of older systems. A particularly exciting area for development is the use of high pressure (in the kilobar regime) to make the 5f orbitals more available for hybridization in metals and in compounds. Such techniques are now at a stage where experiments on the several-microgram scale are possible, thus opening the area to study of the heavier transcurium elements. With californium as an example, an appropriate reaction is $Cf + Cf_2O_3 \rightarrow 3CfO$, which should be feasible, based on successful preparation of rare earth monoxides. With berkelium, the reaction $Bk + 2BkCl_3 \rightarrow 3BkCl_2$ is an obvious candidate.

Although details of the metallic state will be presented in another resource paper, here we consider certain information to have chemical implications. For example, a large metallic radius, implying "divalency", as well as a high metal vapor pressure suggests that the reaction of the metal with its heavier trihalides, e.g., $M + 2MBr_3 \rightarrow 3MBr_2$, will proceed to the right.

Pitfalls

X-ray diffraction is a major tool for identification of compounds containing actinides in their various valences. One of the pitfalls which plagues those who work with small amounts of these reactive actinide metals is their "getter" action for residual gases. The resulting surface can thus be stabilized by certain phases or compounds such as oxides/nitrides/hydrides whose lines then appear in the diffraction pattern, and can mislead the investigator. For example, even in an excellent vacuum, quenched samples of Am and Cm metal showed x-ray patterns corresponding to cells with $a_0 = 5.004$ Å (Am) and $a_0 = 5.038$ Å (Cm).[1] Both have been reported as high temperature fcc forms of the metals. However, this interpretation must be questioned when it is recalled that their binary nitrides have nearly identical cell constants: AmN, fcc, $a_0 = 5.002$ Å and CmN, fcc, $a_0 = 5.041$ Å,[2] and further, that the accepted value for the fcc phase of Am metal is much smaller: ($a_0 = 4.8868 \pm 0.007$ Å).[1] Similarly, a poor pattern of Cf_2O_{3+x} with $a_0 = 10.80$ Å can be indexed as $a_0 = 5.40$ Å which is similar to one of the phases reported for metallic Cf.[3] Since small preparations cannot usually be analyzed, the observed interconversion to another metallic phase is certainly the minimum requirement to establish the existence of a metallic phase. A few lines on a diffraction pattern are not sufficient. A catalog of binary compounds is critical to such work.

As larger sources of the heavier elements become available to more than one laboratory, work has been repeated, often with purer materials. Such work has often produced significant alterations in important data and their interpretation. With americium, for example, the actual existence of the true fcc phase was long questioned. Haire notes that californium requires precisely such extended work, especially on the divalent forms of the metal.[3] This general observation applies equally to other actinide elements.

COMPOUNDS AND VALENCE STATES

As mentioned in the introduction, americium and curium will be present in significant quantities in wastes from processing power reactor fuels.* Therefore, studies are needed to establish the long term chemical behavior of these elements in proposed waste forms and in their migrational behavior in the environment. Curium will likely remain trivalent, but the stabilization of americium in oxide matrices can easily involve the tetravalent or higher states. This is especially true since excess base and high oxygen fugacity can lead to Am(V) and Am(VI) during high temperature waste form preparation. Long term radiation stabilities of such oxidation states are subjects worthy of investigation.

Complexation chemistry involving carbonates, ion-exchange with clays and other important soil and rock constituents are also needed to establish a scientific base for modeling the behavior of curium and americium in the environment. In anhydrous systems for these elements particularly, the technique of using atomic fluorine to obtain higher fluorides should be investigated. Already mentioned were the limited

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* Although of less importance than Np and Pu on a relative weight basis in the nuclear waste, they are important because of their high activity.

studies made thus far with long-lived ^{248}Cm, and the need for an expansion of studies of curium chemistry using this isotope. The possibility of laser activity for curium was not pursued. Valences of curium greater than four need substantially more work, including investigations in carbonate and of other complexes in alkaline media.

In the case of berkelium, the divalent state has not been found except possibly as an intermediate during the decay of Es(II) → Bk(II) → Cf(II).[4,5] The Bk/$BkBr_3$ (or iodide system) should be investigated, perhaps also using high pressure techniques to define stability limits of the Bk(II) state. There are still unanswered questions about californium in the solid state: much work remains to be done even on simple compounds. The oxidation states 0, II, III, and IV have been established for californium, but little is known of their aqueous chemistry except for that of the (III) state. Future investigations should emphasize stabilizing other possible states, such as Cf(V) and characterizing solids containing the various valences.

We emphasize that since both Bk and Cf are the last two elements which can be studied on a several milligram scale, studies of these elements are important in order to establish the best data base on which to plan experiments for the heavier elements which are more radioactive and much less available. As we noted, no complexation constants have yet been reported for Bk(IV).

Not only is extensive work required to characterize properly the solid phases of the transplutonium elements, but a wide variety of new compounds needs to be prepared and studied with the longer-lived isotopes. These studies will be critical to extending our understanding of the role and relative stabilities of the different oxidation states. Moreover, such systems will elucidate the role of the 5f orbitals and the trends in periodic relationships at the heaviest end of the periodic table. In this regard, spectroscopic studies should be particularly valuable.

SOLUTION CHEMISTRY

The radioactive nature of the transuranium elements places limitations on the techniques which can be used to study inherent oxidation state stability and even of complexation in solution since the radiolysis accompanying macroscopic concentrations of many of these elements can seriously perturb the measurements. Consequently, many complexation studies have used tracer concentrations with a two-phase distribution technique such as ion-exchange or solvent extraction. The first hydrolysis constant of fermium shows it to be more acidic than earlier actinides.

Even the heaviest, most radioactive elements can be studied by tracer techniques in ultrafast, automated systems, provided that adequate amounts of transplutonium elements are produced for targets for accelerator production of the heaviest elements. Such research in the transactinide elements can clarify the role of relativistic effects, a question of considerable theoretical interest.

While optical spectroscopy and magnetic measurements have been of great value in the study of transition metal complexes, their use is more limited for the actinides since the f → f transitions are much less sensitive to the effect of complexation. There is a class of spectral bands -- the "hypersensitive bands" -- which do show more significant perturbations upon complexation and some use has been made of these spectral transitions.[6-8] With the growing availability of long-lived species (^{243}Am, ^{248}Cm, ^{249}Cf), more extensive investigations are possible using these hypersensitive bands as well as other desirable macroscale techniques such as titration calorimetry, nuclear magnetic resonance, etc.

The strongly ionic character of the bonding of the transplutonium cations has been noted earlier. As a result of this, the number and geometry of the bonding groups around these cations are not restricted or determined by the requirement for metal-ligand orbital overlap. Consequently, primary coordination numbers up to 12 are known with 6 to 10 probably common in solution, depending on the ligand. A corresponding diversity of symmetries is present which makes these transplutonium cation complexes particularly (and, almost uniquely) suitable for studying electrostatic interactions under a wide variety of conditions. Much more research is needed on the thermodynamic and kinetic parameters of the actinide complexes to provide a sufficient data base for sound theory development.

In this regard the trivalent actinides often form more stable complexes than expected from comparison with the lanthanides. For example, Cf^{3+} and Eu^{3+} have similar ionic radii, yet from cation resin exchange column elution with lactic acid solution, we must accept that the californium lactate complexes are significantly more stable. Similarly, the group separation of actinides from lanthanides by ion-exchange elution using concentrated hydrochloric acid or thiocyanate solutions reflects increased complexation for actinides which cannot be related simply to differences in cationic radii. Such increased complexation implies bonding which is not explained simply by electrostatic interaction. Absorption spectroscopy of f-f transitions would be very helpful in clarifying any role of f orbital participation in the bonding.

The structure of hydrated cations in aqueous solutions is a question of considerable interest and debate. New approaches using neutron diffraction,[9] and extended x-ray absorption fine structure (EXAFS) may provide definite insight into this aspect of actinide chemistry as sufficient quantities of these elements become more available.

In Table II the reduction potentials are collected.[3,10-14] As noted in the introduction, there is an abrupt major increase in the difficulty in achieving the aqueous tetravalent state for elements after plutonium, Bk(IV) being the major exception as sole example of a stable, tetravalent aqueous ion. On the other hand, from Cf on, it becomes easier to attain divalency. Since powerful oxidants are involved with the higher valence

TABLE II. REDUCTION POTENTIALS AND SOME THERMODYNAMIC PROPERTIES

	III,0	III,II	IV,III	V,IV	VI,V	ΔH_f° M_{aq}^{3+} kJ/mol	ΔH_f° M_{aq}^{4+} * kJ/mol
Am	-2.07	-2.3	2.6	(0.82)	1.59	-616.7	-406
Cm	-2.		3-4	--	--	-615	--
Bk	-2.0	-2.8	1.6	(3.5)	--	-601	-483
Cf	-2.	-1.6	~3.2			-576	
Es	-1.98	-1.55				(-596)	
Fm	-(1.95)	-1.15	(4.9)				
Md	-(1.7)	-0.2					
No	-(1.18)	+(1.4)					
Lr	-(2.06)						
104							
105							
106							
107							

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* Other Values: ΔH_f° for AmO_2^{+}(aq) = -805, and for AmO_2^{++}(aq) = -652 kJ/mol.

states, a more expanded chemistry is possible by avoiding the limiting nature of the solvent water. An area which may be very fruitful for study is that of non-aqueous solutions utilizing organic and molten salt solvents. Particularly the enthalpy and entropy changes for complexation in aqueous solutions of actinides are governed by solvation effects. Moreover, water obscures spectral features in many interesting regions. Different geometries, complexing strengths and even oxidation states can be realized by use of non-aqueous solvents. However, such studies are not as amenable to tracer distribution as are studies of aqueous systems, and the long-lived isotopes from TRU/HFIR are necessary.

The rich chemistry of the variable redox behavior of neptunium and plutonium has been a source of very interesting research. The non-aqueous solution chemistry of the transplutonium elements may be even more fruitful. Jørgensen has suggested a way to combine values of the gaseous ionization potentials of atoms with empirical hydration energies to predict stabilities of the simple aquo ions with respect to their oxidation or reduction by solvent water.[15] This approach leads to a smoothly decreasing stability of the trivalent state in favor of the dipositive state as Z increases from Am to Md.[16] The increase in stability of the divalent state reaches a maximum at nobelium, which is shown to be the stable aqueous state. There is then an abrupt discontinuity occurring at element 103, the end of the actinide series, with trivalent Lr^{3+} showing the widest range of aqueous stability.[16] More theoretical work is needed to account for the special stability of the aquo MO_2^+ and MO_2^{2+} ions, and to provide means of predicting their occurrence. Study in non-aqueous systems, e.g., electrochemistry, complexation, spectroscopy, photochemistry, as well as other areas can provide information to extend our models and can open a whole new field of actinide research. Preliminary studies in such solvents have indicated a significant degree of covalency in actinide-soft base ligand (e.g., N_3^-) interaction.[17]

The whole area of the kinetics of oxidation-reduction reactions of Bk, Cf, Es, and Fm is virtually unexplored territory, although accessible to experiment. Since the increase in binding energy of 5f electrons in this region becomes acute, a combination of theoretical and experimental studies should shed new light on the influence of relativistic effects that will augment the limited thermodynamic knowledge in hand.

The architecture of the periodic table is an important consideration for chemists, and the experimental establishment of the end of the actinide series at Lr is an especially significant accomplishment by the "one-atom" chemists at Berkeley, Livermore, and Dubna. The challenges which remain are impressive. Most important is the elucidation of the character of the new transactinide series, but the chemistry of Lr is still based on sparse data, and much more remains to be done in establishing the chemistry of Md and No in order to understand $5f^{14}$ closed shells and the increased binding of 5f electrons relative to 4f. Perhaps, in studying Lr chemistry, we can learn something about the stability of $7p_{1/2}$ shells under strong relativistic conditions. We mentioned earlier that Md^+ work could be pursued to elucidate the stability of the $5f^{14}$ closed shell.

Experience with "time capsules" and their errant predictions, indeed the history of chemical research itself, shows the folly of attempting to predict too closely the direction or even the value of "new directions" very far in the future. Particularly with the transplutonium elements we are concerned with the end of the periodic table and "normal relationships" are perturbed by stronger spin-orbit coupling, higher nuclear charges, relativistic effects, etc. We can only "see darkly" at this time, and theory needs the helping hand of the experimental studies yet to come. However, we can be confident that these studies will provide significant new understanding of these heaviest elements and their place in the nature of matter.

In the description of individual elements we have not discussed potential new directions in reprocessing, such as the possible use of liquid membranes or pyrochemistry, utilizing molten salt solvents and electrochemistry. However, the use of non-aqueous solvents and the molten salt chemistry of the transplutonium elements are believed to be areas which should be exploited. Analytical chemistry was omitted, but the structural advances in neutron diffraction and EXAFS should permit studies of inner sphere coordination in these elements. We have described briefly other areas of needed work, including the following subjects:

solution chemistry, coordination, complexation,
valence stabilization and kinetics;
thermodynamics (obvious lack of data);
organometallic chemistry; chemistry in nonaqueous solvents;
actinides, $5f^{14}$ closure;
transactinides, electronic structure, relativistic effects;
solid state chemistry, need for data on more compounds;
high pressure studies;
waste problems, immobilization and aquatic chemistry.

Finally, few would argue that the problem of transplutonium elements and their disposal will go quietly away. Even if the use of nuclear power diminishes in the United States, it will not disappear in the rest of the world. Furthermore, military needs will result unavoidably in transplutonium element production. Few universities can offer appropriate training. Post-doctoral programs at the national laboratories presently offer valuable but limited assistance, and there is little opportunity for the trainees to remain. We cannot ignore addressing the practical matter of maintaining U.S. expertise in the area.

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APPENDIX G

SPECTROSCOPIC STUDIES OF THE TRANSPLUTONIUM ELEMENTS*

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1. Introduction

The challenging opportunity to develop insights into both atomic structure and the effects of bonding in compounds makes the study of actinide spectroscopy a particularly fruitful and exciting area of scientific endeavor. It is also the interpretation of f-element spectra that has stimulated the development of the most sophisticated theoretical modeling attempted for any elements in the periodic table. The unique nature of the spectra and the wealth of fine detail revealed make possible sensitive tests of both physical models and the results of Hartree-Fock type ab initio calculations.

In many respects there is a similarity between the spectra of the lanthanides and those of the actinides, but in the 5f-series, the f-electrons are less well shielded from potential interaction with ligands. There is consequently a discernible approach to the character of the d-transition elements in certain actinide compounds. Nevertheless, the essential f-element character of sharply defined transition energies is retained, so that the interplay between the electrostatic and spin-orbit interaction of the non-bonding f-electrons, and the nature of the bonding and site symmetry can be explored in detail. In contrast to the atomic spectra of the lanthanides, the actinides exhibit an even more complex and scientifically challenging spectra because energy levels characteristic of many more electronic configurations occur at relatively low energies.

What then can be said about the unique character of heavy-actinide spectroscopy, which is the focus of the present discussion? How does it differ from that of the lighter members of the series, and what are the special properties that are manifest? What properties particularly recommend study of the heavier members of the series?

When one has available a large number of levels of a given configuration, these levels may be used as input to calculations that yield the model Slater (electrostatic) and spin-orbit interaction parameters for the configuration. If several configurations are known, then interactions between configurations can be calculated. These data and calculations for the lighter actinides together with Hartree-Fock calculations are significantly increasing our insight into the structure of the atoms. The transplutonium elements provide a unique area to test atomic theory because the coupling of electrons is not pure and because relativistic effects are so important.

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The distinct changes that occur in the character of actinide spectra in condensed phases as atomic number is increased are related to the increasing stabilization of lower-valence states. The higher multiple valence states that are characteristic of the light half of the series provide an as yet almost untapped and challenging area for theoretical interpretation. In contrast, the increased stability of lower oxidation states in the heavy members of the series provides an experimental basis for exploring the character of the electronic structure resulting from a quite different hierarchy of interactions. As a result the spectra of the light and heavy actinides provide complementary opportunities for theoretical analysis. The spectra of divalent compounds of Cf and Es are just beginning to be interpreted, but predictions regarding the nature of similar spectra for the lighter actinides where no experimental data exist can already be made based on the limited available information. These predictions confirm the potential importance of spectroscopic observations in the ongoing attempts to synthesize such compounds as $PuCl_2$. Of course the position can also be taken that one of the very interesting aspects of heavy-actinide chemistry lies in the challenge of stabilizing the elements in higher-valence states.

Spectroscopic studies that are part of attempts to synthesize compounds with unusual actinide-ion oxidation states provide potential high detection sensitivity and the basis for definitive valence state characterization. In this connection it is useful to point out that spectroscopic data have also been used as the sole basis of identifying valence states in some instances. In a recent series of innovative experiments, changes in the crystallographic structure and oxidation state of heavy-actinide compounds ($EsCl_3$, $BkCl_3$) induced by radioactive decay were sensitively monitored by spectroscopic techniques. This work showed that while the absence of long range order in a crystalline environment precluded obtaining structural information from x-ray patterns, the shorter range order determined by the arrangement of nearest neighbor ions about the central actinide ion yielded spectra that could be uniquely interpreted.

2. The Role of Systematic Studies and the Relationship of Heavy-Actinide Spectroscopy to Ongoing Spectroscopic Investigations of the Lighter Members of the Series

The importance of a systematic theoretical analysis of the atomic spectra across a series of elements such as the actinides is well established. One result can be the essential insight provided into the special interpretive problems encountered for an individual element. The importance of the systematic approach is somewhat less clearly documented for the spectra of actinide compounds. Indeed, the only relatively well-established analysis of the latter type involves the trivalent series. However, even here the guidance provided by averaged theoretical-model parameter values can be clearly demonstrated. In part this is because the spectra of the trivalent actinides have been found to exhibit an increasingly lanthanide-type character with increasing atomic number. It is instructive to point out that it was more difficult to interpret the spectrum of $U^{3+}:LaCl_3$ than of $Np^{3+}:LaCl_3$ or $Pu^{3+}:LaCl_3$ and important insights into the nature of the appropriate physical model for the actinide series as a whole were gained in the analysis of $Cm^{3+}:LaCl_3$, $BkCl_3$ and $CfCl_3$. In part our interest in heavy-actinide spectra also derives from special situations. For example, a great deal of interest continues to center on the chemistry of Pu^{4+} in neutral to basic solutions. To the the extent that any comparisons can be made on the basis of spectroscopic studies, Bk is the first heavier actinide after Pu to exhibit a stable 4+ oxidation state in neutral-to-basic solution.

The importance of systematic investigations of energy-level structure is also apparent as we attempt to extrapolate into uncharted, and perhaps experimentally unchartable, areas of heavy-element spectroscopy. Einsteinium is the last element in the periodic table that can be studied by conventional techniques. It is thus the springboard from which predictions of structure of yet heavier actinides will be launched. Its spectral properties and characteristics consequently take on a special significance as we model the spectra of Fm and No and examine the potential use of the highest-sensitivity techniques that might permit experimental detection of selected states.

One of the important applications of actinide spectroscopy has come in connection with the development of isotope-separation processes. Both in the case of uranium and plutonium, ongoing experimental and interpretive investigations of atomic spectra have been directly instrumental in the development of new concepts for separations that are progressing toward commercialization. Part of the longer-range research effort in heavy-element spectroscopy is devoted to exploring the photophysics and photochemistry of PuF_6 based on the observation of isotope shifts in the vibronic structure which accompanies electronic transitions. The latter investigation takes advantage of the volatility of the higher fluorides of the light actinides. Analogous studies of the most volatile compounds available for lower valence states will also be of interest. While higher-valent, volatile heavy-actinide compounds have not yet been prepared, they may exist. Certainly with 3+ and 4+ compounds analogous examination for isotope separation potential will be important over the whole series. While the present practical application lies in the light end of the series, insights into mechanisms or the role of a particular variable may come from investigations involving the heavier actinides.

Similarly, the development of sensitive methods of detection of actinides in waste streams, in the environment, and as part of waste-management scenarios (primarily associated with the light actinides at present) is an area to which actinide spectroscopy is making very important contributions. The question of detection sensitivity is strongly dependent upon a knowledge of the details of the electronic energy levels.

3. Atomic (free-ion) Spectra

A. Summary of the Present Status of Spectroscopic Studies with the Transplutonium Elements

While americium is the first transplutonium element, its production is not associated with the (HFIR-TRU) facility. Its early availability resulted in some work being done on its atomic spectra and the publication of a partial term analysis, (Fred and Tomkins 1957). In large part, the previous statement regarding availability not associated with HFIR-TRU also applies to Cm. Much of the published spectroscopic data, both atomic and that involving compounds, was obtained using ^{244}Cm. The longer-lived ^{248}Cm isotope, a product of the

TRU facility, can be useful for spectroscopic studies in connection with isotope-shift determinations and where marginal phase or valence stability is expected to be a controlling factor. The status of the energy-level analysis in Cm I was recently given by Worden and Conway (1976). The literature prior to ~1970 for all transuranium element atomic spectra was surveyed by Carnall (1971).

Atomic spectra data and the current status of the analysis in terms of levels and configurations is for the most part unpublished. The extensive nature of the line lists makes it difficult to find suitable avenues for publication, especially since there are revisions as new information is developed. Publications of transcurium atomic spectra data include: for Bk, Worden and Conway (1978); for Cf, Worden and Conway (1970); and for Es, Worden et al. (1970). Extensive experimental data, primarily for Es I, were obtained subsequently in a cooperative effort between groups at Argonne National Laboratory, Lawrence Berkeley Laboratory and Lawrence Livermore National Laboratory. These data are presently being analyzed.

B. Future Needs and Directions in Atomic Spectroscopy

Free-ion spectroscopy of the actinides has provided the basis for present understanding of the electronic structure of that group of elements. The problem is complicated by the fact that there are electrons formally belonging to four different orbitals that can combine in various ways to produce a given configuration (5f,6d,7s,7p). Table I lists the pertinent configurations, most of which were derived from free-ion work. The results given in Table II indicate the present state of affairs with respect to the classification of the spectral lines in terms of levels. The best studied and understood are uranium and plutonium; for einsteinium there are only a few hundred lines that have been measured and a mere tens of levels. A need for more work on americium, berkelium, californium and einsteinium is apparent in order to even begin to appreciate the unique challenges and insights that will develop in the study of these elements. It should be emphasized again that work on one spectrum is greatly aided by the results for others and that for maximum productivity there should be closely correlated studies of many spectra by different research groups. Fourteen configurations have been identified in the neutral spectrum of plutonium and nine configurations in the first ion. The requirements for the analysis are at the limits of present theoretical understanding and computational abilities and stimulate both new approaches and methods. Similar results could be obtained for other members of the series.

Experimentally, Fourier Transform Spectroscopy which has been developed in the last five to eight years, has made it possible to improve measurement accuracy by a factor of ten, and for the first time to obtain meaningful intensity information. Improved accuracy reduces the statistical errors in coincidence searches among wavelength lists that can typically contain 20,000 entries. There are now only two instruments in the world, one at Kitt Peak National Observatory and one at Orsay, France, capable of the required precision. In addition to the instrumental needs, there is also a great need for source development to produce the spectra. A source which produces a rich spectrum but uses one to ten micrograms of material and which lasts a very long time is needed. Practical sources must also produce the spectra of the higher ionization states using microgram size samples.

The atomic spectra of the higher ions, i.e. An^{2+}, An^{3+}, etc., have not been produced for the transplutonium elements; in fact only in the cases of thorium and uranium have experimental studies been reported. These ions are the species that occur in solids and solutions. Consequently, insights gained from analysis of such spectra are of particular interest to chemistry.

Studies of the hyperfine structure and isotope-shift of the spectral lines provide an insight as to the size and structure of the nucleus. Nuclear moments and spin are derived from such studies. It is possible to conceive of the day when laser isotopic separation methods will be used to prepare small samples for nuclear experiment targets as well as for other studies. Such methods can enrich a given isotope or remove an isotope, thus making the sample more suitable to the scientific purposes of the experimenter. The basic data come from measurements of the isotope shift of spectra lines, some of which have already been observed. Laser spectroscopy methods for achieving separation have already been perfected in programs relevant to uranium. If this separation equipment were properly configured, it would be possible to measure the first and second ionization potentials of all the transplutonium elements.

Analytical chemists and astrophysicists are also users of wavelength data. There are a number of papers dealing with the spectrochemical analysis of americium and curium, and in a few cases the other elements have also been analyzed both as an impurity in a sample or to determine the purity of the elemental sample. Astrophysicists have looked for the presence of the actinides in the sun and stars. There are certain types of stars which contain rare earths, and a few of these stars have been looked at to see if actinides occur. The stellar line lists used contained spectral lines of the neutral and first ion whereas the stars usually have lines of the first and second ion, so without good data on the second ion not many firm conclusions may be drawn. Curium-247 because of its half-life ($\sim 10^7$ y) is a likely candidate to be found in stars.

4. The Spectra of Actinide Compounds

A. Summary of the Present Status of Spectroscopic Studies with Compounds of the Transplutonium Elements

Because of its long and widespread availability, a great deal of spectroscopic information relative to Am compounds is available. In much of this spectroscopy, there is a pronounced similarity to that of the light actinides U, Np, Pu. Only reference to divalent compound spectra will be made here. In contrast to the case for the lighter actinides, published data relative to the optical spectra of Cm and the heavier actinides are essentially limited to the lower-oxidation states, as indicated below:

Valence States for which Characteristic Optical Absorption Spectra Have Been Reported

Cm	Bk	Cf	Es
4	4		
3	3	3	3
		2	2

While only tracer-scale studies with Fm have been carried out, the 3+ and 2+ valence states are well characterized. Available sensitive methods of detection make it highly probable that the energies of at least one or two of the excited states in the energy-level schemes could be established for both the indicated valences.

Absorption spectra for $Am^{2+}:CaF_2$ have been published by Edelstein et al. (1967) and for $Es^{2+}:CaF_2$ by Edelstein et al. (1970). Characteristics of the pure dihalide spectra of Cf and Es have been reported in a number of communications, for example, see Haire and Young (1978).

Spectra of the trivalent state for each actinide from U^{3+} through Es^{3+} have been reported, and systematic theoretical analyses of the crystal-field states in D_{3h}-symmetry, while not complete, are well advanced (Hessler and Carnall 1980); more recent studies have addressed investigations of transition probabilities (Carnall et al. 1982), and the mechanisms of excited-state relaxation (Hessler et al. 1980).

While spectra characteristic of Cm(IV) both as solid CmF_4 and in solution in 15 M HF were measured some years ago (Keenan 1961), the solid state spectrum of BkF_4 (Ensor et al. 1981) has just recently been published. This extends the data previously limited to observations of Bk(IV) solution spectra in 0.4 M D_2SO_4 (Carnall et al. 1971). Absorption bands attributed to Am^{4+} stabilized in solutions of unsaturated heteropoly tungstates $K_7PW_{11}O_{39}$ or $K_{10}P_2W_{17}O_{61}$ have also been reported for Am^{4+} and Cm^{4+} (Saprykin et al. 1976), and for Cf^{4+} (Kosyakov et al. 1977), but no clearly defined spectra of Cf^{4+} (or Es^{4+}) showing characteristic sharp f→f bands appear to be available. The only report involving Es^{4+} was made on the basis of thermochromatographic experiments. EsF_4 was postulated to have been formed in the gas phase (Bouissieres et al. 1980).

Interesting reports of the stabilization of unusual oxidation states, Am(VII) (Krot et al. 1974) and Cm(VI) (Peretruchin et al. 1978), have been made.

B. Future Directions

One of the aspects of heavy-actinide spectroscopy that can be identified as having significant potential for rewarding future work is illustrated in Fig. 1. Although based on model calculations for both the $5f^N$ (Carnall and Crosswhite 1982) and higher-lying configurations (Brewer 1971), the level energies shown in the figure indicate that experimental data on the energy-level structure for a number of different configurations should be accessible in the optical range in divalent actinide spectra; however, based on work done to date, the most productive experiments will be those involving the heavy actinides. Since in comparison to similar spectra of the lanthanides, the An(II) excited configurations lie much lower in energy, characterization of the An(II) spectra should lead to valuable additions to our understanding of configuration interaction. There is a similar tabulation for Ln(II) in Dieke (1968).

Figure 1 also suggests that spectroscopic methods of detection should be suitable for establishing the existence of the elusive Bk(II) species. One of the interesting facets of recent work has been the inability to observe absorption bands characteristic of Bk^{2+}, even in the decay chain of $EsCl_2 \rightarrow (BkCl_x) \rightarrow CfCl_2$ where both the Es^{2+} and Cf^{2+} spectra were well characterized (Young et al. 1981). In well-characterized Am^{2+}, Cf^{2+} and Es^{2+} samples, the ability to detect fluorescence in the near-infrared range should make it possible to explore excited-state relaxation phenomena in a class of compounds that is unique, since available experimental evidence indicates that the crystal-field splitting of the free-ion manifolds is relatively small, comparable to that for Ln^{3+}.

The broad outlines of the energy level structure for An^{3+} appear to be well established. Consequently, we have the required basis for future work devoted to exploring both the models for computing transition intensities as well as relaxation and energy transfer mechanisms. The latter type of study has exciting potential for new-frontier science. The degree of agreement attained in the comparison between experimental and model-computed intensities for the An^{3+} aquo ion (Carnall et al. 1982) was sufficient to encourage refinement of the model and to suggest that it would be appropriate to devote considerable effort to the next step in the analysis, namely, the computation of oscillator strengths for the crystal-field components for An^{3+} and Ln^{3+} in appropriate matrices.

Attempts to observe fluorescence in the aqueous solution spectra of the actinides have only been successful for the heavy actinides where the energy gaps between the ground and first excited states are sufficiently large to permit fluorescence to compete with non-radiative modes of decay (Beitz et al. 1981). Since sensitive laser-based methods exist for determining the extent of non-radiative decay in such systems, both radiative and non-radiative relaxation can be monitored to probe the mechanisms involved.

The spectra of organometallic compounds of a number of An^{3+} ions are known, but this area of spectroscopy merits further exploitation. There are many opportunities here to examine and characterize the relative influences of structure and bonding on the spectra. The somewhat greater isolation of free-ion groups in the heavy members of the trivalent series provides added opportunity for developing the interpretation. The large organoligands are also of interest because they make it possible to insulate one actinide-ion center from the influence of other neighboring actinide-ion centers and this in principle gives rise to narrow-band spectroscopic structure.

The spectra of quadrivalent Am, Cm, Bk, and Cf can play an important role in the development of a systematic interpretation of the spectra of An^{4+} if, as seems to be the case, the observed absorption bands are relatively more isolated in energy and there is less overlap of different free-ion manifolds than for the light actinides. The theoretical treatment of An^{4+} spectra has long been a source of contradictory interpretations. Little progress has been made in the last 20 years toward a unified and consistent analysis of An(IV) spectra compared to the successful and increasingly detailed analysis of An^{3+} spectra that has developed. The indicated heavier actinides may well contribute the type of experimental data that are necessary for progress in this area. Since the +4 compounds in question are all powerful oxidants, the conditions under which stable compounds can be prepared will be limited, and little if any opportunity to stabilize quadrivalent actinide organometallic compounds would be expected. Interest does focus on development of a detailed interpretation of the ligand- (or crystal-) field interaction which is at present poorly understood. Part of the long-term problem of interpretation lies in the lack of well-characterized spectroscopic data for which the quantum description of each state has been established by model independent methods such as spectroscopic polarization or Zeeman studies.

As indicated earlier, evidence for the existence of some heavier actinide compounds with oxidation number >4 has been presented. There is little doubt that under the proper stabilizing conditions, such compounds can be prepared and that their spectra would offer exciting insights into the type and nature of bonding involved. In such work it is clear that spectroscopy can provide evidence for the stabilization of a new valence state (in some cases the only reliable evidence if x-ray patterns are not clear) and can also provide evidence for changes in the symmetry of the actinide site where more than one phase can be stabilized.

Important chemical information concerning the heavier actinides can be derived from spectral studies in complexing solutions or molten salts, particularly when spectroelectrochemical techniques are employed. The monitoring of oxidation-state changes as a function of applied potential can yield information on quantities characterizing the nature of the species formed: the oxidation states, stabilities and redox potentials. The spectroelectrochemical technique is particularly well suited to exploring the possible production of unusual valence states in the heavier actinides (Hobart et al. 1981).

Along a quite different line of spectroscopic research it should be noted that heavy-ion-induced x-ray fluorescence is a technique which may provide new insight into the valence states of actinide metals, particularly the transplutonium metals, and their alloys. The metallic valence state of the transplutonium metals has been a subject of debate over a number of years.

Another potential area for study would involve determining the variation in spectral properties of transplutonium compounds as a function of pressure. Examination of transplutonium metals under high pressures using x-ray diffraction techniques suggests a discernible influence on the 5f electron orbitals. The effect of pressure on the optical spectra of transplutonium compounds is also a new area that has exciting possibilities for providing information about bonding and structure relationships.

Resonance Ionization Spectroscopy (RIS) or Resonance Ionization Mass Spectrometry (RIMS) are two new laser ionization techniques that can be applied to the transplutonium elements to further our knowledge of these materials. One interesting application of RIMS would be in differentiating between Bk-249 and Cf-249 in vapor species/reaction mechanism studies, where the Cf-249 daughter signal cannot be differentiated from its parent by conventional mass spectroscopy.

Most of the spectroscopic investigations cited here involve application of more or less conventional spectroscopic techniques. However, the past decade has seen the development of (1) greatly improved Fourier Transform instrumentation, which improves the precision of atomic-spectra data by an order of magnitude; (2) laser spectroscopy, which not only is capable of higher precision for both vapor- and condensed-phase spectroscopic studies, but also introduces a broad range of new methods for analysis; (3) accelerator technology, which combined with laser techniques, permits nuclear spin and moment studies of short-lived isotopes, and which should be particularly interesting for isotopes in the transplutonium region which are far from stability; and, of course (4) the great extensions that have been made in computer capabilities. It is clear that the extent to which advantage can be taken of these opportunities depends on the extent to which the laboratories developing these methods are also properly equipped to handle the whole complement of these highly radioactive samples. There is therefore a special need for the national laboratories engaging in this critical research to be as well appointed as possible to conduct these experiments, which by their very nature require efficient and tightly controlled timing. Production of large quantities of the heavier actinides will have no purpose unless both equipment and personnel are available to ensure efficient and creative use.

5. Other Spectroscopies

Mössbauer Spectroscopy

There are serious problems arising with the potential use of Mössbauer spectroscopy in work with the heavier actinides. Line broadening can be expected to be a problem. It is doubtful if the Mössbauer technique would yield useful information even if suitable source-sample couples could be identified. See Dunlap and Kalvius (1974).

Neutron Spectroscopy

The ability to explore higher-energy ranges--for example, to ~2000 cm^{-1} in some cases of crystal-field split levels, makes the neutron a useful tool where photons cannot yield the desired information. The problem is sample size and type--single crystals are greatly to be desired.

Further references to optical and magnetic properties of the transplutonium elements are to be found in the publication, "A Review of the Accomplishments and Promise of U. S. Transplutonium Research 1940-1981", National Academy of Sciences, Washington, D.C. (1982).

TABLE I.

Ground-State Configurations for the Actinides in Various Charge States.

	I	II	III	IV	
Actinium	Ac	$6d7s^2$	$7s^2$	$7s$	
Thorium	Th	$6d^27s^2$	$6d7s^2$	$5f6d$	$5f$
Protactinium	Pa	$5f^26d7s^2$	$5f^27s^2$		
Uranium**	U	$5f^36d7s^2$	$5f^37s^2$		$5f^3$*
Neptunium	Np	$5f^46d7s^2$	$5f^46d7s$		$5f^4$*
Plutonium	Pu	$5f^6\ 7s^2$	$5f^67s$		$5f^5$*
Americium	Am	$5f^7\ 7s^2$	$5f^77s$	$5f^7$*	$5f^6$*
Curium	Cm	$5f^76d7s^2$	$5f^77s^2$		$5f^7$*
Berkelium	Bk	$5f^9\ 7s^2$	$5f^97s$		$5f^8$*
Californium	Cf	$5f^{10}\ 7s^2$	$5f^{10}7s$		$5f^9$*
Einsteinium	Es	$5f^{11}\ 7s^2$	$5f^{11}7s$	$5f^{11}$*	$5f^{10}$*
Fermium	Fm	$5f^{12}\ 7s^2$			

*From crystal work.

**U V $5f^2$ and U VI $5f$ free-ion analyses have also been completed.

TABLE II.

Status of the Number of Lines Measured and Levels Assigned for the First and Second Spectra of the Actinides.

				Number of Levels			
	U	Np	Pu	Am	Cm	Bk	
I	Even	1307	181	601	39	348	186
	Odd	405	284	585	12	335	166
II	Even	518	30	239	63	415	97
	Odd	178	46	743	5	441	38
#	Lines	100000	6000	20000	3000	13000	5000

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APPENDIX H

Magnetic and Solid State Properties

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Introduction

The open shell of 5f electrons dominates the magnetic and many solid state properties of the actinide elements and their compounds. For the early part of the actinide series, the 5f electrons have a much greater radial extent than their 4f counterparts, with the concomitant result that they interact much more strongly with their neighbors.[1] As the nuclear charge increases for a given oxidation state, the additional 5f electrons experience a greater nuclear attraction due to imperfect shielding; this results in the contraction of the 5f shell. The effects of the actinide contraction are clearly shown for the actinide metals which have properties intermediate between the delocalized 3d elements and the localized 4f elements.[2,3]

Thus two of the more outstanding problems in metals, the onset and description of magnetism in the 3d transition metals (chromium through nickel), and interpretation of certain experimental phenomena in cerium materials are relevant to the actinide metals. These two problems are connected by the actinide series, which is situated between the 3d and 4f elements in the progression of these transition metal series towards localized (magnetic, nonbonding) behavior.[4] The actinides exhibit many similar phenomena common in cerium materials, such as mixed valence, localization, heavy fermions, and dense Kondo systems. A consistent description of these phenomena in the actinides will aid in understanding both the 3d transition series and the cerium materials, because the actinide metals begin as f-bonding, d-like transition metals and cross over to localized f-electron, more lanthanide-like behavior at americium. This result is paralleled in the chemistry of the actinide elements and is the reason why the actinides were not recognized as a second f-transition series until the discovery of the transuranium elements.[5] Indeed, transplutonium work has been most important in assessing the electronic structure of the earlier actinide elements.

It is fortunate that the actual crossover region between d-like (itinerant) and f-like (localized) behavior occurs between the relatively manageable and plentiful elements plutonium and americium. However a full description and manipulation of the crossover region requires studies of the heavier actinides which are more radioactive and more costly to produce, but are currently under production.

Because of this crossover region the elements (and compounds) in roughly the U to Cm region can be made to exhibit a multiplicity of crystal structures and valence states, chemical and catalytic activity, a high density of electronic states, nearly magnetic behavior, and many other important properties as temperatures, pressures, and mixtures with other elements are varied. Nonetheless, beyond this region there exists an almost completely unexplored region when taken in the broader context of current physics and chemistry. It is not sufficient to deny further study of the transplutonium elements with a simple affirmation that the actinides become trivial once they exhibit lanthanide-like behavior. Within specific research areas, lanthanides are considered to exhibit a rich variety of behavior, for example, the subtle differences in magnetic exchange. Furthermore the difference between 4f- and 5f-electron behavior does show itself even in the heavier elements since the actinides do become divalent metals at einsteinium. This paper presents various areas where important work remains to be done.[6]

Elements and Alloys

During the seventies it has become increasingly clear that the physics and chemistry of the actinide elements in many respects are of an intermediate type between the d transition elements and the lanthanides. This means that very interesting physical phenomena for such a borderline situation already can be found for the pure actinide metals, while these phenomena otherwise normally appear only in more complicated binary and ternary systems for d transition elements. This is an important simplification, and this absolutely unique role of the actinides in the Periodic Table means that information from this series of elements will be of central importance in other areas of solid state and materials science. However, much more still has to be determined about actinide systems before the fertilization to other branches of condensed matter physics can take place. In this respect the transplutonium elements play a most significant role.

The lanthanide series of elements provide an excellent opportunity to study the effect of small changes in electronic structure on bulk properties. Fundamental questions concerning the relation between electronic structure and melting point or crystal structure can then be addressed in great detail. Since the transplutonium elements seem to form a second rare-earth series, such "simple" characterizations as crystal structure and melting temperature are already of immediate interest. Thus, a complete and accurate determination of the structures as a function of temperature, as well as the melting points, are of fundamental importance even in areas far outside the realm of the actinides.

In this connection high pressure crystallographic investigations of the transplutonium elements are most significant. The elements Am, Bk and Es are strong candidates for dramatic electronic transitions, all of which are expected to be of a different nature. In the case of curium it would be interesting to see if the distorted fcc structure, recently found for some compressed lanthanides, will appear at high pressure. Also lanthanum and cerium based alloys with the transplutonium elements ought to be studied under compression. For americium it would be particularly important if the high pressure studies could be extended into the low temperature region.[7] This brings us to another significant experiment, namely, the study of the occurrence of superconductivity in americium as a function of pressure.[8] Absorption edge shifts under high pressure should also be determined, as well as extended X-ray absorption fine structure (EXAFS), positron annihilation and Compton scattering, just to mention a few of the many possibilities.

Photoelectron spectroscopic studies would be extremely valuable for the transplutonium metals, especially for locating the energies of the 5f levels. Such studies would give a direct fingerprint of the valence state of the metal. A most interesting case would then be californium, where a divalent surface layer on top of the trivalent bulk metal is expected. It would also be of considerable spectroscopic interest to follow the evolution of the $5d_{3/2}$ and the $5p_{1/2,\,3/2}$ lines as well as the $4f_{7/2}$ line and its shake-down satellite through the transplutonium series. Also surface core level shifts should be possible to investigate with ultraviolet photoelectron spectroscopy (UPS).

"Classical" experiments like specific heat, resistivity and magnetic susceptibility[9] are, of course, all of high priority.[10] Magnetic phase transitions in curium, berkelium and californium should be looked at in detail, and any possible description of the magnetic structures present would be useful. The specific heat anomaly at about 60°K in americium has to be clarified. Investigations of Cm, Bk and Cf acting as magnetic impurities in various metallic hosts should be performed by resistivity or NMR measurements. If treated as noninteracting impurities, then the production of daughters and the problem of self-heating are minimized in such dilute systems.

Actinide Compounds

The early part of the actinide series is characterized by multiple oxidation states as shown in Table I. This behavior resembles that of the d transition series rather than the 4f transition series. Towards the middle of the series the lower oxidation states become the most stable. For example, it is possible to obtain Am^{6+} compounds as AmO_2^{2+} species, but the existence of Cm^{6+} is still under investigation. For the transplutonium elements, the trivalent state is the most common, as for the lanthanide series, but at Cf a new trend appears, that of increasing stability of the divalent state. Divalent compounds have been prepared and characterized for the $5f^7$, $5f^{10}$, and $5f^{11}$ ions Am^{2+}, Cf^{2+}, and Es^{2+}; and Es metal itself appears to be completely divalent, like Eu or Yb. From radioactive tracer experiments for the transeinsteinium actinides both the trivalent and divalent oxidation are accessible (except for lawrencium) with the divalent state unexpectedly being the most stable state in aqueous solution for nobelium. Table I also indicates the state of magnetic measurements for transplutonium compounds.

Actinide compounds offer the advantages found for the lanthanide series for magnetic and spectroscopic studies in that the optical spectra consist of narrow, sharp lines which provide information about the electronic structure of the 5f shell. In contrast to the lanthanide series many oxidation states are available for study, so that trends of electrostatic, spin-orbit, and ligand field parameters may be followed for the same element as a function of oxidation state, or for the same oxidation state as a function of atomic number. In the actinide series, only the trivalent state has been systematically characterized spectroscopically. The other oxidation states are now under active investigation. The transplutonium elements are of course a necessity for the systematic investigation of the magnetic and spectroscopic properties of the trivalent and tetravalent states, but in addition allow data to be obtained for the unique divalent states of Cf and Es. It is possible also that Bk may be stabilized in the divalent state.

At this time only some of the transplutonium dihalides have been characterized. It would be fascinating to determine if the monoxides or monosulphides are stable. The compound CfS would be of great interest since it would be expected to undergo a valence transition at a modest pressure (provided it is a divalent semiconductor at zero pressure). The question of the occurrence of "conventional" mixed valence states in actinide systems could thereby get its first clear-cut answer.

Mixed valence states have become a very popular and active field of research among rare-earth scientists. If the point of view is taken that cerium exhibits a localization phenomenon, then mixed valence (as referred to by physicists) occurs with two discrete but degenerate valences and is seen in Sm, Eu, Tm, and Yb materials. It appears that the same mixed valence might be seen in the actinides as early as plutonium in PuB_6, which should be analogous to SmB_6. The compound AmB_6 should also be mixed valent but would be particularly important because its two states would have the f^6 and f^7 configurations, which are the two simplest, partially filled f-shell configurations to treat.[10] In order to look for mixed valence in transplutonium compounds all that is necessary is the preparation and room temperature x-ray diffraction measurements on a large number of compounds. Discontinuities in smoothly varying lattice parameters across the series are the clear signature of mixed valency compounds.

In the general characterization of elemental solids, the cohesive energy plays a special role.[11] However, in order to fully exploit the information contained in this quantity, one needs to know the energy levels of the free atoms. Thus, atomic spectroscopic investigations for various ionization stages would be of great value for solid state physics as well as for the understanding of the chemical oxidation numbers. Furthermore, this will be tremendously useful for predicting the physical and chemical solid state behavior of the transeinsteinium elements,[12] and would be most helpful in trying to assess the validity of the startling chemical properties of the heavy actinides claimed by Soviet scientists.

Thermochemical measurements of the heat of formation of various transplutonium compounds would also be of great utility for the understanding of compound formation and stability. This would, in particular, be very helpful in clarifying the chemistry of the earlier actinide elements.

Relativistic Effects

For the heaviest elements in the Periodic Table, relativistic effects play an increasingly important role. This is clearly shown by the increase in the magnitude of spin-orbit interaction, which for the actinides is of the same order of magnitude as the electrostatic interaction. This results in $5f^n$ systems being best described by intermediate-coupled wavefunctions, i.e., somewhere between the Russell-Saunders and the j-j coupling limits. Relativistic effects are of major importance for s electrons and the hyperfine structure of electronic configurations with an open s shell will show such effects.

The hyperfine anomaly Δ is, for two isotopes, a measure of the difference between the distribution of nuclear magnetism over the finite size of each of the nuclei. It is defined as

$$\Delta = \frac{a_1 g_2}{a_2 g_1} - 1,$$

where the parameters a_1 and a_2 are the hyperfine structure constants for a particular level of an open s-shell configuration and g_1 and g_2 are the nuclear g values for each of the two isotopes, respectively. Experimentally, the hyperfine structure anomaly can be obtained by analysis of high resolution optical or atomic beam data for the free ion to determine the hyperfine structure constants of particular levels of a $5f^n7s^2$ and a $5f^n7s$ configuration. Solid state electron paramagnetic resonance data on other oxidation states of the two isotopes can also provide useful information for this determination.[13]

From the Bohr-Weisskopf theory[14] it can be shown that the magnitude of the hyperfine anomaly is proportional to a certain factor b which is calculated by evaluating the relativistic electronic wave function over the finite size of the nucleus. This factor has been tabulated and changes in magnitude from approximately 0.08% for $Z = 10$ to 4.8% at $Z = 90$. Extrapolation to $Z = 99$ gives $b \simeq 6.3\%$. Thus, a hyperfine anomaly, which is usually less than 1%, could be magnified in the heavy elements by the relativistic increase in the s-electron density at the nucleus.

Measurements of this quantity can provide information about s-electron density at the nucleus including configuration interaction effects, the distribution of nuclear magnetism, and the coupling of nuclear angular momenta for a particular nuclear state. Furthermore, with the use of high resolution laser sources, it should be possible to measure hyperfine effects for excited electronic levels in actinide compounds.

Conclusions

As already indicated, the actinides constitute "the missing link" between the d transition elements and the lanthanides. It is fascinating that among the actinides the critical region for the crossover is located between plutonium and americium. Here, as in any other branch of science, it is clear that much attention should be concentrated on such a borderline situation. To be able to do this fruitfully and in order to make the correct conclusions, it is important that the ranges before and after the transition region are well characterized and understood. Hence, transplutonium research is extremely important for a correct assessment of this physical crossover region. In addition, every means (for example high pressure and chemical manipulation) to bring a system into the critical region should be applied.

Actinide surface physics and chemistry and catalytic studies are almost totally unexplored fields. The easily accessible f-electrons should provide unique chemical bonding situations and may therefore influence catalytic reactions in a previously unknown way. Unusual surface properties are likely to be seen, where the 5f electrons play a predominant role. Surface induced electronic transitions would be fascinating subjects for study. Again transplutonium research would be extremely useful for our understanding of the earlier actinides. Intensified research in this area should greatly enhance our knowledge about electronic structure in general.

Table I - Chemical Oxidation States of the Actinides and the Status of Magnetic Measurements for Transplutonium Compounds

	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
1^+													E		
2^+							G			X	G	X	X	X	
3^+	+	E	E	+	+	+	O	G	G	G	X	X	X	X	X
4^+		+	+	+	+	+	G	O	G	X					
5^+			+	+	+	+	X								
6^+				+	+	+	X	E							
7^+					+	+	E								

+ - Accessible oxidation state.

E - Oxidation state reported under extreme conditions.

X - No magnetic measurements for this accessible oxidation state.

O - Anomalous magnetic results for a localized $5f^n$ system.

G - Consistent magnetic results assuming a localized $5f^n$ system.

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APPENDIX I

INDUSTRIAL USAGE OF CALIFORNIUM-252

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1. SUMMARY OF INDUSTRIAL USAGE OF ^{252}CF

Californium-252 became available to commercial source fabricators in 1971. This isotope was then, and remains today, the sole commercially available isotope capable of fabrication into physically small sources which emit neutrons intensely over a practical period of time. ^{252}Cf sources have significantly smaller physical dimensions than alpha-neutron or gamma-neutron sources of the same neutron output, and less free space is required within ^{252}Cf sources to accommodate decay and reaction-produced gases.

Industrial users of neutron sources began purchasing ^{252}Cf sources in 1971 for development purposes. By 1975, the major industrial users were well established. The approximate percentages of industrial ^{252}Cf sources and isotope quantities used for the major applications are shown in Table 1-1. Start-up sources for commercial nuclear reactors account for about one-half of industrial ^{252}Cf usage, both in terms of number of sources and in terms of quantity of ^{252}Cf. Approximately one-fourth of the ^{252}Cf isotope used by industry (about 8% of the industrial sources) is employed in nuclear fuel rod scanners, and an additional 19% is used for other activation analysis applications. Other users of industrial ^{252}Cf sources include education, research, instrument calibration, dosimetry, industrial guaging, and neutron radiography.

TABLE 1-1. INDUSTRIAL CF SOURCES (1971-1982)

	Per cent of Sources	Per Cent of Cf-252
Reactor Start-Up	55.3	48.3
Fuel Rod Scanners	8.2	25.3
Activation Analysis	18.9	19.4
Education & Reserch	5.0	2.4
Medical Research	3.1	0.7
Calibration & Dosimetry	3.1	0.1
Miscellaneous Other	6.3	3.8
	99.9	100

2. NUCLEAR REACTOR START-UP SOURCES

2.1 APPLICATION DESCRIPTION

Commerical nuclear power reactors use isotopic neutron sources to provide sufficient neutrons in the core prior to start-up to allow instrument calibration and observation of the approach to criticality. Two classes of sources are usually present in the core: primary and regenerative. Primary sources are those which emit neutrons at the time of insertion into the core. The great majority of such sources at this time are ^{252}Cf spontaneous fission sources. Prior to the commerical availability of ^{252}Cf, ^{238}PuBe alpha-neutron sources were preferred for primary start-up, with ^{210}PoBe alpha-neutron sources being used prior to about 1970. ^{124}SbBe photo-neutron sources have been used by one U.S. reactor manufacturer since the 1960's, and a few sources of this type are still being made for primary start-up today. Regenerative start-up sources are non-radioactive when placed in the core, and are activated within the core for subsequent start-ups. ^{123}SbBe sources are universally used for this purpose. The ^{123}Sb is activated to 60-day ^{124}Sb by core neutrons, and thence neutrons are produced by the ^{124}SbBe photo-neutron reaction. Combination sources consisting typically of a ^{252}Cf primary source and an unactivated ^{123}SbBe regenerative source in a single assembly become available in the mid-1970's.

2.2 GROWTH OF ^{252}CF USAGE

Start-up sources are in-core components and such must be designed, analyzed, and approved for use in a manner similar to fuel rods. The time-consuming design and approval process delayed the initial use of ^{252}Cf for commercial reactor start-up until late 1973, some two years after the isotope became commercially available. Figure 2-1 shows the usage of ^{252}Cf for primary start-up sources compared to ^{238}PuBe sources. As can be seen from the Figure,

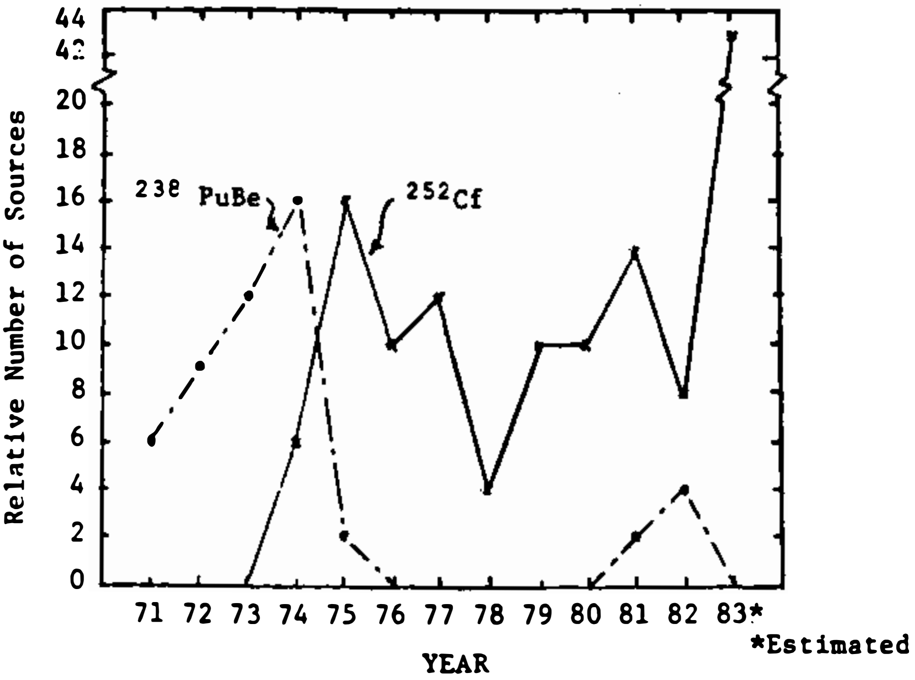

Figure 2-1. Relative numbers of reactor primary start-up sources.

^{252}Cf has essentially replaced ^{238}PuBe sources for commerical reactor start-up applications.* Californium sources have been used for commerical reactor start-up purposes in West Germany, Japan, Korea, Sweden, Brazil, Yugoslavia, Spain, France, and Italy as well as in the United States.

2.3 ADVANTAGES OF ^{252}CF FOR PRIMARY START-UP USE

2.3.1 Small Physical Size

Start-up source neutron output requirements range from approximately 5 x 10^7 neutrons/second (n/sec) up to approximatley 1 x 10^{10} n/sec. Required output depends upon reactor type and size, source placement, detector efficiency, country in which located and other factors. From two to seven sources are employed to generate the total neutron output required for a particular reactor. ^{252}Cf emits 2.311 x 10^{12} n/sec/g, so that the physical volume of a 1 x 10^9 n/sec ^{252}Cf source theoretically could be less then 1 mm^3. The minimum volume of practical ^{252}Cf sources of this output, including fission gas plenum and containment capsule, is about 0.6 cm^3. A practical ^{238}PuBe source of 1 x 10^9 n/sec output would require about 75 cm^3 for the PuBe material, plus an additional volume of the same order of magnitude as a plenum for reaction gases. The volume required for ^{124}SbBe sources depends upon the activation time and neutron flux; a 1 x 10^9 n/sec source typically would require 25 to 50 cm^3 of SbBe material, plus a gas plenum.

That ^{252}Cf sources are about two orders of magnitude smaller in volume than ^{238}PuBe or ^{124}SbBe sources of the same neutron output permits greater flexibility in design for sources using californium, and in particular makes high-output combination primary/regenerative sources feasible.

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*^{124}SbBe start-up sources are not shown in Figure 2.1 because accurate data on their use are not available to the author. Their use has been limited due to the short (60-day) half-life and high radiation field of ^{124}Sb, and is believed to have steadily decreased since peak usage in the mid-1970's.

2.3.2 Lower Heat Generation and Temperatures

Heat is generated within reactor start-up sources during reactor operation as a result both of neutron-induded reactions and of gamma heating. The preferred physical form of ^{252}Cf for use in reactor start-up sources is that of the californium sesquioxide-palladium cermet wire produced by the U.S. Department of Energy. The wire material contains a maximum of two per cent of Cf_2O_3 in a palladium metal matrix compacted to nearly theoretical density (1). The wires are roughly 0.040 inches square, and are available with ^{252}Cf concentrations of approximately 2, 20, and 200 μg/cm (1). The wire cermet form distributes the ^{252}Cf over a volume two orders of magnitude greater than that of the californium itself, thereby reducing volumetric heat generation rates by two orders of magnitude. In this form, a 1 x 10^9 n/sec ^{252}Cf source wire located in a reactor in a thermal neutron flux of 6 x 10^{13} n/cm^2-sec generates approximately 1.6 watts of which about 0.9 watt is due to decay and fission in the californium isotopes and about 0.7 watt is due to gamma heating in the Cf_2O_3/Pd cermet. The volumetric heat generation rate is approximately 50 watts/ cm^3. For comparison a 1 x 10^9 n/sec SbBe source in the same neutron flux would generate approximately 310 watts or 16.6 watts/cm^3 (7.2 watts/cm^3 from gamma and neutron heating, 0.5 from neutron thermalization in Be, 2.8 from ^{124}Sb reactions and subsequent decay, and 6.0 from ^{122}Sb reactions and subsequent decay) and a 1 x 10^9 n/sec ^{238}PuBe source in the same neutron flux would generate approximately 60,000 watts or 4410 watts/cm^3 (19 watts/cm^3 from gamma heating and 4390 from fission of Pu isotopes). It should be noted that ^{238}PuBe sources for this set of conditions are infeasible because of their very high heat generation rate and associated temperatures. Practical ^{238}PuBe start-up sources are limited to outputs on the order of 10^8 n/sec and thermal flux levels of about 3 x 10^{13} n/cm^2-sec.

Temperatures inside start-up sources during reactor operation are strongly dependent upon the mechanical design of the source, and upon coolant temperature, flow rate, and composition as well as upon the source intensity and type and the local gamma and neutron fluxes. Source design must be such as to maintain both the active materials and structural materials at acceptable temperatures during reactor operation. This requirement is easily met in ^{252}Cf sources utilizing Cf_2O_3/Pd cermet wire as the source material. Wire centerline temperatures on the order of 1500°F are acceptable due to the high (2800°F) melting temperature of palladium. The high temperature capability combined with the low total heat generation and moderate power density of this material allow simple, conservative source designs to be used even for high neutron output sources in high neutron and gamma flux environments. SbBe sources typically have source material power densities on the same order as ^{252}Cf sources (i.e., 25-50 watts/cm^3) but have total source material heat generation rates several hundred times those of ^{252}Cf sources. Since the melting temperature of antimony is 1167°F, source material temperatures must be held below about 850°F. While SbBe sources may be designed to meet the requirements of most applications where sufficient physical space is available, their design is typically more complex and less conservative than is the of ^{252}Cf sources. ^{238}PuBe source material has both a high power density and a high total heat generation rate. Even though source material temperatures on the order of 2000°F are acceptable in these sources, centerline temperature is frequently a limiting factor in their design. Typical design features employed to limit certerline temperature include annular geometry for the fuel material and small (a few thousandths of an inch) clearances between the source components to enhanc heat transfer. ^{238}PuBe sources are generally significantly more complex and costly to fabricate than either ^{252}Cf or SbBe sources for the same design conditions. Source material centerline temperature and/or source structural material (cladding) temperature limitations restrict ^{238}PuBe sources to neutron output levels less than about 1 x 10^8 n/sec and neutron flux environments less than about 3 x 10^{13} n/cm^2-sec.

2.3.3 Lower Gas Generation

Neutron sources of all types generate gas from nuclear reactions during reactor operation. Source designs must provide a plenum inside the source cladding to retain gases and to prevent excessive pressure buildup over the design life of the source (design life ranges from a few years up to forty years). Typical end-of-life gas pressures at reactor operating temperature are in the range of 1500 psi. The greater the quantity of gas generated over the source life, the greater is the required volume of the gas plenum, and therefore the thicker are the walls of pressure vessel (cladding) which retains the gas. For a given neutron output and reactor environment, ^{252}Cf sources generate less gas than sources made from any other available radiosotope.

^{252}Cf sources generate gas from ^{252}Cf and other Cf isotopes by fission (spontaneous and neutron-induced) and by alpha decay. Approximatley 0.3 gas atom is produced per fission (2) and approximately 1 gas atom is produced per alpha decay. A ^{252}Cf source having an initial output of 1×10^9 n/sec in a thermal flux of 6.1×10^{13} n/cm^2-sec produces 2.2×10^{17} gas atoms (of which 30.5% are fission gas) in the first six months. At the end of ten and twenty years, the total numbers of gas atoms generated are 1.02×10^{18} and 1.04×10^{18}, respectively, of which about 15% are fission gas. ^{252}Cf is unique among practical neutron source materials in that higher reactor neutron fluxes result in lower total gas generation. This is becuase higher neutron fluxes increase the number of californium atoms undergoing fission (and therby producing an average of 0.3 gas atom per reaction) relative to those undergoing alpha decay (which results in 1 He atom per reaction). In a flux of 1.1×10^{14} n/sec-cm^2, a 1×10^9 n/sec ^{252}Cf source will produce a total of 9.1×10^{17} gas atoms in twenty years, of which 22% are fission gas.

SbBe sources generate gas primarily from the (n, 2n) and (n, γ) fast neutron reactions in beryllium. Gamma-induced reactions generate negligible quantities of gas relative to the neutron-induced reactions. The reactions of interest are:

$$Be^9\ (n,\ 2n)Be^8$$

$$Be^8 \xrightarrow{1 \times 10^{-16} S} 2\ He^4$$

$$Be^9\ (n,\gamma)He^6$$

$$He^6 \xrightarrow{\beta^-,\ 0.8\ s} Li^6$$

$$Li^6\ (n,\ \gamma)\ H^3$$

In a commercial reactor, with a thermal flux of 6.1 x 10^{13} n/cm^2-sec, approximate 2 x 10^{22} gas atoms will be generated by a 1 x 10^9 n/sec SbBe source over twenty years of commerical operation. The rate of gas generation is proportional to the fast neutron flux, and the toal gas generation is proportional to the integrated fast flux over the reactor life.

^{238}PuBe sources generate gas both by fission of the ^{238}Pu (and other plutonium isotopes present) and by fast neutron reactions in beryllium. A 1 x 10^9 n/sec ^{238}PuBe source in a reactor having a thermal flux of 6.1 x 10^{13} n/cm^2-sec would generate approximately 2.4 x 10^{24} atoms in twenty years, of which about 3% are fission gases.

Gas generation by ^{252}Cf is seen to be approximately four and six orders of magnitude less than that generated by equivalent SbBe and ^{238}PuBe sources, respectively.

2.3.4 Neglible Swelling Problems

The palladium matrix surrounding the $^{252}Cf_2O_3$ particles in the Cf_2O_3/Pd cermet wire used in reactor start-up sources serves as a mechanical barrier to fission fragments and alpha particles, thus protecting the capsule wall from direct impact. Some gas atoms generated within the cermet diffuse to the surface and are released into the gas plenum, others are retained in the metal matrix and may eventually cause swelling of the matrix material by atomic displacement or by agglomeration into gas pockets. Due to the low rate of heat generation in ^{252}Cf sources, cermet to capsule wall gaps allowing for 100% or greater volumetric growth of the cermet are both feasible and typical. Such swelling of the Cf_2O_3 cermet as may occur is readily accommodated with no contact forces on the encapsulation materials, and is not a significant factor in ^{252}Cf source design.

Swelling in sources containing beryllium occurs both by atomic displacement and as a result of helium generation within the beryllium. Above an integrated fast flux (E > 1 Mev) of 10^{21} n/cm^2, swelling occurs primarily as a result of gas generation and agglomeration into bubbles (3). Growth rates for Be are reasonably linear with fast neutron fluence up to about 3 x 10^{22} n/cm^2(4). In a reactor having a thermal flux of 6.1 x 10^{13} n/cm^2-sec, volumetric swelling of typical SbBe pressed-powder pellets over a 20-year life would be on the order of 0.6%, and linear pellet dimensions would increase by about 0.2%. Solid beryllium would increase in linear dimensions under these conditions by roughly 0.4%. Typical SbBe or ^{238}PuBe source pellet diameters range from 0.2 to 0.8 inches; diametral swelling on the order of 0.0004 to 0.0030 inches will occur depending upon source design. The need to provide space for pellet swelling, along with the high heat generation rates in SbBe and especially ^{238}PuBe sources, imposes design restraints on these sources which are not present with ^{252}Cf sources.

2.3.5 Pre-Installation Timing Considerations

^{252}Cf and ^{238}PuBe sources have out-of-reactor half-lives of 2.6 years and 89 years, respectively. These sources emit their design output of neutrons when fabricated, and are delivered directly to the reactor site from the source manufacturer.

Their half-lives are such that delays in start-up of the reactor of several months have little effect on the source neutron output. SbBe sources, however, are fabricated from non-radioactive ^{123}Sb and therefore require activation in a reactor prior to delivery to the reactor site. Typical activation periods range from 120 days to one year, depending upon the flux level in the reactor used for activation. The activated ^{124}SbBe source has a half-life of 60 days; delays in the reactor start-up result in significant decreases in source neutron output. The relative scarcity of reactors suitable for commerical activation, and the scheduling problems inherently associated with SbBe sources make these sources unattractive for primary start-up. The major use of SbBe start-up sources is now as regenerative sources which are non-radioactive when placed into the reactor, are subsequently activated by the reactor, and are used for re-starts of the reactor in which they are activated.

2.3.6 Other Considerations

U.S. and IAEA shipping regulations allow up to 2 Ci (curies) of ^{252}Cf in "Special Form" capsules to be shipped in a single Type A cask. Since ^{252}Cf emits 4.3×10^{9} n/sec/Ci, start-up source sets adequate for nearly any commercial reactor may be shipped in a single Type A cask.

^{238}PuBe sources emit about 2.5×10^{6} n/sec/Ci; sources for most reactors would exceed the IAEA Type A limit of 8 Ci for ^{238}Pu in "Special Form" (the U.S. limit is 20 Ci), and would have to be shipped in Type B casks.

^{124}SbBe sources emit about 4×10^{5} n/sec/Ci. An activated start-up source set contains on the order of 10,000 Ci, and must be shipped in Type B casks.

Design, fabrication, and regulatory approval of Type B casks are much more difficult, time-consuming, and costly than is the case for Type A casks.

2.3.7 Start-Up Source Summary

The great majority of commercial nuclear reactor primary start-up sources fabricated in the last several years, and planned for fabrication in the next several years, are ^{252}Cf start-up sources. The characteristics of ^{252}Cf start-up sources are shown in Table 2-1 along with the corresponding characteristics of other types of start-up sources. It is seen from the comparison that ^{252}Cf is far superior to other available isotopes for primary start-up source applications. For reactors requiring greater than about 2×10^{9} n/sec for start-up, only ^{252}Cf sources are practical. At least two U.S. reactor manufacturers, and the major reactor manufacturers in West Germany, Japan, France, and Sweden, use ^{252}Cf sources exclusively for primary start-up. Table 2-2 is a partial list of reactors using ^{252}Cf start-up sources.

TABLE 2-1. COMPARISON OF ^{252}CF AND OTHER START-UP SOURCES

(For: 1 x 10^9 n/sec initial output and use in a reactor having a thermal flux of 6.1 x 10^{13} n/sec-cm^2)

	^{252}Cf	^{238}PuBe	^{24}SbBe
Volumetric	50 watts/cm^3	4,410 watts/cm^3	16.6 watts/cm^3
Source volume	0.6 cm^3	75 cm^3	50-100 cm^3
Heat generation			
TOTAL	1.6 watts	60,000 watts	310 watts
Volumetric	50 watts/cm^3	4,410 watts/cm^3	16.6 watts/cm^3
Internal temperature limit	~1500°F	~2000°F	~850°F
Gas generation			
10 years	1.02 x 10^{18} atoms	1.2 x 10^{24}	1 x 10^{22}
20 years	1.04 x 10^{18}	2.4 x 10^{24}	2 x 10^{22}
Swelling problems	No	Yes	Yes
Shelf half-life	2.6 years	89 years	60 days
Activation required	None	None	120-360 days
Radiation content	0.23 ci	400 ci	2,500 ci
Shipping cask type	A	B	B

TABLE 2-2. PARTIAL LIST OF REACTOR START-UP SOURCES BY TYPE

Year	Reactor type	Nuclear power plant	Source type	Purchased by
1964	PWR	Indian Point 1	PoBe	Babcock & Wilcox
1965 & earlier	PWR	Various	SbBe	Westinghouse
1966	PWR	Indian Point 1	PoBe	Westinghouse
1966	HTGR	Peach Bottom 1	PoBe	Gulf General Atomic
1966	PWR	Chooz (SENA)	PoBe	Westinghouse
1966	PWR	San Onofre 1	PoBe	Westinghouse
1967	Research	Lynchburg Research Center	PoBe	Babcock & Wilcox
1967	PWR	Yankee Rowe (Replacement)	PoBe	Westinghouse
1968	PWR	Obrigheim (KWO)	SbBe	Siemens
1968	PWR	Jose Cabrera	PoBe	Westinghouse
1968	PWR	Obrigheim (KWO)	PoBe	Siemens
1968	Marine	S. S. Savannah	PoBe	Todd Shipbuilding
1969	PWR	Beznau (NOK)	PoBe	Westinghouse
1969	PWR	Robert E. Ginna 1	PoBe	Westinghouse
1969	PWR	SELNI (Restart)	PoBe	Westinghouse
1970	PWR	Palisades	PoBe	Combustion Engineering
1970	PWR	Mihama 1	PoBe	Westinghouse
1970	PWR	H. B. Robinson 2	PoBe	Westinghouse
1970	PWR	Chooz (SENA) (Restart)	PoBe	Westinghouse
1970	HTGR	Peach Bottom 1	PoBe	Gulf General Atomic

(continued)

TABLE 2-2 (continued)

Year	Reactor type	Nuclear power plant	Source type	Purchased by
1970	PWR	Point Beach 1	PoBe	Westinghouse
1970	BWR	Big Rock Point	SbBe	Consumers Power
1971	PWR	Point Beach 2	Pu8Be	Westinghouse
1971	PWR	Indian Point 2	Pu8Be	Westinghouse
1971	PWR	Stade (KKS)	Pu8Be	Siemens
1971	PWR	Mihama 2	Pu8Be	Westinghouse
1972	PWR	Turkey Point 3	Pu8Be	Westinghouse
1972	PWR	Surry 1	Pu8Be	Westinghouse
1972	PWR	Main Yankee	Pu8Be	Combustion Engineering
1972	PWR	Surry 2	Pu8Be	Westinghouse
1973	BWR	Big Rock Point	SbBe	Consumers Power
1973	PWR	Zion 1	Pu8Be	Westinghouse
1973	PWR	Turkey Point 4	Pu8Be	Westinghouse
1973	PWR	Omaha I	Pu8Be	Combustion Engineering
1973	PWR	Prairie Island I	Pu8Be	Westinghouse
1973	PWR	Kewaunee	Pu8Be	Westinghouse
1973	PWR	Zion 2	Cf-252	Westinghouse
1974	PWR	Takahama I	Pu8Be	Westinghouse
1974	PWR	Ringhals II	CF-252	Westinghouse
1974	PWR	Indian Point 3	Pu8Be	Westinghouse

(continued)

TABLE 2-2 (continued)

Year	Reactor type	Nuclear power plant	Source type	Purchased by
1974	PWR	Calvert Cliffs 1	Pu8Be	Combustion Engineering
1974	PWR	Calvert Cliffs 2	Pu8Be	Combustion Engineering
1974	PWR	Donald C. Cook I	Cf-252	Westinghouse
1974	PWR	NSS - Oconee I, II, III	SbBe	Babcock & Wilcox
1974	PWR	NSS - Arkansas Nuclear One	SbBe	Babcock & Wilcox
1974	PWR	NSS - Rancho Seco	SbBe	Babcock & Wilcox
1974	PWR	NSS - Three Mile Island I	SbBe	Babcock & Wilsox
1974	PWR	Prairie Island II	Cf-252	Westinghouse
1974	PWR	Genkai I	Pu8Be	Westinghouse
1974	PWR	Takahama II	Pu8Be	Westinghouse
1975	PWR	Millstone 2	Pu8Be	Combustion Engineering
1975	PWR	St. Lucie 1	Pu8Be	Combustion Engineering
1975	BWR	Brunsbuttel (KKB)	Cf-252	Krafwerk Union
1975	PWR	Trojan	Cf-252	Westinghouse
1975	PWR	Milhama 3	Pu8Be	Westinghouse
1975	PWR	Biblis (KWB-B)	Cf-252	Kraftwerk Union
1976	PWR	Beaver Valley 1	Cf-252	Westinghouse
1976	PWR	Unterweser (KKU)	Cf-252	Kraftwerk Union
1976	PWR	Salem 1	Cf-252	Westinghouse

(continued)

TABLE 2-2 (continued)

Year	Reactor type	Nuclear power plant	Source type	Purchased by
1976	BWR	Isar (KKI)	Cf-252	Kraftwerk Union
1976	PWR	Ikata Machi I	Cf-252	Westinghouse
1976	PWR	Mihama I (Restart)	Cf-252	Westinghouse
1976	BWR	Phillippsburg (KKP-1)	Cf-252	Kraftwerk Union
1977	PWR	Kori	Cf-252	Westinghouse
1977	PWR	Joseph F. Farley 1	Cf-252	Westinghouse
1977	PWR	North Anna 1	Cf-252	Westinghouse
1977	PWR	Ohi 1	Cf-252	Westinghouse
1977	LWBR	Shipping port	Cf-252	Westinghouse
1977	Research	Idaho LOFT	Cf-252	Exxon Nuclear
1977	PWR	Diablo Canyon 1	Cf-252	Westinghouse
1977	PWR	ANO-2	Pu8Be	Combustion Engineering
1977	PWR	Donald C. Cook 2	Cf-252	Westinghouse
1977	PWR	Ohi 2	Cf-252	Westinghouse
1979	PWR	Salem 2	Cf-252	Westinghouse
1979	PWR	North Anna 2	Cf-252	Westinghouse
1979	PWR	Stade (KKS)	Cf-252	Kraftwerk Union
1979	PWR	Surry 2 (Restart)	Cf-252	Westinghouse
1979	PWR	Sequoyah 1	Cf-252	Westinghouse

(continued)

TABLE 2-2 (continued)

Year	Reactor type	Nuclear power plant	Source type	Purchased by
1979	PWR	Genkai 2	Cf-252	Westinghouse
1979	PWR	Crystal River	SbBe	Babcock & Wilcox
1979	BWR	Big Rock Point	SbBe	Consumers Power
1979	PWR	Mihama 2 (Restart)	Cf-252	Westinghouse
1980	PWR	Mihama 3 (Restart)	Cf-252	Westinghouse
1980	PWR	Indian Point 2 (Restart)	Cf-252	Westinghouse
1980	PWR	Takahama 2 (Restart)	Cf-252	Westinghouse
1980	PWR	Farley 2	Cf-252	Westinghouse
1980	PWR	Takahama 1 (Restart)	Cf-252	Westinghouse
1890	PWR	McGuire 1	Cf-252	Westinghouse
1980	PWR	OHI 2 (Restart)	Cf-252	Westinghouse
1980	PWR	Almaraz 1	Cf-252	Westinghouse
1981	PWR	Surry 1 (Restart)	Cf-252	Westinghouse
1981	PWR	Asco	Cf-252	Westinghouse
1981	PWR	Ikata Machi 2	Cf-252	Westinghouse
1981	PWR	Kresko	Cf-252	Westinghouse
1981	PWR	Genkai 1 (Restart)	Cf-252	Westinghouse
1981	PWR	Sequoyah 2	Cf-252	Westinghouse
1981	PWR	Ohi (Restart)	Cf-252	Westinghouse
1981	PWR	Angra 1	Cf-252	Westinghouse

3. REACTOR FUEL ROD SCANNERS

Nuclear fuel rod scanners are the second largest industrial use of ^{252}Cf. The scanners use activation by ^{252}Cf neutrons to assure the uniformity of fissile material loading in fuel rods, and to measure the quantity of fissile material in the rods. Uniformity of the quantity of fissile material per unit length of the fuel rod is necessary to prevent hot spots in the rod during reactor operation, and thereby to avoid possible fuel clad rupture and release of radioactive materials. Total fissile content of a fuel rod must be controlled to prevent excessive heating of the individual rod in the reactor. The degree of uncertainty in fissile material uniformity within individual rods and between rods in a reactor directly affects the allowable power level for the reactor. Greater uncertainties require lower power levels to assure that the hottest spot of the hottest rod will not fail.

Accurate measurement of the total fissile material content of each fuel rod fabricated in a plant restricts the pathways for diversion of mateiral to waste and scrap outputs and to the uncertainty of the quantity of material in process.

Automated scanners for UO_2 or mixed UO_2-PuO_2 fuel rods are available which operate with sufficient speed to permit assay of all fuel rods prior to their shipment from the fabricating plants. At scanning speeds up to 2000 feet of rod per hour, total fissile content may be measured to an accuracy of ±1%, and pellet loading variations greater than ±5% relative may be found, both with a confidence level of 95%.(5)

A typical fuel rod scanner employs 600 to 1500 μg of ^{252}Cf in a moderator to irradiate a fuel rod passing through the moderator on a conveyer at a uniform speed. Fission-product gamma radiation resulting from fissions induced by the californium neutrons is measured by one or more detectors located downstream of the irradiator. One commercial manufacturer of fuel rod scanners achieves count rates on the order of 300,000 counts/sec using two NaI scintillation detectors and a deadtime-less counting system.(6) Analysis and comparison to stored calibration data are performed by a minicomputer; defective rods are identified automatically. Scanning of several rods at once, and automatic sorting of accepted and rejected rods are optional.

Precision of measurement depends upon the number of neutrons available for activation. Approximate minimum source size is 600 μg of ^{252}Cf, equivalent to 1.4 x 10^9 n/sec. Sources for this application usually contain about 1500 μg of ^{252}Cf when manufactured, and are replaced after they have decayed to about 750 μg, i.e., after about three years of use. Cost of a 1500 μg source is roughly $30,000, and cost of the entire scanner is in the range from $150,000 to $250,000.(5) ^{238}PuBe or ^{241}AmBe sources having neutron outputs equivalent to 750μg of ^{252}Cf (i.e., to 1.7 x 10^9 n/sec) would contain about 690 Ci of alpha emitter. Commercial ^{238}PuBe and ^{241}AmBe sources are limited to about 50 Ci of either isotope per source; thus, about 14 sources would be required to substitute for the single ^{252}Cf source of minimum neutron output, each of which would be about 1.5 inches in diameter by 2.5 inches long. The large physical size of ^{238}PuBe and AmBe souces relative to ^{252}Cf sources of equivalent neutron output limits the thermal neutron flux attainable from these alpha-neutron souces in a moderator to a samll fraction of that attainable from ^{252}Cf. The high-specific-activity alpha emitter ^{210}Po offers physical size reduction and higher thermal neutron potential relative to ^{238}Pu or ^{242}Am, but is available only in small quantities in purities adequate for static eliminators. Cost of ^{210}Po is prohibitive for use in fuel rod scanners (i.e., about $300/Ci or $207,000 minimum per scanner) and has only a 210-day half-life. No commercially-available isotope other than ^{252}Cf is suitable for fuel rod scanner use.

4. ACTIVATION ANALYSIS

Activation analysis applications (other than fuel rod scanners) account for roughly 19% of the industrial use of ^{252}Cf, both in terms of numbers of sources and in terms of quantity of isotope.

Elemental analysis of a sample by neutron activation techniques involves irradiating the sample with neutrons to induce activity in the samples and either gamma ray spectrometry or neutron measurement to determine the concentrations of specific elements in the sample.

Prompt gamma ray techniques analyze those gamma rays emitted essentially instantaneously following neutron capture; detection of the induced radiation is performed simultaneously with the neutron irradiation. In addition to prompt gamma rays, some activated elements emit delayed gamma rays for a time following neutron capture. The analysis of the delayed gamma radiation is best performed after neutron irradiation has stopped, and at a location away from the neutron source, to minimize background radiation.

The gamma rays emitted by the elements in the sample are characteristic of the emitting element. Such gamma rays are emitted with specific discrete energies, usually in the several Mev range. The energy specturm of gamma rays recorded by the detector and associated electronics generally consists of broadened peaks superimposed on a smooth background. The peaks are centered around the energies characteristic of the corresponding elements, with the degree of broadening depending on the detector and electronics resolution. Background results from the detection of radiation from sources other than the sample, from gamma rays emitted from other elements in the sample whose energies have been reduced by scattering reactions, and from electronic noise. The concentration of the emitting element within the sample is proportional to the number of gamma rays contributing to the corresponding characteirstic peak in the spectrum. The coefficient of proportionality for a given system is best determiend by calibration measurements on samples having known concentrations. Accurate determination of concentration requires sophisticated data reduction to resolve closely spaced peaks, compensate for background and noise, and calculate the area under particular peaks. Such data reduction is usually performed by computer. Sensitivity and accuracy vary greatly depending on the element of interest, strength of the neutron source used for irradiation, activation time, detector and electronics resolution, and the presence of elements which emit radiation having energies sufficiently close to those of the element of interest to interfere with the interpretation of the detected gamma spectrum. Most elements are detectable at parts per million concentration with suitable equipment. Extensive literature is available on the subject of neutron activation analysis. Reference 7 is an excellent textbook on the subject, and reference 8 contains recent papers describing applications related to fossil fuels exploration and use.

The source used in neutron activation/gamma spectrum analysis are typically ^{252}Cf sources having outputs ranging from 10^9 to 10^{10} n/sec. Applications involving physically large samples (such as the core analyses discussed in Section 4.3 of this paper) irradiate the sample with source neutrons in order to assure neutron penetration throughout the sample. Applications involving physically small samples generally thermalize the source neutrons outside the sample to achieve maximum capture within the sample. Thermalization is achieved by immersing the neutron souce in a moderator such as water; the sample to be activated is placed in the water at the location of peak thermal flux. For a physically samll ^{252}Cf source (0.92 cm diameter by 1.9 cm long) the maximum thermal neutron flux in water is approximately 0.013 thermal neutrons per centimeter squared per source neutron, and occurs at a distance of approximately 0.6 cm from the source center.(9) Thermal fluxes as high as 0.024 n/cm^2 per source neutron are attainable at 1 cm from the center of ^{252}Cf source in a polehtylene (CH_2) sphere of 4 cm radius inside a spherical beryllium reflector hving a radius of 34 cm.(10) Californium-252 is the only commercially available isotope which combines high neutron output with sources of small physical size; small physical size is essential for this application since the thermal flux is a maximum approximately 1 cm from the source center and decreases rapidly with increasing distance.

Neutron activation/neutron analyis techniques are limited to those isotopes which emit neutrons subsequent to neutron capture, i.e., to fissile isotopes. One application is uranium borehole logging (discussed in Section 4.2 of this paper). Other applications include quantitative assay of the fissile contents of closed containers of material and theft-prevention devices for fissile materials.

Several specific activation analysis applications are discussed briefly in the following sections.

4.1 ASSAY SYSTEMS FOR FISSILE AND/OR FERTILE MATERIAL

Assay systems for the quantitative measuremnt of fissile and/or fertile material contained in closed vessels are commercially available. Various models accommodate vessel sizes ranging from a few cubic centimeters to 55-gallon drums. The fissile/fertile material may be in any form within the vessel: solid chunks mixed with inert material, dissolved or suspended material in a liquid, etc. One such commerical system can accept vessels up to 8 inches in diameter by 51 inches in length(11) and under "average conditions" can detect 0.25 g of fissile material disbursed in a gallon of bulk matrix material.(12) Accuracy of measurement ranges from ±100% for 0.1 g of fissile material per gallon to ±0.7% for contents of 50 g/gallons (both at one standard deviation).(12)

Systems of this type generally irradiate the vessel with unmoderated ^{252}Cf neutrons to induce fission, and monitor fission gammas and/or neutrons plus gammas using coincidence counting. Source size required for these systems ranges from about 20 μg of ^{252}Cf up to about 500/μg depending upon system design and upon the size of the containers to be assayed.

4.2 URANIUM BOREHOLE LOGGING

Uranium borehole logging is a specialized application of neutron activation analysis which permits accurate determination of uranium concentration in formations outside of cased or uncased boreholes. Present systems are capable of measuring uranium concentrations as low as 100 parts per million U_3O_8.(13)

A sonde containing a ^{252}Cf neutron source and a neutron detector located sufficiently far from the source to detect very few neutrons from the source is lowered into the borehole, then withdrawn at a speed of approximately 3.5 feet per minute. Neutrons from the source penetrate approximatley 15 cm into the formation outside the borehole while slowing to thermal energies. If uranium is present, some of the thermal neutrons are captured by ^{235}U nuclei, which then fission. Certain of the resulting fission products decay by neutron emission after a short time, and these "delyaed" neutrons are detected as the neutron detector moves upward through the activated region. The high sensitivity of the system for uranium is a result of the negligible level of naturally occurring neutrons, and of the fact that ^{235}U is the only naturally occurring isotope which undergoes fission following capture of a thermal neutron.

Neutron sources used for this application must produce neutrons at rates on the order of 10^9 n/sec, and must be physically small enough to fit into boreholes having dimaters as small as 2-1/4 inches. Of the commercially available neutrons sources, only those using ^{252}Cf (which produces neutrons by spontaneous fission) can meet both the neutron output and physical size requirements at reasonable cost.

4.3 CORE SAMPLE ELEMENTAL ANALYSIS

Exploration for hydrocarbon reservoirs or for mineral deposits frequently involves core drilling into a formation followed by analysis of core samples for the presence and content of the desired mineral. Rapid, non-destructive analyses of core samples up to about 5 inches in diamter and 18 inches in length may be performed in the field using neutron activation techniques.(14) The core sample to be analyzed is placed between a high-output neutron source and a gamma detector capable of high energy resolution (such as a lithium-doped germanium detector). The sample is rotated and translated such that the entire volume of the sample is exposed to the neutrons form the source. Elements within the sample capture neutrons and emit gamma radiation having energies characteristic of the absorbing element. Both prompt gamma radiation (emitted within approximately 10^{-13} sec after neutron capture) and delayed gamma radiation are emitted at discrete energy levels characteristic of the emitting element. Core sample analysis is preformed by energy analysis of both prompt and delayed gamma rediation (the techniqures are described in the section of this paper dealing with neutron activation analysis). Sensitivities vary depending upon the activation period, neutron source strength, and element of interest. For neutron source strengths on the order of 7×10^9 n/sec and activation times of 15 to 20 minutes, elements such as iron, sulfur and copper may be detected at concentrations as low as 0.2 weight percent. Some elements may be detected at much lower concentrations. Vanadium, for example, may be detected at concentrations of only 3 parts per million by weight.

The source requirements for this application are high neutron output and small physical size; the only practical commercially available source material is ^{252}Cf. Since the analysis is performed aboveground, the environmental requirements are minimal, and standard source designs adequate.

4.4 OTHER ACTIVATION ANALYSIS APPLICATIONS

Other industiral devices involving activation analysis using ^{252}Cf include continuous monitoring of the composition (especially sulfur and ash content) of coal on a moving conveyor at rates up to 50 tons per hour(15, 16, 17) and batch analysis of the vanadium content of crude oil.(18) The common element in each application is that each requires an intense neutron source of small physical dimensions.

5. OTHER INDUSTRIAL USES OF ^{252}CF

Approximately 10% of the industrial ^{252}Cf sources (about 4% of the ^{252}Cf isotope) go into application other than those discussed in previous sections, education and research. Such applications include instrument calibration, dosimetry, industrial gauging, and neutron radiography. In most cases, ^{252}Cf is selected because it is the only isotope adequate for the particular intended use.

6. CONCLUSIONS

The isotope ^{252}Cf is unique among commercially available radioistopes because it is the only such material with a reasonably long half-life capable of being fabricated into intense neutron sources of small physical size. That ^{252}Cf produces neutrons from spontaneous fission eliminates the need for target materials required for other neutron source types and thereby eliminates target-related restrictions (target material volume, gas and heat generation in the target). Neutron production by spontaneous fission is more than six orders of magnitude greater in efficiency of neutron production than either alpha-neutron or gamma-neutron reactions; radioistope-related restrictions (heating and gas generation due to natural decay or neutron-induced reactions) are therefore minimal in ^{252}Cf sources.

Becuase of its short half-life (relative to ^{241}Am and ^{238}Pu), ^{252}Cf is rarely used in industrial applications in which other types of neutron sources could be used. In most cases, no adequate substitute exists for ^{252}Cf. Substantial investments in research, development, and equipment have been made by industry on the assumption that ^{252}Cf will continue to be available in adequate quantities at reasonable cost. Should ^{252}Cf cease to be available, these investments will be lost. In those applications where substitutes are feasible, extensive development and re-design would be required piror to use of the substitute; many applications would become infeasible due to the unavailability of a suitable substitute for ^{252}Cf.

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APPENDIX J

Cf-252: NEW RADIOISOTOPE FOR HUMAN CANCER THERAPY

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HISTORICAL

In 1895, Roentgen discovered X-rays which led to the application of photon radiation to human cancer therapy. In 1898, M. Curie discovered radium Ra-226, a radioactive material whose biological potency in humans was discovered soon afterward by Becquerel and P. Curie (see 47). Ra-226 and related photon emitting radioactive isotopes have since been applied *in extenso* and very successfully to human cancer therapy. Neutron therapy has generated considerable interest in recent years as a modality for treating more resistant tumors. Neutron beam radiation was first tested in man by Stone *et al*. (60) beginning in 1939 using the cyclotron developed by E. O. Lawrence. In 1950, the group at the University of California Berkeley Laboratory isolated and identified the radioactive isotope Cf-252 (64) which was later characterized in detail and found to be a neutron emitter. The potential of the material and of neutron brachytherapy was not appreciated for a long time. Shlea and Stoddard (59) in 1965 finally postulated that such therapy might be useful for hypoxic tumor therapy and determined isodose curves which might be expected near linear Cf-252 sources, e.g., for use in intracavitary therapy. Fast neutron beam therapy has now become an active ongoing project, with studies of neutron only (7) and mixed beam studies (21) being carried out in the United States, England, Europe, and Japan.

A number of centers in several countries undertook early clinical trials using Cf-252 (6, 54, 66, 69) and radiobiological studies. However, Cf-252 as an isotope for human cancer therapy was shortly abandoned by most of those who conducted those early clinical trials (6, 54, 69). The major conclusions of this period were concern about its very high relative biological effectiveness (RBE) and the hazards to personnel during clinical use. Calculations by Rossi and Kellerer (30, 56) led to estimates of RBE for small doses and low dose rates (57) of 10-100 times greater than equivalent doses of photon radiation. The estimates were based upon the dual radiation action (DRA) theory (31).

This initial era yielded a number of careful studies of dosimetry of the difficult-to-measure neutrons. The works of Colvett and Krishnaswamy were most important [(12,29) and see review by Anderson (1)]. A large number of radiobiological experiments were also conducted to assess RBE (see 25) and the oxygen enhancement ratio (OER) (see 26) which were felt to represent the important parameters upon which to base therapy [see reviews, e.g., (19), Feola *et al*. (14), Maruyama *et al*. (43), Maruyama and van Nagell (47)]. Kal recently summarized much of the diverse data on this subject (24, 25, 26). From early clinical trials a very high RBE was identified for Cf-252 over conventional brachytherapy using Ra-226 or radium equivalent isotopes such as Co-60, Cs-137, Ir-192, Au-198, etc. For GYN tumor intracavitary therapy, this era is analogous to the early exploratory studies by the French, Swedish and Manchester groups (see 47). These various groups eventually systematized their methods of therapy so that outstanding results were obtained for tumor therapy. Fletcher and the M.D. Anderson Hospital group

(15) evolved, by very careful and individualized studies, the next generation approach founded upon the European systems. That system has been highly successful and widely emulated.

The early trials of Cf-252 neutron brachytherapy were regarded as failures, and no significant interest focused on the isotope until we began our studies in the mid-1970's. This led to a reawakening of interest in the study of this more complex neutron emitting isotope for cancer therapy (59). Studies carried out at the University of Kentucky A.B. Chandler Medical Center (UKMC) in Lexington led to a new interest in neutrons for the brachytherapy of unfavorable presentations of pelvic tumors. Basically, by applying systematic (46), computerized, and optimized (10, 63) high dose conventional photon radiotherapy to cervix cancer, we recognized shortcomings in our system (46, 47). The control of low stage cervical cancers was very satisfactory. However, tumor control for high stage cervical cancers was far from satisfactory, and failure was almost invariably due to tumor persistence and local failure (23, 47, 70). Thus, while most other reports were preoccupied with frequency of success in low stage disease, we became very interested in the frequency of failures in stage IIB, IIIA, IIIB, and IVA disease (43) and reasons for failure in stages IB-IVA (70). Similar results have been reported by most major cancer centers [see review by Kademian and Bosch (23)]. One alternative therapy was the use of very high dose photon beam and brachytherapy, but the result of that study revealed such a disastrous frequency of major complications of bladder, rectum, vagina and small bowel (5) that such studies were abandoned to return to more conventional dose schedules. Since local failure is seen in 50-100% of all the failures of radiation therapy in advanced tumor stages, there exists a real need to develop more effective local therapy for those tumors (43) and that is where we felt a potential application existed.

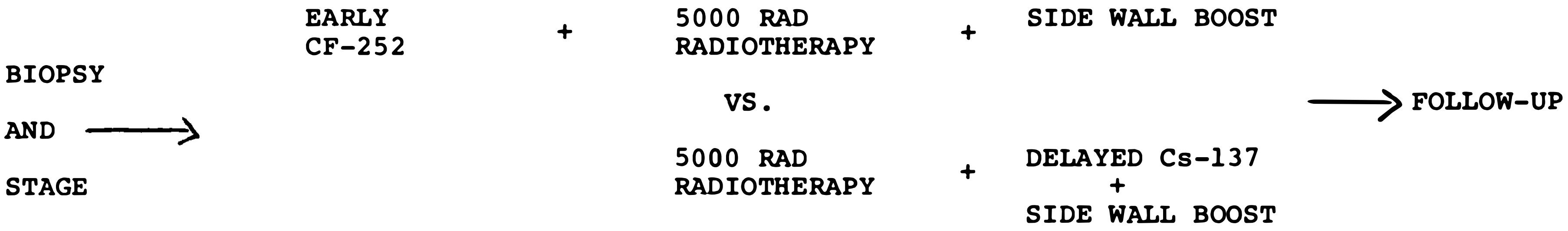
During this era, unique attributes were ascribed to photon beam energy which are unlikely to ultimately ever be shown to be due to anything more important than adequate field size and adequate coverage of central and lateral pelvic structure by a uniform high dose of radiation. Such therapy reduces the primary tumor's size and bulk, reduces sepsis, allows drainage of infected organs, clears minimal or microscopic disease in vessels, lymphatics, lymph nodes and adjacent pelvic structures, and reoxygenates the tumor mass. The standard practice as based upon the radiobiological principles to 1977 (16) was to shrink the tumor bulk to its resistant core and to boost the residual tumor core using interstitial/intracavitary photon radiation. If hypoxia is the major factor in tumor radioresistance as postulated by Gray et al. (18), then this approach is sound, provided tumor bulk is small. However, it should be possible to devise better methods to treat bulky tumor hypoxia than by the slow process of giving small doses in a protracted course of fractionated radiotherapy and waiting for the unpredictable process of tumor reoxygenation and tumor shrinkage to occur (27).

Our studies addressed the question of tumor bulk and hypoxia and we began testing neutron brachytherapy, as it is much more effective against hypoxic tumors (43). This led us to the use of neutrons in different schedules (34) and our observations of rapid tumor clearance. We postulated that the schedule-dependent clearance of bulky cervical cancer was due to more effective antihypoxic tumor therapy. This was done by starting with Cf-252 neutron ("early") brachytherapy (34) and following with photon radiation (51). This was found to be twice as effective as neutron or photon therapy done after photon radiotherapy ("delayed") (34, 51). We (39) postulated that the sparse but densely ionizing events from neutron therapy destroyed hypoxic tumor better. But, it may also miss many hypoxic tumor cells when the tumor is small. By early Cf-252 therapy, one destroys a large quantity of hypoxic tumor, and this leads to rapid shrinkage of the bulky tumor masses (34) and probably to better tumor reoxygenation (27). This could lead to an advantage for later fractionated radiotherapy for destroying residual tumor since by destroying a large quantity of resistant tumor, one leaves a more responsive tumor. Our results could not be explained by differences in patients' disease stages or medical conditions (51). The differences observed and our failure pattern were postulated to also be affected by differences in the vascular supply or tumor bed (40). A number of factors important to neutron therapy (NT) were identified (39, 40). Table 1 summarizes some of the factors felt to be important in the application of hypoxic tumor therapy using neutrons.

Table 2 presents some of the reasons proposed for the use of brachytherapy in a delayed sequence. Also shown is the rationale for the use of early brachytherapy using agents effective against hypoxic tumor. Figure 1 shows the early Cf-252 implant schedule and contrasts it to the delayed implant schedule done with photon emitting radioisotopes. That protocol is now being evaluated in our clinic.

PROTOCOL KY CX NT

Cancer of Cervix IB-IVA



ENDPOINT: LOCAL TUMOR CLEARANCE
LOCAL TUMOR CONTROL
RECURRENCE-FREE SURVIVAL
SURGERY + HISTOLOGY
(STAGE IB-II)

Figure 1

TABLE 1

FACTORS IN TUMOR RADIATION RESPONSE TO NEUTRONS

1. TUMOR BULK AND VOLUME
2. HYPOXIA AND NECROTIC ZONES
3. VIABLE HYPOXIC TUMOR CELLS
4. REOXYGENATION
5. DECREASED TUMOR BLOOD FLOW/INCREASED WITH TUMOR SHRINKAGE
6. TUMOR MICROVASCULARITY/REVASCULARIZATION
7. TUMOR CELL KILLING AND LYSIS

Table 2

REASONS FOR BRACHYTHERAPY SEQUENCE IN RADIATION THERAPY

DELAYED (Conventional)	EARLY
1. Reduce Tumor Bulk to Minimal and Resistant Core	1. Attack Hypoxic Tumor
2. Minimize Regional Tumor Burden	2. Produce Rapid Reduction of Tumor Bulk
3. Attack Residual Tumor Core	3. Allow Tumor Reoxygenation
4. Treat Residual Tumor Core with High Dose	4. Increase Efficacy of Low L.E.T. Radiation
	5. Increase Likelihood of Regional Tumor Clearance by Low L.E.T.

BASIC RADIOBIOLOGY

Concepts derived from basic cellular radiobiology dating back to the research of Puck and Marcus on human cervical cancer cells (55) guided our first radiotherapy clinical trial. Puck identified a single-hit multitarget model for photon inactivation of human cervix cancer (Hela) cells. Research by Lockhart et al. for human Hela cells (32) based upon the split-dose radiation technique and the concept of repair of sublethal damage (SLD) for mammalian cells by Elkind for photon radiation have shown SLD repair capacity of human cancer cells. But a large body of research on high linear energy transfer LET radiation showed that no SLD repair should be observed for highly ionizing radiation such as low dose rate (LDR), low energy neutrons emitted from Cf-252. This was confirmed in our laboratory by Todd et al. for human T-1 cells (65) and for other tumor cells by Feola (14). LDR photon radiobiology by Bedford (3) indicated that SLD for low LET photon radiations delivered at low dose rate is continually repaired by the Hela cells. Thus larger doses of photons are required to obtain a lethal lesion in the cell, whereas any dose of neutrons is lethal. Using LDR Cf-252 neutron radiation it was postulated that no dose rate effect should be observed since the high LET lesions represent one-hit inactivating events and are incapable of SLD repair (39). Therefore, neutron dose need not be protracted over a treatment time of days or weeks. Large cell killing effects occur with neutrons regardless of dose rate, and it does not make any difference whether dose is given in a few hours or a few days. Dose rate independent cell killing allowed us to make our treatment time short, i.e., 7-8 hours. Efficient cell killing also may cause tumors to shrink more rapidly, so there are reasons to destroy tumor more rapidly. The important type of radioresistance to overcome is that due to the hypoxia based upon the tumor outgrowing its blood supply. This type of radioresistance was shown by Gray et al. (18) to be overcome very effectively by neutron irradiation. Neutrons reduce the oxygen enhancement ratio (OER) or dose to overcome the increased resistance of hypoxic cells from 3.0 to 1.5. That is, there is a large oxygen gain factor of 2 by using neutron radiation. These advantages led us to utilize Cf-252 for our clinical trial.

However, an important constraint was that radiation dose should not exceed normal tissue tolerance, as an excessive complication rate would not allow neutron brachytherapy to have a fair evaluation or clinical trial. Above all, it should not irradiate personnel, create hazards or cause late effects or tumors in visitors, hospital workers or occupationally exposed staff.

RESULTS

Number of Patients Treated. We have treated a variety of patients with different tumors in 6+ years in our studies of Cf-252 for neutron brachytherapy. This largest single experience has been accumulated a a remarkably rapid rate and was based upon the fact that we see many patients with bulky, advanced localized neoplasms which are poorly controlled by presently available cancer treatment. We are also the major provider of specialized cancer therapy in our region, and many problems were sent to us because they were very complicated and obviously could not be dealt with by standard surgical, radiation or chemo-radiation protocols. From 1976 until the end of 1982 we treated 307 patients and carried out 516 procedures (Table 3). We treated over 50 patients per year and those usually 1.7 times each with Cf-252. This is a sizeable experience and included tumors of many types and primary sites (Table 3). About two-thirds were those of the female pelvis and this represented our greatest experience to date. Most of the sites are those that are also treated by standard photon brachytherapy with well-established outcomes. Kaplan has discussed tumors that are appropriate to high LET and hypoxia-directed therapy (28).

Advanced Pelvic Cancers. Our very first trial using Cf-252 can now be analyzed, since they took place over five years ago. In 1976-1977, we tested a schedule in those early days which can be considered conventional. It was of interest to see what the outcome of that therapy was (Tables 4 and 5). We used a conventional photon irradiation schedule, and Cf-252 was used exactly as a radium-equivalent substitute (lower half of Figure 1). The group of patients selected for therapy had advanced stages of cervix and pelvic cancer (i.e., stages III and IV). If low stage cervix tumors responded poorly to standard radiation schedules, they were transferred to the Cf-252 neutron therapy arm. A comparison group of patients treated with conventional photon therapy during this time period was also analyzed (49). In Tables 4 and 5 I present the five year survival results of Cf-252 or Cs-137 brachytherapy and whole pelvis and side wall photon beam radiation. Overall, 100% of stage I tumors, 50% of stage II tumors, 29% of stage III tumors and 0% of stage IV tumors were absolute 5 year NED (no evidence of disease) survivors when treated with Cf-252. Also, 57% of stage III uterine adenocarcinomas and 50% of stage III vagina cancers were 5 year cures. Thus, 10 of 27, or 37%, survived among the primary tumors we treated. One patient, or 3.7% developed a possible neutron related delayed effect (49); hence, unusual tissue complications were not observed (5% is considered average).

Complications. As noted above, an unusual frequency of delayed complications has not been observed (49,50,51). We do have patients with high radiosensitivities (47) and, in particular, they are small and susceptible to enteric problems (48). In the first group of patients we treated 6 years ago (49), complications have not exceeded 5% (51).

Table 3

SOME PRIMARY AND RECURRENT TUMORS TREATED WITH Cf-252

Cervix	202	(66%)
Vagina	10	
Uterus	29	
Tonsil--Oropharynx	8	
Brain (Hemispheric)	20	
Sinuses (Maxillary Antrum)	4	
Alveolar Ridge	2	
Nasal Cavity	1	
Tongue	5	
Urethra	6	
Hard Palate	1	
Floor of Mouth	2	
Malignant Melanoma	1	(1 other vagina)
Laryngopharynx	2	
Lymph Node Metastasis in Neck	2	
Pyriform Sinus	2	
Rectum	6	
Breast	1	
Laryngeal Stoma	1	
Vulva	2	
	307	

TABLE 4

Five-YEAR SURVIVAL OF STAGE I AND SQUAMOUS CELL CARCINOMA OF CERVIX TREATED WITH CONVENTIONAL VS. Cf-252 NEUTRON THERAPY

	NEUTRON BRACHYTHERAPY			PHOTON BRACHYTHERAPY				
	No.	Alive		No.	Alive		Survivors / Total	%
Stage I	1[+]	1		13	11		12/14	86
Stage IIA	4[*]	2		7	7		9/11	82
Stage IIB	1[o]	0		20	11		11/21	52
	6	3	(50%)	40	29	(73%)	32/46	(70%)

[+] Barrel

[*] Slow Regressors

[o] Bulky 12 cm Diameter Tumor

TABLE 5
FIVE-YEAR SURVIVAL OF STAGE III AND IV SQUAMOUS CELL CARCINOMA OF CERVIX TREATED WITH CONVENTIONAL VS. CF-252 NEUTRON THERAPY

	NEUTRON BRACHYTHERAPY			PHOTON BRACHYTHERAPY			SURVIVAL TOTAL	%
	No.	Alive		No.	Alive			
STAGE IIIA	2	2	29%	2	0	25%	2/4	50
STAGE IIIB	12	2		2	1		3/14	21
STAGE IVA	2	0		1	0		0/3	0
	16	4 (25%)		5	1 (20%)		5/21	(24%)

REPRESENTATIVE CASE REPORTS

Stage IB Barrel Shaped Cancer S. O., a 48 year old white female, gravida (G), para (P), G12, P12, developed an abnormal PAP test and was found to have an 8 cm barrel shaped large cell non-keratinizing carcinoma (LCNK) of the cervix with endometrial extension. The patient was treated with whole pelvis radiation to 4000 rads in 4.5 weeks without evidence of tumor response. Because of this slow responder tumor, a Cf-252 implant was carried out and 4 weeks later, a total abdominal hysterectomy and bilateral salpingo-oophorectomy (TAHBSO) was carried out. The specimen and examination at surgery were negative for tumor. The patient is alive and well 5 years later without disease (NED).

Stage IIA Poor Responder Cancer L. R., a 41 year old G5 P5 white female, developed an abnormal PAP test and was found to have a 6-7 cm stage IIA mixed LCNK and large cell keratinizing carcinoma (LCKC) of the cervix. She was treated with 4000 rads, but this required 6 weeks because of her small habitus (88 lbs.) and poor tolerance to radiation. She had a Cs-137 implant after pelvic radiation, but that produced such severe symptoms and diarrhea that she did not return for 4 months. Because of abnormal findings and persistent irregularity in the tumor site, and the extremely protracted treatment schedule, the patient received a Cf-252 implant for 7.5 hours. The patient is NED and well 5.5 years later.

Stage IIIA Cervix Cancer J. C. is a 75 year old G11 P9 white female who developed an abnormal PAP test and was diagnosed to have a stage IIIA carcinoma of the cervix. She was a diabetic and was on 20 units of insulin per day. She had severe cardiovascular disease and had had a right leg amputation. The LCNK tumor replaced the cervix and the vagina and measured 6 cm in length by 6 cm wide with the entire anterior and posterior vaginal wall infiltrated to the introitus. The patient received 5000 rads in 6.5 weeks of whole pelvis radiation. She had a Cf-252 and a Cs-137 implant after the pelvic radiation followed by transvaginal cone therapy with 80 kilovolt (Kvp) x-rays to 2000 rad surface dose. The patient has been continuously NED for 5 years since.

Stage IIIB Cervix Cancer The patient is a 33 year old white female G0 P0 who developed profuse vaginal bleeding and was diagnosed to have a poorly differentiated LCNK of the cervix. The tumor measured 4 X 4 cm at the cervix, extended to the left pelvis sidewall, and extended halfway through the right parametrium on the right side (total diameter 13 cm). The patient received a Cf-252 implant early, i.e., 4 days after the start of pelvic radiation. Whole pelvic radiation dose was 5040 rads in 6 weeks. Two months later she had a second Cf-252 insertion. One month after the implant the cervix was completely clear. At the end of therapy there was only some thickening and fibrosis discernible in the left parametrium but the tumor had cleared completely. The patient is NED 4.8 years later.

Stage III Adenocarcinoma of the Uterus. R. W., a 43 year old white female, developed profuse and heavy vaginal bleeding requiring many blood transfusions. She had had irregular menses for 4 years. The patient had a large fungating vaginal mass and a huge mass that filled the whole pelvis (15 cm in diameter) and had a massively enlarged uterus. Biopsies showed a moderately differentiated adenocarcinoma. The patient received whole pelvis radiation to 4000 rads in 5 weeks and a single intrauterine-vaginal Cf-252 implant. Tumor response was dramatic. Because of this the patient had a TAHBSO done. Some residual tumor was found in the uterus so the patient had post surgical pelvic sidewall and vaginal vault irradiation. The patient is 6 years since therapy without problems.

CHARACTERISTICS IN CERVIX TUMOR RESPONSE

Since the earliest trial, we have found many characteristics of tumor response to NT which are different from conventional radiation response. I became interested in different schedules of NT brachytherapy, especially before external radiation (early schedule) or afterwards (delayed schedule). By early versus delayed NT we have made observations on NT brachytherapy response of cervix carcinomas. These include the following.

Rapid Clearance (34) High stage cancers cleared more rapidly by early versus delayed NT application (51). Our observations were remarkable in that they were made entirely clinically and after only one year of testing the delayed implant schedule. Since the clearance results with delayed implants were not very impressive or different from conventional photon radiation, we went to an early (before external beam treatment) schedule. The rapid clearance observations followed shortly thereafter (34).

Latent Period for Tumor Clearance of Stage IB Cervix Cancers. We developed a model to analyze the clearance pattern of stage IB cervix cancers [Maruyama and Muir (44)]. A logistic tumor regression model was used to analyze the serial data obtained on tumor clearance pattern made at weekly to biweekly intervals. It was found that the clearance pattern for photon radiation therapy (PT) had three components, i.e., a latent period, a rapid clearance component and a delayed clearance component. The latent period was 12 days for conventional PT. For NT radiation, the latent period was 0.0 days. Since NT is not affected by tumor hypoxia, apparently the tumor clearance pattern was greatly altered.

Tumor Clearance Time. The half tumor clearance period (TCP) for the NT vs. PT, i.e., Cf-252 vs. Cs-137, for stage IB tumors was compared (47). The half clearance period (TCP_{50}) for stage IB tumors (44) treated by NT was 8.0 days; for those treated by PT it was 32 days ($P < 10^{-6}$). This proved that NT was much more effective in clearing bulky, probably hypoxic tumors than conventional therapy. For this stage tumor, PT is considered effective therapy. Nonetheless, for slow responder tumors the findings are significant and suggest alternate therapy for tumors that respond poorly using PT (slow responders) (Figure 2).

Histological Clearance of Stage IB and II Cervix Tumors. For low stage tumors of bulky size our standard therapy procedure has been to give radiotherapy first and to follow that with extrafascial hysterectomy (52, 70). By this protocol, and by using careful histological study of the resected specimen, we can assess the efficacy of timing the procedure by the histological clearance of tumors. Our study using NT showed that by scheduling the NT implant early, it was much more effective in clearing stage IB-II tumors (75% of specimens were negative for tumor) compared to the delayed schedule [37% were negative for tumor (52)]. The results were significant ($P < 0.05$), again proving that NT scheduling was very important to tumor clearance.

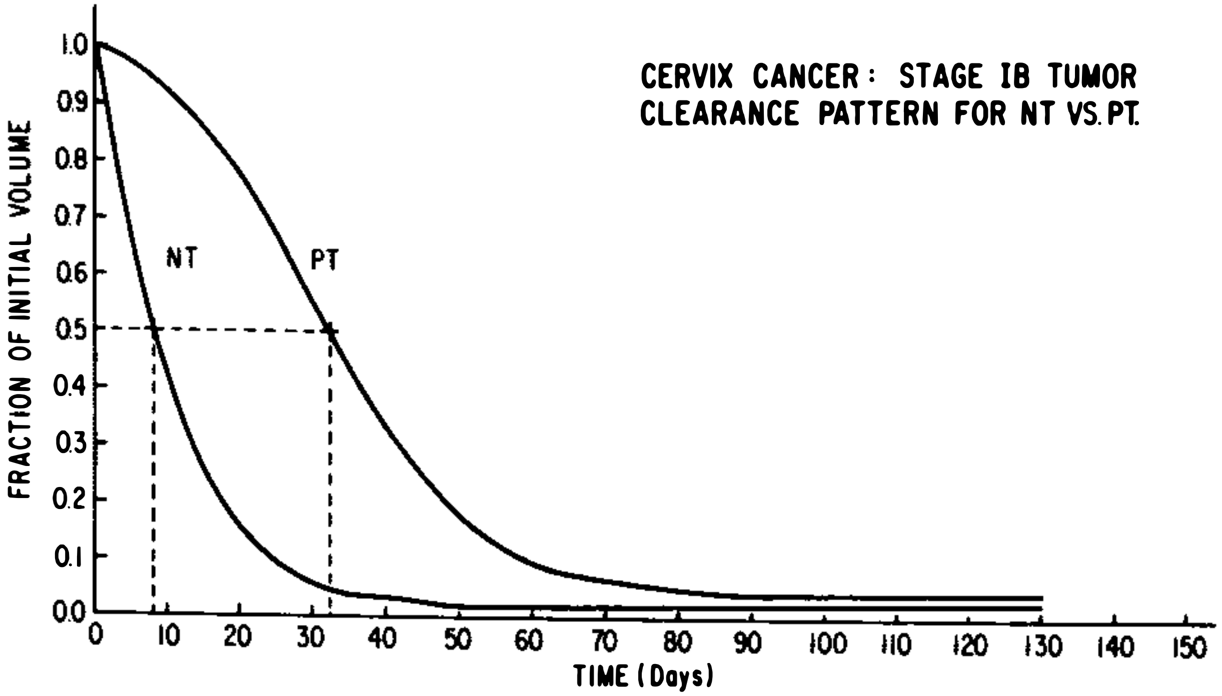


Figure 2

Tumor clearance pattern for stage IB cervix cancers treated with early Cf-252 NT and whole pelvis radiation vs. whole pelvis radiation followed by Cs-137 implant therapy (conventional). Tumor clearance pattern and period (TCP_{50}) were significantly different, the latter was highly significant with $P < 10^{-6}$ (44).

TUMOR CLEARANCE AND SURVIVAL

Figure 2 shows our results for stage IB and small stage II cervix cancers treated with radiation and surgery. Eighty percent actuarial 5-year survivals were observed and represents an outstanding experience, as good as any reported with conventional photon radiotherapy (47). Table 6 shows the clearance rate of cervical cancers treated with NT during the period 1976-1980 and followed for 2 year recurrence-free survival. For comparison, the photon tumor clearance data of Hardt et al. (20), reviewing our UKMC experience, are shown. For stage IIB cancers, preliminary data show that delayed NT cleared 0%, PT 57%, and early NT 81% of treated tumors. For stage IIIA cancer, delayed NT cleared 67% and PT 50%, but no early NT cases were studied. For stage IIIB cancer, delayed NT cleared 24%, PT 37%, and early NT 87%. For stage IV, delayed NT cleared 0%, PT 16%, and early NT 100%. However, 2 year recurrence-free survivals were less than the tumor clearance rates. For stage IIB, NT given early cleared 95% of tumors but only 81% were 2 year survivors. For stage IIIB cancers, early NT cleared 87% of the tumors but only 42% were 2 year recurrence-free survivors. For stage IV cancers, early NT cleared 100% of the tumors but 0% survived 2 years without recurrence. Comparative data for conventional Cs-137 therapy show that there was 57% complete regression (CR) or partial regression (PR) clearance of stage IIB cancers and 65% were recurrence-free for 2 years or longer. In stage IIIB cancers, 37% were CR and PR responders and 33% survived two years disease-free. For stage IV cancers, only 16% were CR and PR responders and 17% survived two years recurrence-free.

For delayed Cf-252 NT implants, for stage II disease, 0% were CR responders and 0% survived 2 years. For stage IIIB cancers 29% were CR responders and 24% were 2 year survivors. For stage IV disease, 0% cleared their tumors and 0% were 2 year survivors. The results indicate that clearance frequency was greatly increased with early NT compared to delayed NT or conventional PT. Delayed NT and conventional PT therapy results were very similar. Early NT cleared stage IIB tumors much more effectively (95%) and controlled tumors for 2 years (81%) compared to only 57% for conventional radiation therapy. The early NT results were for the bulkier and larger stage IIB cancers, whereas our recent experience (Tables 4 and 5) selectively used conventional PT for the smaller and more favorable tumors.

For stage IIIB cancer, 87% were cleared but 13% persisted. Almost half recurred locally, or distantly, or both so that only 42% remained recurrence-free at 2 years. Compared to PT only, 37% were CR and PR responders and 31% were recurrence-free for 2+ years. For stage IV cancer, results were poor even with local clearance of tumor for NT and likewise for PT. While local failure has been the dominant pattern for conventional PT, extrapelvic, para-aortic, bone,* lung, liver, skin and nodal metastases are now much more frequently seen.

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* Kamath, Maruyama, DeLand and vanNagell, GYN Oncol. in press, 1982.

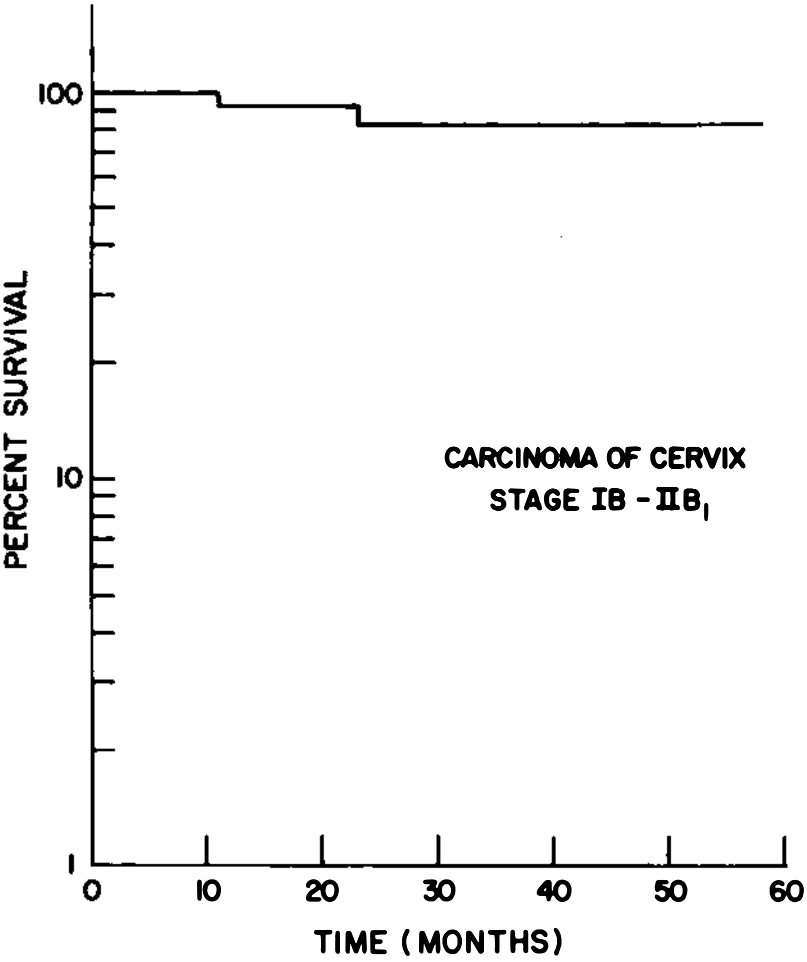

Figure 3. Survival curve by Cutler method for bulky stage IB and small stage IIA, IIB cervix tumor treated by NT and fractionated radiation followed by extrafascial hysterectomy. By combined therapy central failure was eliminated. Eighty percent actuarial 5-year survivals were observed (52).

TABLE 6
NT OF ADVANCED CERVIX CANCER[***]
PRELIMINARY DATA ON SCHEDULING OF NT, TUMOR CLEARANCE AND 2-yr SURVIVAL FOR Cf-252 BRACHYTHERAPY
(UNIVERSITY OF KENTUCKY 1976-1980)

	Early Implant		Delayed Implant		Photon Radiation Response[+]		
STAGE	CR[+] RESPONSE	2 yr RECURRENCE	CR[+] RESPONSE	2 yr RECURRENCE	CR[+] RESPONSE	CR+PR[o]	RECURRENCE[**]
IIB	20/21 (95%)	4/21 (19%)	0/2 (0%)	2/2 (100%)	24/75 (32%)	43/75 (57%)	26/75 (35%)
IIIA	—	-	2/3	1/3 (33%)	1/6 (17%)	3/6 (50%)	5/6 (83%)
IIIB	27/31 (87%)	18/31 (58%)	5/17 (29%)	12/17 (71%)	5/48 (10%)	18/48 (37%)	34/48 (69%)
IV	2/2 (100%)	2/2 (100%)	0/1 (0%)	1/1 (100%)	1/12 (8%)	2/12 (16%)	10/12 (83%)

[***] Only squamous cell and small cell carcinoma (no adenocarcinomas)

[+]CR Complete regression and clearance of tumor

PR Partial regression and clearance of tumor

[*] From Hardt et al. (1982)

[**] Minimum period 2 years

[o] Includes both CR and PR responders

(see 56)

OTHER TUMORS SUCCESSFULLY TREATED BY Cf-252

Brain Tumors

We studied 20 patients with hemispheric malignant gliomas using Cf-252 neutron brachytherapy combined with 5000-6000 cGy of planned whole brain radiation in collaboration with our neuro-surgeons (41, 42). We found that 90% had improvement in performance status and also decrease in enhancing computed tomography (CT) tumor dimensions. Therapy was carried out by localizing the tumor with CT scans. A burr hole was placed in the skull over the tumor. A specially constructed "ice-pick" applicator was placed into the tumor site and the Cf-252 afterloaded into the applicator. We usually followed the implant with whole brain radiotherapy using a variety of therapy schedules. The improvement in performance status was rapid and most impressive to us who have been treating malignant gliomas with photon radiation only (Table 7) or chemoradiotherapy for many years [H. W. Chin *et al*. (9)].

T4 Tonsillar Cancers

We recently reported studies of Cf-252 therapy of large T4 tumors of the tonsillar fossa (38). Seven of these were primary (Table 8) and one was recurrent after radiotherapy. Eight of eight tumors treated (100%) had a complete regression response. They were treated by placing tubes in the tonsillar fossa against the tumors. Seven of seven primary tumors (100%) cleared up completely when combined with high doses (4500-6000 rads) of fractionated Co-60 radiotherapy (Table 8). This was encouraging since 65-90% of these tumors usually fail to be controlled by standard radiation or radiation and surgery (see 38). Two out of six are 15-24 month survivors NED and two others of these elderly patients died of other causes NED (67%). This reflects a good response for a group of patients of advanced age, severe medical illnesses and poor tolerance to therapy.

Case Report: T4 Tonsillar Cancer. O. R., a 58 year old white male, developed a sore throat and was found to have a 4 x 6 cm mass of the right tonsillar fossa. The tumor involved the soft palate, tonsil, retromolar triangle, lingual-alveolar sulcus and lateral tongue (T4). He had a high right cervical lymph node metastasis (N1). The patient had a Cf-252 implant followed by 6000 rad of Co-60 radiation therapy in 6 weeks. The tumor cleared completely. The patient had a mucosal ulceration 1 cm in diameter appear shortly after radiotherapy, but that cleared with conservative treatments. He is NED 2+ years after treatment.

We have found that female urethral cancers also respond well.

Case Report: Urethral Cancer. I. R., an 89 year old female developed a urethral squamous cell carcinoma for which she consulted her urologist. It involved the urethra, vagina, and labia minora. The bulk of the superficial tumor was partially resected but the

TABLE 7
NT RESPONSE OF GLIOBLASTOMA AND MALIGNANT GLIOMA
CLINICAL RESPONSE TO A COMBINATION OF SURGERY, NEUTRON THERAPY, AND RADIATION THERAPY

		KPS*		Tumor Size@						
Patient	Age/ Sex	Prior to therapy(s)	After therapy(s)	Pre-craniotomy	Prior tc therapy	After therapy	Clinical Response+	Radiation cGY	Dose F‾	Schedule days
1	63/M	30	75	5.5x7	5.3x5.3	—	+2	6,240	34	61
2	52/M	30	70	6x4	3x4	1x1	+3	6,000	49	40
3	61/M	30	65	3x4	3x4	2x2.3	+2	6,000	32	46
4	70/M	20	10	5x6	4x5	—	-2	2,200	22	16
5	52/M	30	80	7x7	6.5x5	5x3	+3	6,000	60	42
6	68/M	30	60	3.9x3.1	3.3x4.2	2.3x3	+3	6,000	59	34
7	52/M	40	90	6.3x4.6	3.3x2.5	—	+3	5,000	45	34
8	56/M	30	75	10x6.3	8.5x63	3.3x3.3	+3	6,000	33	55
9	64/F	30	60	5.5x5	4.6x3.8	2.5x3.3	+3	6,000	60	45
10	65/F	30	65	—	6.5x5.6	5x4	+3	6,000	60	48

* Karnofsky performance status.

@ By CT scan in two dimensions only, measured in cm.

\+ +3 = markedly better, +2 = definitely better, +1 = possibly better, 0 = unchanged, -1 = possibly worse, -2 = definitely worse, and -3 = markedly worse.

‾F Number of fractions

From (41)

TABLE 8

NT OF ADVANCED CARCINOMA OF THE TONSIL (T4)
PATIENT AGE, SEX, PERFORMANCE STATUS AND MEDICAL CONDITIONS

Sex	Age	KPS[o]	Tumor Stage	Tumor Size (cm) (pattern)[#]	Primary Tumor (Sites of Tumor involvement)	Neutron Therapy		Photon Therapy		Response	Outcome
						D_n (cGy)[##]	Implants No.	(Ret) cGy/fraction no/days	Total Dose (req)		
F	83	70	$T_4N_0M_0$	4x4 cm. (ulc)	RMT (4)	293[##]	x1	$\frac{4900}{14F\ 56d}$(1600)	6658	CR	Deceased . NED 14 months
F	87	60	$T_4N_0M_0$	6x6 cm. (exo)	Tonsil (5)	278[##]	x2	$\frac{5000}{25F\ 45d}$(1519)	6668	CR	Deceased 9 mont NED
F	72	90	$T_4N_1M_0$	5x5 cm. (ulc)	Tonsil (5)	181[##]	x1	$\frac{6000}{30F\ 46d}$(1741)	7086	CR	Recurred 10 mon. surgery. Deceased of surgical complication.
M	58	90	$T_4N_1M_0$	4x6 cm. (exo)	Tonsil (5)	240[##]	x1	$\frac{6000}{30F\ 46d}$(1733)	7440	CR	MMB[a], healed NED 25 months
M	74	90	$T_4N_0M_0$	5x6 cm. (exo ulc)	Tonsil (6)	248[##]	x1	$\frac{6000}{30F\ 48d}$(1729)	7488	CR	MMB[a], healed NED 17 months
M	59	50	$T_4N_1M_0$	6x8[+] cm. (exo ulc)	Tonsil (9)	414[##]	x2	$\frac{6000}{30F\ 46d}$(1741)	8484	CR	MMB[a], healed, Recurred in base of skull at 9 months
M	84	50	$T_4N_0M_0$	6x6 cm. (exo)	Tonsil (6)	138[##]	x1	$\frac{4500}{9F\ 37d}$(1723)	5328	CR	Tonsillary fossa cleared, recurred and deceased @ 13 mon.

[*] Number of anatomic sites include the following: tonsil, RMT (retromolar triangle, soft palate, pharynx, tongue, alveolar ridge, anterior faucial pillar, lingual tonsillar sulcus, temporo mandibular joint

[+] Massive, ulcerative and invasive, and destroyed the medial mandible.

[o] Karnofsky performance status

[#] exo = exophytic; ulc = ulcerative

[a] MMB = mucous membrane breakdown

[##] req = rad equivalent where neutron RBE = 6.0

(see 38)

margins were all positive. She was referred for post-operative radiotherapy. An early Cf-252 neutron implant was done, followed by 5000 rad of pelvic irradiation to this cut-across tumor. The patient had CR response of the tumor and is 2 years NED since treatment. She has full bladder control, but is minimally incontinent with sneezing.

CONCEPTS IMPORTANT IN USE

Many properties of neutron radiations are different from photon radiation. Some of those which are important have been identified.

Relative Biological Effectiveness (RBE). The identification of an accurate value for RBE has been studied *in extenso* and predicted and found to be high for Cf-252 (19, 25, 43). Our studies have found that RBE value depends upon tissue and end point being studied. RBE value is higher under hypoxic (14) than oxic conditions; hence, a larger gain factor and advantage exists for the therapy of oxygen deprived hypoxic tumors (43), e.g., human cervix cancers (65). There is no single simple value for RBE for use in clinical therapy. The most important organ for determining a reference value is probably the most sensitive normal tissue in the irradiation field. For the pelvis, we use the small bowel where the RBE is 5.2 (11, 73), but the tumor value is probably very close to 6.0 (14, 65). The RBE for hematopoietic RBE was found to be 2 in our studies (to be published) elsewhere (17).

Oxygen Enhancement Ratio (OER). Very important to the use of Cf-252 for pelvic tumor brachytherapy is its efficacy against hypoxic tumor (43). The OER for neutrons is small, probably about 1.4-1.5 (26). Since the OER for acute photon radiation is approximately 3.0 (61), an oxygen gain factor of two-fold may exist relative to acute radiation and 1.4 for LDR radiation where OER is 2.0 (3). Compared to LDR photon radiation, significant gain factors may exist (39).

Dose Rate Independence. An important consideration from neutron radiobiology is that the shape of the dose response curve is exponential and no SLD repair is possible (39). Radiation can be given at rapid or very low dose rates (e.g., 40 rad equivalent dose per hour). Since dose rate makes no difference (13, 14), the prescribed dose can be given rapidly for greater convenience and safety (e.g., 200 rad per hour) at reference tumor sites.

Reoxygenation (27). A tumor becomes hypoxic with progressive tumor growth (61). By crowding and by competition for nutrients, O_2, and blood supply, a tumor becomes more and more severely hypoxic. The process is reversed by destroying tumors with, e.g., radiation. This reduction in the tumor cell population allows previously hypoxic cells to become reoxygenated (39). Rapid tumor debulking and shrinkage may allow tumor to become reoxygenated more effectively. However, there may be real differences in our ability to deal with acute versus chronic hypoxia (see 36). Other factors may also contribute to radioresistance in ulcerated, deeply infiltrated and infected tumors with extensive tissue destruction.

Neutron Brachytherapy: Principal Postulates. Our clinical experience and observations suggest that the rules governing clinical application of neutrons are greatly different when compared to photon emitting isotopes. These are summarized in Table 2, where delayed photon emitting isotopes is considered conventional. Early scheduled NT brachytherapy, i.e., before external beam radiation, appears to be important if the intent of therapy is to attack and destroy hypoxic tumor (34). This more effective destruction of tumor bulk (and hypoxic tumor) leads to rapid reduction of the quantity of tumor and of tumor size. This may allow more effective reoxygenation to occur. By adding low LET radiation as tumor is reoxygenating, greater effectiveness was observed (51). This means that greater likelihoood of achieving tumor destruction and regional tumor clearance of tumor is possible with the added low LET (2) radiation in high dose. Some of these parameters represent important differences between photon and neutron brachytherapy and need to be appreciated and applied in order to obtain good tumor clearance. Microdosimetry of Cf-252 events has been proposed by us to be important (2) to our observed clinical results.

Need for Photon Radiation in Neutron Brachytherapy. Neutron radiation produces a small number of highly ionizing events in the cell target and produces lethality very efficiently, even with a single event. Some of the cellular lesions may be potentially lethal or of the PLD type (39). Probably it would be useful to call these single-event neutron PLD lesions. Such a postulated lesion could perhaps be made lethal by the addition of further dose using photon radiation (2). Photon radiation produces a large number of lesions of the single strand break type in DNA, and more of the SLD or photon PLD type in the cell.

PROTECTION AND Cf-252

One of the principal problems in the use of any radioactive material for implant therapy is the radiation exposures of humans occupationally or inadvertently exposed to the emitted radiations. We know a great deal about the safety, containment, permissible doses, acute and late effects, carcinogenesis, leukemogenesis and epidemiological consequences of acute or chronic exposure to sparsely ionizing radiations such as X- and γ-rays. No such literature or knowledge is available for the person occupationally, accidentally, or otherwise exposed to neutron radiation. Recently, Kelleher and Rossi (30) and Rossi and Kelleher (56) considered the hazards and biological effects of neutrons based upon a consideration of the basic biological lesions and factors involved, such as low dose and low dose rate (57). The data suggest that late effects RBE is high (58, 68, 72). Current radiation protection guidelines affix a higher biological effectiveness for neutrons by adding a quality factor of 10 for neutron dose. Thus, one of the principal concerns in the clinical use of neutron emitters for brachytherapy is to ensure adequate personnel protection and environmental safety. Since the biological effectiveness of neutrons relative to gamma rays may reach values as high as 50X or even 100X at low doses and low dose rates (57), clinical studies have been few throughout the world. Among those who carried out the first trials, the work was soon abandoned after a few years because of the concern for personnel safety and the hazards in use. It was also felt that Cf-252 had no advantages over Ra-226 or its substitutes. We were not inattentive to this concern as we began our research.

In planning our project I felt it important to not regard Cf-252 as just a radium substitute. This was one of the major problems of the earlier workers and much thought was given to equivalent doses and time-dose schedules chosen to match radium experience (19). For example, sublethal damage (SLD) recovery is a major concern in photon use in radiotherapy, and it is well known that there are marked differences in biological effects at different low dose rates [lower the dose rate, the more reduced the effects (3)]. For neutron radiation, no SLD repair should occur because of one-hit cell inactivation by the neutrons. Therefore, regardless of dose rate, no differences in cellular dose response were anticipated (13, 14). To capitalize on this effect, we obtained heavily loaded sources and used the absence of a dose rate effect to our advantage. That is, since it did not make any difference in effect whether a 1 week application or a 1 hour application were performed, I used the shorter period and settled on a very practical period of ~8 hours. This made the duration of the implant a very convenient time period, and all treatments could be given and completed in a single work shift. To accomplish this, we obtained the most heavily loaded sources then available and used 50-200 micrograms per application. Afterloading applicators were routinely used, and we used commercially available devices but also designed and built a large number for different problems. During this time period we planned to deliver a therapeutic dose of about 150-200 neutron rads delivered at point A and a larger dose to a reference tumor point (point T) in the para-cervical region of the uterus (46, 47). Allowing for RBE it was estimated that this was a dose equivalent to about 1000 reqs (cGy equivalents, i.e., cGy_n X RBE_n + cGy_γ X 1.0). As experience evolved we learned to work very rapidly with this material, to use lucite or steel tanks filled with water as personnel shields, lucite source transporting carts, and also the patient's body as a shield for the neutrons. A large room was used in our work from the start, and a similar room was designed by Onai et al. (53). When the sources are placed in the patient's body (mostly water), neutrons are absorbed and the radiation flux around the patient becomes largely photon radiations.

Table 9 presents the cadre of personnel that we developed to deliver neutron brachytherapy to the patient. Each of these persons has a different and important role in the application of neutron brachytherapy. The physician needs to be a radiotherapist who is principally concerned with patient problems and treatment. Since my principal interests at Kentucky have been gynecological tumors, it was natural that Gyn tumors were treated with highest priority in our early studies in conjunction with my Gyn colleagues (Drs. J. R. van Nagell, Chief of Gyn Oncology, E. S. Donaldson and M. Hanson). The radiation safety officer, Mr. L. C. Wilson, is an important member of our team and wrote and implemented the procedural protocols for persons working in the neutron program. An implant procedure nurse (Mrs. Ann Martin) supervised the implant suite and its procedures, and attended to the patients' needs for medication, meals, and procedures while in the neutron therapy suite. The radiological technologists (Mrs. Jackie Sims and Janet Sanford) were involved in loading and unloading the patients and providing back-up. The neutron curator (and radiobiologist) became an important member of our team (Dr. Jose Feola) and recorded and signed out all Cf-252 sources, analyzed the configuration and loadings of the Cf-252 prescribed, transported the arrangement to the nurse-radiographers to place in the patient and returned them to the safe. He also recorded data in our files on each patient treated, and film recorded the Cf-252 sources used. Our neutron therapy physicist (Dr. J. Lawrence Beach) calibrated our sources, directly measured neutron dosimetry and microdosimetry, established and monitored the dosimetry system and wrote our treatment planning and isodose plotting programs. The problems of neutron dosimetry and measurement are very complex and very much ongoing for inhomogeneous media and tissues (4). A summary of personal characteristics of this group would show that they were mostly older persons. Many persons were involved and were permitted limited participation to handle certain steps in the procedures, but only for very limited and highly restricted time intervals.

Time was strictly limited to approximately 1.5 minutes per person per day in the neutron therapy room. We started out with more liberal time allowances (e.g., 3 minutes) but after noting that the staff could work at reduced times, reduced the allowed time. All room times were strictly recorded and personnel were badged with neutron sensitive badges. For each person we have data right back to the very first time we used Cf-252.

TABLE 9

SPECIAL PERSONNEL REQUIREMENTS FOR Cf-252 NEUTRON BRACHYTHERAPY

1. Physician Radiotherapist - Requires special training and experience in neutron therapy.
2. Physicist - Knowledge of neutron physics, measurement and calibration.
3. Radiation Safety Officer - Authority to control personnel exposure time.
4. Nurse(s) - Implant suite experience. Patient care in neutron therapy holding suite.
5. Neutron Curator - Monitors sources, source selection, source strength in each application. Keeps records.
6. Radiotherapy Technologist(s) - Knowledge of special handling requirements of neutron emitting sources.
7. Radiobiologist - Neutron and high LET, RBE, safety knowledge.
8. Engineer - Building and maintenance of special equipment, devising and constructing special equipment requirements.
9. (And) Other Surgeons, Gynecologists, and Physicians - Collaborator on joint study using protocols and orderly approach to therapy.

The Neutron Therapy Room for UKMC has always been one of our unused megavoltage therapy rooms. These are large rooms with heavily shielded walls and mazes designed for photon therapy use. The rooms are provided with a hospital bed, TV monitor cameras and TV sets, personnel shields and area survey meters (Table 10). The room is large so that neutron scatter off the walls is minimized.

While there were few interstitial or intracavitary implants that we did not try at least once, we have thus far continued only those that were effective and led to good results. To pursue the more difficult implants will require better and smaller sources of high activity. It will require automatic afterloading machines and probably some robotic support. A single afterloading machine will not be suitable for all implant procedures, e.g., Gyn implants require one type of machine while oral, brain, interstitial, body cavity, and lung implants will require others. A department engineer has worked with me extensively on designing and building applicators. At the same time we have not had the support to build all the adequate and properly designed machines we would have liked for this project.

Since one of the principal problems in the use of Cf-252 is the protection of the medical, nursing and technical staff, radiation safety must be provided by any user who contemplates a human clinical trial. We have welcomed external reviewers to evaluate and view our safety procedures repeatedly to ensure compliance with safety in neutron use. It is apparent that Cf-252 use is expensive in terms of space, personnel, and monitoring equipment. Personnel must also be badged with standard and neutron sensitive detectors. Currently, track etch films appear to be most suitable for routine use. Since these personnel detectors are not very sensitive to neutron radiations, it is essential that, in addition, timing, barrier, and remote handling devices be available. The difficulties are real and significant but certainly not insurmountable. While the safe usage of Cf-252 has been accomplished, it is very important that the safety officer be granted the authority to control access to the room and time limits on all who handle Cf-252. Those individuals are sometimes not appreciated but are very important to this type of work.

TABLE 10

CHARACTERISTICS OF Cf-252 NEUTRON THERAPY ROOM

1. Large 20' x 20' room.
2. High ceilings - intermediate absorper
3. Thick walls (3')
4. Personnel shields
   a. Bedside
   b. Source
5. Patient facilities
   a. Bed with TV monitors
   b. TV set/radio
   c. Bathroom/toilet
   d. Meal service
   e. Voice communicator
6. Cf-252 storage photon therapy
7. Cf-252 source selection and delivery system
8. Transport cart
9. Afterloading machine(s)
10. Handling tongs
11. Room monitor(s) for neutron
12. Door interlocks

PROBLEMS FOR FUTURE STUDIES OF CANCER USING Cf-252

The rules for the use of neutron brachytherapy for human cancer treatment are still evolving. They clearly are not like Ra-226 rules, and this means the average radiotherapist does not know how to work with neutrons since he knows only photon effects. We have studied a sufficient number of cases that a few general rules have become apparent. It is clear that Cf-252 allows new and more effective therapy against bulky localized hypoxic and radioresistant tumors. While such antihypoxic tumor therapy in our hands has had dramatic effects and produced remarkable tumor clearance rates and frequencies for advanced gyn tumors that we had not seen before, it has also become clear that there are other bases of tumor radioresistance that do not appear to be based solely upon hypoxia. A number of these relate to the tumor itself, but in general we have noted that the tumor bed and the extent of infiltration and ulceration of tumor, and infection is also very important, as are the characteristics of the vascular supply. Several factors appear to be of importance, as follows:

Hypoxia Which Does Not Reoxygenate. In some patients with severe arteriosclerosis, hypertension and small vessel disease, very poor tumor responses were observed because tumors were perhaps incapable of revascularizing and reoxygenating. In a review by Bell, myself, *et al*. (40), we discussed some of these factors. In these tumors much more neutron radiation therapy is probably required, or perhaps neutron beam therapy combined with hypoxic radiosensitizers. We have scheduled more implants now (up to 5-6X) with some, but not with outstanding success for the far advanced stages of cervix cancer.

Rapid Tumor Growth. In some patients, tumors responded rapidly and grossly disappeared. Tumors then reappeared and very rapidly regrew [see Young (74)] . To get ahead by radiotherapy, this group of patients probably requires adjuvant therapy and a means to recognize the rapid growth and DNA-synthetic activity of tumor (33) by some non-invasive diagnostic test. In these patients adjuvant chemotherapy may be needed (probably antimetabolite in type) and a schedule to sequence and combine chemotherapy and radiotherapy once this pattern is recognized (37).

Infection and Deeply Ulcerating and Necrotic Tumors. These tumors are clearly severely hypoxic and very resistant to radiation, including neutrons. I have tried Metronidazole (MTZL) in large systemic, oral and intravaginal doses to treat both the hypoxia and the infection in conjunction with the Cf-252 neutron implants. I have also combined MTZL with broad spectrum antibiotics and Clindamycin in order to treat what I believed to be anaerobic infection. The results were satisfactory for low stage tumors, but were not as satisfactory as I would have liked to see for high stage tumors. Further study of combination therapy with antibiotics and hypoxic sensitizers is needed to determine whether the infections and the extreme radioresistance of these types of tumors can be overcome. Both hypoxic radiosensitizers and antibiotics need to be developed to address this difficult group of tumors, and to be tested for efficacy in controlling these infected tumors.

REQUIREMENTS AND PROSPECTS FOR NEUTRON BRACHYTHERAPY

Table 11 lists the requirements for a Cf-252 treatment program. Bulky, localized and accessible tumors, applicators for therapy and capability for afterloading all applications is needed. This could be machine afterloaded, but need not be. A special small operating room (implant suite) situated close to the neutron holding room is needed. One does not wish to wait for surgeons to finish and then follow them late in the day. One must have radiographic rooms and implant localization facilities run by experienced radiographers, physicists and treatment planning personnel, who must be immediately available. The cadre of personnel involved is extremely important and needs to be educated and experienced in Cf-252 use and safety. In our new cancer center we are building a neutron brachytherapy suite.

Table 10 listed the characteristics of our neutron therapy holding room. It is a large room with heavily shielded walls. The neutrons scatter readily, so personnel shields are needed to protect against the neutrons. Creature comfort facilities are needed for the approximately 8-hour implant procedure, as are storage and transportation facilities for the Cf-252 sources, handling trays, room monitors and foor interlocks. Our NT facility will be in the UK Lucille Parker Markey Cancer Center to be built next year in Lexington, Kentucky. It will represent the first facility planned for Cf-252 neutron therapy in this country. The plan of this large facility will allow us to apply either neutron or photon brachytherapy. There are beds in the new center for holding patients for photon implants or for several serial one-day implants. We can do two implants per day, and this reflects our view that our present approximate 100 NT implants per year will double to approximately 200 NT implants per year and that we can provide an important regional specialized cancer therapy center. The cost per treatment will be much less than conventional Ra-226, Co-60 or Cs-137 therapy since the therapy only takes a couple of hours, and the patient need not be hospitalized. Three to seven days of hospitalization are needed with standard gamma emitters. We also do not need general anesthesia or recovery room time (45).

At the present time one can only conjecture about the national needs. The NCI has not assigned the Cf-252 neutron brachytherapy program any priority for study, but it is clear that more exciting observations are being made in our clinical NT therapy program than in many of the well funded cancer projects. What is needed now are clinical research institutions who wish to conduct studies of Cf-252 neutron brachytherapy and who have quality clinical and research staffs and clinical material to begin to develop facilities of this type (35). Radiation biology, radiation physics and radiation safety staff are needed to provide support for a successful program to evolve.

In Kentucky we have had excellent cooperation from our Gyn oncologists (under Dr. J. R. van Nagell) and neurosurgeons (Dr. A. B. Young), who have been essential and responsible for our large patient experience and for special categories of tumors being made available for study. Without support from colleagues, no neutron brachytherapy program could have made much progress.

Radioprotection of Normal Structures. We have also considered radioprotectors combined with radiosensitizers in order to increase gain factors and normal tissue tolerance (22). In our Kentucky region, C. P. Sigdestad of the University of Louisville (personal communication) has been testing radioprotectors against neutrons and found that radioprotection is possible albeit the dose modifying factor (DMF) are small and better for low doses of neutrons.

Distant Metastases. While our therapy is directed at local tumor bulk, one failure pattern has become very evident, e.g., with small cell carcinomas (71). This is distant metastatic spread. Thus, while local tumor was being controlled, failure was occurring in, e.g., para-aortic lymph nodes, lung, bone and liver. To combat this, effective adjuvant chemotherapy is required, but is not yet available (47). When to use this type of therapy and how to combine it with a very potent and potentially highly toxic form of radiotherapy are questions for future research. Small cell carcinoma of the cervix (71) in Kentucky is an anaplastic, highly metastatic, rapidly growing tumor in need of effective adjuvant chemotherapy.

Hyperthermia. By virtue of the bulk of cervix cancers, hyperthermia, or heat therapy, in conjunction with neutron brachytherapy appears reasonable and obviously needs to be tested. Thus the rapid tumor shrinkage produced by Cf-252 may be further aided by heat therapy applied shortly after the NT treatment. So far, equipment to accomplish this for deeply situated tumors is not completely satisfactory for, e.g., deep pelvic heating. There is the danger that local-regional shrinkage of a tumor mass, if accomplished too rapidly, may create tissue defects leading to complications or the need for major surgical intervention to correct those complications. The combination of heat and NT treatments should be tested.

Our plans are to test intracavitary probe antennas for central pelvic hyperthermia therapy,with LDR NT,for recurrent cervix cancers. The other group where its use can be justified is the poor responder and persistent cancers of high stage tumors. That group has been seen even with LDR NT and exhibits a form of radioresistance not overcome by the LDR NT,even when combined with metronidazole.

TABLE 11

BASIC TOOLS FOR NEUTRON BRACHYTHERAPY

1. CONFINED HOLDING ROOM
2. VARIETY APPLICATORS
3. PHOTON THERAPY
4. OPTIMIZED TREATMENT PLANNING
5. OPTIMIZED LOADING SYSTEMS
6. AFTERLOADING
7. VERIFICATION BY PHANTOM/IN VIVO DOSIMETRY
8. RBE OF TUMOR/NORMAL TISSUE
9. MONITORS OF RESPONSE

Should there be further development of neutron brachytherapy centers? The enormous cost of medical cyclotron beam therapy can be overcome by the development of Cf-252 for medical neutron therapy (35). If 50-100 centers of clinical research excellence in the United States and the world cooperated and carried out the needed trials, I expect that in 5-10 years we could establish many of the properties and characteristics of neutron brachytherapy and expand the scope, varieties and effectiveness of cancer treatments available. There is a need for both protocol and feasibility studies and a lot of imaginative brachytherapy developments. Nuclear engineers would need to fabricate small sources of high activity in needles, narrow diameter sealed sources, beads and wires for afterloading into narrow diameter applicators. We need afterloading machines and robotic developments to avoid personnel exposures and reduce handling times to the lowest possible levels.

Each center would need new sources approximately every 1.5 years. We now have about 500 μg of Cf-252 in mostly 7.5-30 μg loadings and find that that is a good array of source strengths for our clinical treatment doses and times. We could use a linear flexible arrangement for intrauterine use. Our cervix and vaginal loadings were initially a tandem only (62) but are now highly individualized (46, 47) and optimized (11, 63) and reflect our general approach to treatment of this disease (40). If we begin to treat lung, esophagus, pancreas, bladder, prostate and bowel as well as head and neck sites (e.g., 38) and brain (41, 42) regularly, we would be treating many of the more common cancers of humans. For some of the latter sites we would have to utilize combined chemo-radiotherapy as the frequency of extensive tissue infiltration and distant metastases require that adjuvant systemic chemotherapy be administered (e.g., 71). Fifty patients accessioned per year per institution with 100 participating institutions could mean study of 50,000 patients with cancer in 10 years. Cervix, uterus, vagina, tonsil, floor of mouth, alveolar ridge, urethra, and some brain tumors may be much better controlled by neutron brachytherapy than by currently available modalities of treatment. If the cancers were advanced primary female pelvis cancers, about 20,000-30,000 (approximately 40-50%) would be alive NED 5+ years later as our earliest schedule showed (Tables 4 and 5). The economic value of saving human life from a disease such as cancer is not easily calculable, but is worth the investment.

New neutron emitting isotopes for future brachytherapy studies are needed. While Cf-252 is the best isotope found so far, possibly others of the transplutonium series can be tested, e.g., Cf-254. Tandem transplutonium isotopes should be studied for their potential for neutron therapy. Perhaps beryllium may be useful combined with an alpha emitter similar to the original experiments of Chadwick (8). With some of these tandem combinations, long-lived combinations, small configurations and sizes, and high dose rates may be possible. The other important need is for a greater variety of neutron energies. For example, an isotope with 4 Mev or 8 Mev neutrons could be (21) very useful, although it could lead to a higher frequency of late complications (68). Still another possibility is to have sources that produce low energy neutrons that can be thermalized in tissue. Under those conditions, chemicals to enhance the capture event and enhance energy release in tissue such as the boron capture compounds could be of great value in increasing the therapeutic effectiveness of the neutron at greater distances from the primary tumors and sources. If the applications of Cf-252 can be extended, its potential ultimate value for human cancer therapy alone would justify a continuing active investigational and production project as well as biomedical research into human use.

Table 12 lists some possible goals for the study of neutron brachytherapy with Cf-252. This represents the objectives in our continuing studies.

Recommendations

1. Establish a national/international neutron brachytherapy demonstration center which should be provided with a wide variety of neutron emitting sources, detectors, robotic or automated handling device and appropriate equipment. It should have the necessary personnel and staff to thoroughly investigate and to demonstrate the use and applications of Cf-252 neutron brachytherapy in human cancer therapy.

2. Establish 50-100 Cf-252 neutron brachytherapy projects throughout the world in academic clinical research centers which have adequate facilities, personnel, professional physics and radiobiology staff as well as numbers and varieties of cancer patients to carry out clinical research trials. Each center will require ~500 μg of Cf-252 as small sealed sources.

3. Prepare and provide a variety of sources of suitable size, activity and shape to carry out trials of human cancer treatment using Cf-252.

4. Establish a Cf-252 production program which will renew the sources of the neutron brachytherapy centers at a 1.5 year frequency.

5. Establish a Biomedical committee to advise the Department of Energy on clinical applications of Cf-252 and other transplutonium isotopes and on biological and clinical research studies.

6. Conduct research into other neutron emitting isotopes with suitable properties for human cancer therapy, specifically those with different half lives and neutron energies.

TABLE 12

GOALS IN NEUTRON BRACHYTHERAPY

1. OPTIMAL COMBINATIONS WITH EXTERNAL BEAM THERAPY
2. ACCURACY IN DOSIMETRY
3. REPRODUCIBILITY
4. DOSE DISTRIBUTIONS TO MATCH TUMOR BULK
5. PERSONNEL SAFETY IN USE
6. INSIGHT INTO TUMOR RESPONSE

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