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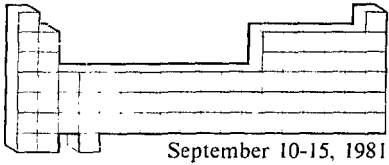
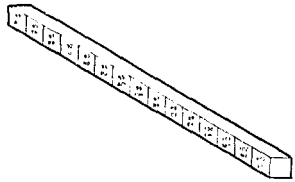
ACTINIDES-1981



September 10-15, 1981



ABSTRACTS

September 1981

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA

Prepared for the U.S. Department of Energy
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ACTINIDES-1981

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ABSTRACTS

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CA 94720

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PREFACE

"Actinides-1981" follows directly from the "5th International Conference on Plutonium and Other Actinides" and the "4th International Transplutonium Element Symposium" which were held in consecutive sessions in Baden-Baden in 1975. The merging of these two conferences represents an attempt to bridge the gap between scientists in specialized disciplines.

This conference also marks the fortieth anniversary of the discovery of plutonium and the fiftieth anniversary of the Lawrence Berkeley Laboratory.

One of the primary objectives of this conference is to assess progress in present programs and to identify directions for future research.

Inevitably in a conference covering a wide variety of topics and techniques applied to a particular chemical series, some subjects will be emphasized more than others according to the interests of the majority of participants. Approximately half of the contributed papers deals with electronic structure of the actinides, and will be covered in two poster sessions. Other topics will be presented in two further poster sessions. A diversity of subjects will be covered in the invited lectures, which have been scheduled so that several topics will be covered in each session. The invited lectures will be published by Pergamon Press as the Proceedings of the Actinides-1981 Conference.

I would like to thank the members of the International Advisory Committee and the American Organizing Committee, especially W. T. Carnall and D. J. Lam, for their valuable advice. Special thanks also go to LBL staff members: S. Ovuka for the day-to-day planning and organizing of this conference, L. Lizama for editing the brochures and abstract volume, and B. Komatsu for handling the extensive correspondence for the conference.

Norman Edelstein
Chairman

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INVITED LECTURES

THE PLUTONIUM STORY*

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This year marks the fortieth anniversary of the synthesis and identification (i.e., the discovery) of plutonium. I believe that this "Actinide-1981" conference is an appropriate place to recount some of the history and describe the present status of this element.

The story of plutonium is one of the most dramatic in the history of science. For many reasons this unusual element holds a unique position among the chemical elements. It is a synthetic element, the first realization of the alchemist's dream of large-scale transmutation. It was the first synthetic element to be seen by man. One of its isotopes has special nuclear properties which give it overwhelming importance in the affairs of man. It has unusual and very interesting chemical properties. It is rated as a dangerous poison. It was discovered and methods for its production were developed during the last war, under circumstances that make a fascinating and intriguing story.

In the fall of 1940 I asked a graduate student, A.C. Wahl, to consider the possibility of studying the tracer chemical properties of element 93 as a thesis problem, a suggestion which he was happy to accept. This, and related work on element 94, was carried on in collaboration with J.W. Kennedy, who, like myself, was at that time an instructor in the Department of Chemistry at the University of California. After McMillan's departure from Berkeley in November 1940, and his gracious assent to our continuation of the work he had begun on the search for and possible identification of element 94, our group turned its major efforts to this problem.

Our first bombardment of uranium oxide with the 16-Mev deuterons from the 60-inch cyclotron was performed on December 14, 1940. Alpha radioactivity was found to grow into the chemically separated element 93 fraction during the following weeks, and this alpha activity was chemically separated from the neighboring elements, especially elements 90 to 93 inclusive, in experiments performed during the next two months. These experiments, which constituted the positive identification of element 94, showed that this element has at least two oxidation states, distinguishable by their precipitation chemistry, and that it requires stronger oxidizing agents to oxidize element 94 to the upper state than is the case for element 93. The first successful oxidation of element 94, which probably represents the key step in its discovery, was effected through the use of peroxydisulfate ion and silver ion catalyst on the night of February 23-24, 1941, in a small room (no. 307) on the third floor of Gilman Hall on the University of California campus in Berkeley.

The plutonium isotope of major importance is the one with

mass number 239. The search for this isotope, as a decay product of Np^{239}, was being conducted by the same group, with the collaboration of E. Segre, simultaneously with the experiments leading to the discovery of plutonium. The isotope Pu^{239} was identified, and its possibilities as a nuclear energy source were established during the spring of 1941, using a sample prepared by the decay of Np^{239} produced by neutrons from the 60-inch cyclotron, and it was later purified by taking advantage of the then-known chemistry of plutonium. Using neutrons produced by the 37-inch cyclotron in the University of California Radiation Laboratory, the group first demonstrated on March 28, 1941, with the sample containing 0.5 microgram of Pu^{239}, that this isotope undergoes slow neutron-induced fission with a cross section even larger than that of U^{235}.

The early work of the chemistry group at the University of California formed the basis for the later development of the process used in the separation of plutonium from uranium and fission products in the large manufacturing plants. This process was based upon the use of the two oxidation states of plutonium, and a great deal of our earliest work was concerned with the study of these states on the tracer scale. The conception and early development of the process for use in the large-scale manufacture of plutonium in the plants in Clinton, Tennessee and Hanford, Washington took place at the war-time Metallurgical Laboratory of the University of Chicago.

On December 19, 1942, S.G. Thompson, who was probably the first to recognize the possibilities and advantages of a phosphate process, attempted the precipitation of a relatively large concentration of bismuth (III) as bismuth phosphate. Upon digestion of the uranyl nitrate solutions ocntaining bismuth (III) and phosphoric acid at elevated temperatures, precipitation occurred slowly but fairly completely when the time of digestion was extended. Surprisingly enough, the precipitate carried more than 98 per cent of the plutonium in a lower oxidation state, and frequent repetition led to the conclusion that bismuth phosphate presented attractive possibilities as a carrier in a separations process. This work showed that bismuth phosphate did not carry the highest oxidation state (VI) of plutonium. It was also found that bismuth phosphate is a very specific carrier for the separation of plutonium from fission products.

The isolation of plutonium at the Metallurgical Laboratory, after initial contributions by M. Cefola, was carried on chiefly by B.B. Cunningham and L.B. Werner, who had previously been occupied in the biochemical field. The first pure chemical compound of plutonium, free from carrier material and all other foreign matter, was prepared on August 20, 1942, after starting with a plutonium concentrate in about 10 milligrams of rare earths prepared by A.C. Wahl and co-workers at Berkeley. This historic day marks man's first sight of the element plutonium and, in fact, the first sight of a synthetically produced isotope of any element. The first weighing of a pure compound of plutonium occurred on September 10, 1942, when 2.77 micrograms of the oxide (PuO_2) were weighed by Cunningham and Werner.

From this time until the fall of 1943, cyclotron bombard-

ments were the sole source of plutonium, and over this period of time about 2,000 micrograms, or 2 milligrams, of plutonium were prepared. This material was used to maximum advantage by the ultramicrochemists to prepare compounds of plutonium and to measure properties such as solubilities and oxidation potentials. In particular, it was possible--and this was of inestimable importance--to test the Bismuth Phosphate Process which was under consideration for use at Hanford. The various parts of the complicated separation and isolation procedures were tested at the Hanford concentrations of plutonium in the careful and crucial experiments performed by B.B. Cunningham, L.B. Werner, D.R. Miller, I. Perlman, and others. Without the possibility of these tests early in 1943, I believe it is fair to say that this process, which went into use at Hanford, and turned out exceedingly well, would not have been chosen.

In addition to the need for work with pure plutonium in connection with the separations process, it was necessary to determine a number of the physical and chemical properties of the dry salts of plutonium and of plutonium metal. Therefore, the study on the ultramicroscale had to encompass this field of investigation also. A number of compounds of plutonium were prepared by reactions involving the solid and gas phases--that is, by dry chemical reactions. This work was done in collaboration with W. H. Zachariasen and R.C.L. Mooney of the Univerisity of Chicago staff, who were able to use the x-ray diffraction technique to identify or help identify a number of the compounds that were synthesized and, in many cases, thus to establish their chemical structures.

During the intervening years, plutonium has been prepared in ton quantities in nuclear reactors and chemically isolated, using much more efficient procedures.

Continuing investigations of the chemical properties of plutonium in many laboratories throughout the world, as it has become available, has led to the situation where the chemistry of this relative newcomer is as well understood as is that of the well-studied elements. Thus, plutonium has the four oxidation states--III, IV, V, VI--leading to a chemistry which is as complex as that of any other element. In fact, it is almost unique among the elements in that these four oxidation states can all exist simultaneously in aqueous solution at appreciable concentration. As a metal, too, its properties are unique. It has six allotropic forms in the temperature range from room temperature to its melting point (640°C), and some of these have properties not found in any other known metal.

The nuclear properties of plutonium are also very interesting. All of the isotopes from ^{232}Pu to ^{246}Pu are known. Research in laboratories throughout the world has given us much information about their radioactive decay, and fission properties, and their methods of production by nuclear transmutation reactions.

*This work was supported by the Director, Office of Energy Res., Div. of Nucl. Phys. of the Office of High Energy and Nucl. Phys. of the U. S. Department of Energy.

DISCOVERY OF TRANSPLUTONIUM ELEMENTS

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Since 1944 there have been thirteen elements added to the periodic table of the elements. Elements 96 and 95, curium and americium, were added in that order using rather conventional methods of nuclear chemistry, but the work was very difficult because the tools of discovery had not yet been developed. Bombardments of ^{239}Pu by cyclotron and neutron reactor were used and various laborious chemical procedures were tried until success was achieved, spurred on by Seaborg's advocacy of the actinide concept.

By 1949, enough ^{241}Am and ^{242}Cm had been accumulated from reactor bombardment to be able to make short-lived isotopes of elements 97 and 98, berkelium and californium, by cyclotron reactions; by now more sophistication in chemical procedures and instrumentation techniques had been acquired, but the discoveries required great ingenuity by the late Stanley G. Thompson, the leader of the teams.

Then came the big breakthrough in November, 1952, when all the elements from uranium to fermium, element 100, were made in a microsecond by the successive capture of fast neutrons in the world's first test thermonuclear explosion. Over the next few months, both element 99, einsteinium, and fermium were discovered, as well as a number of neutron-heavy isotopes of the lighter elements. By now the technology had advanced to the point where very small numbers of atoms could be isolated and identified with certainty, but the work was still relatively slow because of the necessity of handling large amounts of intensely radioactive debris from the huge explosion.

Not long after these discoveries, it was found that most of the same nuclides could be made in the U.S. high flux thermal neutron reactors, and after a short period, these became the producers of the necessary materials for further element building. In 1955, element 101, mendelevium, was discovered, the product of bombardment of only 10^9 atoms of ^{253}Es by intense helium ion bombardment in the Berkeley 60" Cyclotron, the same accelerator that had been used for the discovery of elements At, Cm, Bk, and Cf. This became the first time that a new element was produced and identified one atom at a time. For this purpose, the recoil technique was used for the first time wherein the transmuted atom was separated from the target by the energy imparted to it in the reaction.

To go beyond mendelevium required ions heavier than alpha particles because of the limitation of available target material. In 1957 there were few machines capable of accelerating suitable heavy ions. One attempt was made in that year at Stockholm with ^{13}C bombardment of $^{244,246}Cm$ which unfortunately led to an erroneous result. This work was proved to be wrong by the Berkeley group who used the just-completed HILAC to bombard curium targets with carbon ions. Further experiments resulted in the discovery of element 102, and eventually the name nobelium was proposed for the element. In 1961, some of the same group succeeded in finding an isotope of element 103, lawrencium, in bombardments of californium with boron ions.

By now, the instrumental techniques at Berkeley were beginning to develop a high degree of sophistication since there was no possibility of using ordinary chemical methods for separation of the new products from target debris. The helium-gas-jet method was soon developed, and this became the work-horse technique for isolating and identifying elements 104-106 at Berkeley. At the same time, the method of using spontaneous fission track detection was developed at Dubna, U.S.S.R., to use in their searches for these same elements. This method is sensitive but not definitive since, unfortunately, it is impossible to tell from measurement of a fission track alone what the atomic number and mass must be. On the other hand, the Berkeley group pioneered the use of alpha-alpha correlation techniques which allow one to link genetically two or more nuclides, and thus establish a direct decay sequence to known elements. Using our technique, we discovered element 104, rutherfordium, in 1968, and element 105, hahnium, in 1970, by bombardments of ^{249}Cf with ^{12,13}C and ^{15}N. Our discoveries have been corroborated by the Oak Ridge National Laboratory, but the SF nuclides claimed for 104 and 105 by Dubna, made by bombardments of ^{242}Pu and ^{243}Am by ^{22}Ne, have not been shown to be due to those elements.

Element 106, no name yet, was discovered at Berkeley in 1974 in ^{18}O bombardments of ^{249}Cf. Approximately simultaneously, Dubna found a short-lived SF activity in bombardments of ^{208}Pb with ^{54}Cr which they attribute to element 106. By agreement, no name was to be proposed by either side until the priority and validity of the discoveries could be determined

A claim was made to element 107 by Dubna, but the evidence was very indirect and is not given much credence by most researchers in the field. Recently, however, a beautiful experiment with SHIP has been performed at the GSI UNILAC which has identified ^{262}107 in bombardments of ^{209}Bi by ^{54}Cr. In my opinion, this last group deserves the honor of naming this thirteenth element beyond plutonium.

THE ROLE OF ZACHARIASEN IN ACTINIDE RESEARCH*

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Professor (Fredrik) William Houlder Zachariasen began, at age 24, his forty-four years on the University of Chicago faculty, an academic career which progressed through Professor of Physics, Department Head, and Dean of the Physical Sciences. He was a member of the U. S. National Academy of Sciences and of the Norwegian Academy of Sciences. At age 19 he presented his first paper before the Academy in Norway. His long career resulted in an outstanding book and over two hundred publications, most of which were singly authored. They appeared over a period of fifty-five years and covered in depth a range of topics whose central theme was that of x-ray diffraction, spanning both theoretical and experimental advances.

For the purposes of this Symposium and the topic of this paper, the focus will be on that part of Zachariasen's work which had its pervasive influence on studies of the 5f elements. This period began in late 1943 and lasted 36 years, until his death in December 1979. (His last paper was on the subject of bond lengths in 5f element fluorides and appeared in 1980.)

In late 1943, Zachariasen began his fruitful involvement with the Metallurgical Laboratory of the University of Chicago at a very critical point. The Metallurgical Laboratory was the focal point for the intensive studies needed for plutonium separation processes which would be used in the major production facilities being built at Hanford, Washington and for eventual metal production at Los Alamos. In December 1941, two weeks after the Pearl Harbor attack, Nobel Laureate Arthur Compton started in motion an effort which centered this large scale project at the University of Chicago. Fermi, about a year later at Chicago, demonstrated the feasibility of the sustained nuclear chain reaction.

Although the eventual production of plutonium was thus assured, there still remained the unsolved chemical problems of isolating plutonium from uranium and the fission products by remote handling on a large scale and of preparing pure metal. Before reactors could be built to produce plutonium, tedious bombardments of many hundred pounds of uranium by cyclotron-produced neutrons followed by laborious separations had yielded a few hundred micrograms of plutonium. By mid-1943, intensive microscale studies of the chemistry of plutonium, including the chemistry of solids containing it, were well underway. Many parallel studies were being pursued: The bismuth phosphate, wet fluoride, dry fluoride, oxalate and acetate processes, to name a few, as well as studies of fission products behavior, micro preparations of plutonium metal, chemical engineering scale up, and radiation effects (the author became involved in these latter studies in July 1942 at Chicago).

Glenn Seaborg, who was to be awarded the Nobel prize, was in charge of several groups and more than 60 chemists who were developing with great intensity chemical procedures for extraction and purification of plutonium. The wartime threat and the unknown status of the nuclear effort in Germany, the birth place of atomic fission, hung over every one. Would Germany achieve success first? German scientific articles in 1941/42 on the diffusion length of neutrons and their absorption showed such studies to be abreast of our similar efforts at that time. The extraordinary complexity and number of phases of metallic plutonium were stumbling blocks yet to be discovered; unsuspected, as well, was the nearly constant (~1.V) redox potential connecting the four aqueous valence states of plutonium.

Thus it was in 1943 that Zachariasen came to play his role in understanding the puzzling behavior of plutonium, a role he was uniquely equipped to fill. Zach, as he was known to his friends, was already a world figure in x-ray structural work with his landmark paper on glass structures and some 80 publications. As a young student of the great geochemist Goldschmidt, he had studied countless x-ray films of rare earth minerals and compounds; Zach now came to apply his experience and depth of understanding of crystal chemistry to studies of the new rare earth series - the 5f elements man made beyond uranium.

He made early and extraordinary contributions to plutonium chemistry and its separation processes when x-ray powder diffraction was the only analytical tool available to decipher the components present in the microgram samples of (usually impure) plutonium compounds. Zachariasen was simply unique in his ability to derive quantitative information from what is usually regarded as hopelessly complex data -- a powder diffraction pattern of a multicomponent mixture. He studied hundreds of samples and provided identification of most of the plutonium compounds and phases important to separation processes; he first deduced from cell constant data on the dioxides the magnitude of the 5f element contraction, and labeled them thorides; he first deduced from meager data alone, the unique, multiple structures of plutonium metal. Studies of other 5f metals structures would follow, as would studies of many new compounds. Zachariasen established a self-consistent set of atomic and ionic radii and their dependence on coordination number. In the last of his 55 publication years, he formulated and improved his quantitative relationships involving bond lengths, and their dependence on the strength and number of bonds. During this period also he demonstrated that the rare earth element cerium under high pressure became isostructural with α-uranium, hitherto a nearly unique structure.

Parallel to these studies Zachariasen made outstanding contributions to diffraction physics. His work is applicable to broad classes of materials: oxides, sulfides, nitrides, 5f-metals, and fluorides; and to broad classes of problems, including stacking disorders, diffuse scattering, bond lengths and radii, extinction. absorption and to structure solving in the broadest sense. The breadth of his contribution is enormous; there is hardly a major advance in crystallography in one-half

century that does not bear his mark. No other crystallographer has done as much to expand our knowledge of heavy element crystal chemistry or had such a central role in the early development of atomic energy.

* This work was performed under the auspices of the U.S. Dept. of Energy.

PHOTOEMISSION TECHNIQUES

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The recent development of photoemission techniques and other related methods has opened unique possibilities for investigating the electronic structure of solids. Many fascinating properties of the Actinides are related to the presence of the open 5f shell. Spectroscopic studies can therefore be expected to yield a very fundamental contribution to the understanding of their electronic structure. A brief presentation of the photoemission techniques will be given. In these the photon energy is a very important parameter since it mainly determines the type of information which can be obtained. In the high-energy limit (XPS) the core level spectra yield a straightforward chemical analysis. In addition, well resolved spectra can reveal many interesting aspects of the outermost electrons: the variation of the charge distribution around the different atoms (chemical shift), the existence of both localized open shell (multiplet splitting) and of spin (exchange splitting) and the localization of outermost levels (shake-up and shake-down satellites). The XPS valence band spectra can be usually interpreted as the superposition of the partial densities of states weighted by the corresponding cross-sections. In the low energy range, the use of synchrotron radiation allows a detailed investigation of the electronic states in the vicinity of the Fermi energy. By taking advantage of the continuous character and of the polarization of this radiation, the dispersion relations and the symmetry of the electronic states can be now investigated in great detail. Many other related spectroscopies (bremsstrahlung isochromat spectroscopy, appearance potential spectroscopy, energy loss spectroscopy, x-ray absorption and emission spectroscopy ...) must also be mentioned since they allow one to investigate aspects of the electronic structure which are not accessible by photoemission techniques.

The aim of this paper is to give a survey of the existing photoemission studies dealing with Actinides. In view of the numerous possibilities for investigation which are offered by all these techniques, only a small proportion have so far be attempted. This situation is mainly due to the fact that quite special and dedicated equipment is necessary to work with highly radioactive samples. There is little doubt that this field will expand in the next few years since the actinide series offers the unique possibility to follow step by step the gradual localization of the 5f electrons. It is predicted in the metals that these states undergo a transition from extended to localized behaviour between Pu and Am. This situation which can also occur in the 3d elements

(and maybe in Ce) is an extremely interesting subject of comparison between theoretical calculations of the electronic structure and spectroscopic studies. It should allow one to investigate very closely the conditions determining this transition and the resulting breakdown of the Koopmans approximation.

NEUTRON SCATTERING STUDIES OF THE ACTINIDES

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Since the last joint actinide meeting in 1975 a great number of investigations using neutrons on actinide systems have been performed. The relative weakness of neutron beams, together with their weak interaction with nuclei and/or electron spins, means that large samples must be used, thus often confining experiments to uranium systems, and certainly prohibiting investigations of transcurium species for the forseeable future. The last five years have seen a rapid increase in the number of experiments on single crystals. Unfortunately, very few single crystals of transuranium compounds exist. However, despite these obvious disadvantages, neutron studies have contributed to major advances in our understanding of 5f systems. The principal reason for this is the very detailed information in both space and time (energy) coordinates that neutrons provide on the microscope interactions. Some of the basic principles will be explained in this talk.

The unpaired 5f electrons are of major interest in the actinides because their considerable spatial extent implies that they may interact either with neighbouring 5f orbitals, or with other bonding electrons. By virtue of the neutron magnetic moment, neutrons interact with the resultant moments of these unpaired electrons. Experiments at the Centre d'Etude Nucléaires, Grenoble investigating the magnetic structure of, for example, UAs, USb, $NpAs_2$, and U_3P_4 have used high magnetic fields (100 kOe) and uniaxial stress to show that the moments develop complicated arrangements as a consequence of competing interactions. Even in such simple systems as the UX (X = N, As, Sb) we have $1\vec{q}$, $2\vec{q}$, and $3\vec{q}$ magnetic structures.

Another series of experiments aimed at determining the spatial extent of the 5f wavefunctions, are performed with polarized neutrons, mostly at the Institut Laue-Langevin, on compounds such as URh_3, UGe_3, USn_3 and NpO_2. These show the interaction between the 5f and neighbouring atomic wavefunctions. Indirect evidence for such interactions comes also from studies of the critical scattering, which examine the correlations between magnetic moments in the regime around the ordering temperature. These experiments, performed at Argonne, Brookhaven and Chalk River Laboratories, provide conclusive evidence for anisotropic interactions, but the exact microscopic form of these interactions remains controversial.

The studies above involve elastic scattering, i.e. they represent a long-time average and give no information on the excitation spectra. Experiments measuring the inelastic scattering of neutrons are in progress at Chalk River and ILL. With the notable exception of UPd_3, in which 4f like localized behaviour exists, the experiments have found a complex excitation spectra reflecting the localized-itinerant duality of the 5f electrons and, at least in metallic systems, the interaction with the conduction electrons.

Neutron scattering has also been used to investigate atomic ordering processes. The most important discoveries concern the longstanding mystery of the 43K transition in alpha uranium. Experiments at Oak Ridge and ILL have shown that at this temperature a charge-density wave appears in α-U, and the

uranium atoms are shifted a very small amount off their normal positions.

Not all the above examples can be covered in one talk. Our object in this abstract is to illustrate the bradth of neutron scattering and how the results have provoked questions about current theoretical models of 5f systems. Some future experiments and the importance of extending this work into transuranium systems will also be discussed.

BAND STRUCTURE STUDIES

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By recalling the fully relativistic, semi- or pseudo-relativistic and non-relativistic level of effective one-electron Hamiltonians, methods for the calculation of the electronic structure of actinides and actinide compounds are reviewed. This survey relates band structure methods versus cluster methods, reviews some of the linearized approaches to band theory and includes a discussion of methods for alloys and mixed crystals. Examples will illustrate common aspects of these methods. In particular relativistic multiple scattering theory will be used to show the usefulness of model band structure studies of the electronic structure of actinides and their compounds.

The importance of relativistic effects for both, low-lying valence bands and typical f-bands will be discussed in some detail for NaCl-type Uranium compounds.

SINGLE CRYSTAL PREPARATION OF ACTINIDES AND ACTINIDE COMPOUNDS

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I In most cases growing of single crystals is just one part of a larger scientific program. Before starting a project three important questions have to be asked. 1. What do I want to learn? 2. How do I realize it? 3. How much effort and time does it take?

The crystal grower should be consulted before deciding on point 2 and 3. He can estimate the chances to grow crystals of the desired size, and how much time and effort would probably be needed. In many cases it turns out to be easier, faster and more economical to adapt or improve the equipment in order to perform the desired experiments on small or very small crystals (magnetic measurements performed on microgram samples are a good example) rather than trying to grow crystals of utopical size as required for the existing equipment.

II Much effort has already been put into growing single crystals of the actinides and their compounds. Crystals have been grown of some actinide metals and their intermetallic compounds with Mn, Co and Ni, as well as some of their oxides, borides, fluorides, chalcogenides and pnictides. Crystal growth of the actinide metals and their compounds is hampered by their radioactivity (handling in glove boxes), the scarcity of the materials and the high melting points of most of the compounds (2000° C and more) causing problems with the crucible materials. A general tendency is to use low-temperature methods in order to avoid part of the difficulties and to improve crystal perfection.

III The different methods for growing single crystals are therefore classified according to the working temperature T in relation to the melting point T_m of the crystal.

a) $T \ll T_m$
Salt like compounds can be crystallized at or near room temperature. Thus Rb $UO_2(NO_3)_3$ crystals were grown from solution in hot HNO_3.UO_2 and NpO_2 crystals were grown by electrolysis in fused salts solutions.

b) $T \sim 1/2\ T_m$
In this temperature region transport reactions in sealed fused quartz tubes (limiting the temperature to about 1200° C) are commonly used. Transporting agents are HCl, Cl_2, Br_2, I_2, Br_2+S_2 and $TeCl_4$. Crystals of U_xO_y (especially UO_2), $U_{1-x}Th_xO_2$ and polypnictides and chalcogenides of U were obtained. A modification of this method, based on rf-heating of tungsten plates inside the quartz tube allows to extend the temperature range up to 1800°C. Monochalcogenides and monopnictides have successfully been grown with this so-called modified van Arkel technique.

c) $T \lesssim T_m$ (T just below or close to T_m)
Crystals can be grown from a low-temperature melt using a flux. Promising results have been obtained with the following fluxes: $PbF_2.B_2O_3$, $Li_2O.2MoO_3$, $Li_2O.2WO_3$, $NaF.B_2O_3$ and Ga-Al.NpO_2, ThO_2 and ThB_6 crystals were grown by this method. Monopnictide and monochalcogenide crystals are obtained by mineralization. Pressed pellets of the powdered substances are carefully heated in sealed tungsten crucibles up to almost the melting temperature and kept at this temperature for several weeks. Big UO_2 single crystals were grown by elaborate technique of sublimation.

d) $T \gtrsim T_m$ (melt growth)
Arc melting is widely used - UO_2 crystals were successfully grown by this method. Working in crucibles causes serious problems due to the fact that most crucible materials are destroyed by the melt. Water-cooled crucibles corundum- and tantalum-carbide lined tungsten crucibles were used to grow crystals (by the Czochralski technique or by directional cooling) of UO_2, ThO_2, UMn_2, UO_2, UNi_5 and USb_2. Floating zone melting was successful for UO_2 and UN crystals.

IV The decisive parameter needs not to be temperature in all cases, pressure can be of equal importance. High-pressure technique was applied to prepare α-Pu crystals. Desolving PuO_2 in glass and pulling fibres avoided oxygen loss and yielded stoichiometric PuO_2 single crystals encapsulated in the glass fibres.

AB INITIO CALCULATIONS ON ACTINIDE COMPOUNDS*

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The evolution of first principles theories capable of describing the electronic structure of actinide compounds is reviewed. Particular emphasis is placed upon molecular orbital and cluster models for gas phase and solid state systems respectively. Comparisons are made between "direct" methods based upon Dirac-Fock (DF) and local density Dirac-Slater (DS) schemes, and "indirect" pseudopotential or perturbative schemes. Prospects for basing a full many-electron treatment upon the self-consistent DS single particle orbitals are discussed.

The nature and magnitude of relativistic effects on chemical bonding and valence electron level structures have been subjects of perennial interest. DF studies on heavy atom hydrides, using a one-center expansion technique[1], have been used to study the relativistic contraction of bond lengths. Early beliefs that the bond contraction was simply due to contraction of the underlying atomic orbitals; i.e. an overlap effect, have turned out to be incorrect. Recent results[2,3] which throw light on this aspect are discussed.

The development of reliable pseudopotential methods[4,5,6] in a relativistic framework gives hope that rather large systems (both in terms of atomic number, and number of nuclear sites) can be treated by considering only valence electron states explicitly. It is possible at present to carry out all-electron calculations on actinide complexes in local density models, so interesting comparisons between direct and indirect methods become feasible.

Self-consistent DS energy levels and charge distributions are presented for a number of $(AcO_m)^q$ complexes, where Ac=Th,U,Np,Pu, representative of oxide compounds and spectroscopically accessible "free" complexes[7,8]. An effort is made to correlate the f-electron occupation and bonding interactions to the variables; coordination number, formal valency, and bond lengths. The magnetization density in UO_2 is discussed, and preliminary results on some halide compounds are presented.

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COMPLEX OXIDE SYSTEMS OF THE ACTINIDES*

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This article reviews recent research on the structural, spectroscopic, thermodynamic, and magnetic properties of ternary and other complex oxides containing actinide ions. Since complex compounds often exhibit unusual coordination sites and oxidation states for transition elements, the unique properties not found in the binary oxides are emphasized. For completeness, a brief summary of properties of the binary oxides is also given.

Since the last comprehensive reviews of actinide complex oxides,[1,2] much new research has been published. Complete crystallographic studies have shown that relatively few complex oxides have sample high-symmetry structures.[3] New spectroscopic techniques (x-ray photoelectron spectra,[4] Mössbauer spectra[5]) have extended the understanding of electronic structure of actinides. The number of thermodynamic studies[6] of complex actinide oxides has vastly increased, bringing improved correlation of structure, coordination number, acid-base relationships and stability. Magnetic measurements (susceptibility, neutron diffraction, paramagnetic resonances, have reached maturity for simple oxides but are still lacking for complex oxides.

This article classifies complex oxides by structural types and by relative acidities and basicities of component oxides. Within this framework, the recent literature has been assessed to highlight major developments in complex oxide systems:

(a) Structural studies.[7]
(b) X-ray photoelectron spectra.[8]
(c) Vibrational spectra.[9]
(d) Electronic spectra.[10]
(e) Solution calorimetry.[11]
(f) High-temperature EMF studies.[12]
(g) Low-temperature calorimetry.[13]
(h) Vaporization phenomena and phase studies.[14]
(i) Magnetochemistry.[15]

Research advances are summarized in terms of the impact on fundamental solid-state chemistry and thermodynamics, and in terms of their applications to nuclear fuels, radioisotope sources, and long-term nuclear waste disposal.

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FISSION PROPERTIES OF THE ACTINIDES

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Recent progress in the experimental determination of fission barrier and scission properties is reviewed. The importance of deformed nuclear shells in influencing fission decay rates in actinide nuclei is demonstrated. The dramatic influence of shape symmetries on fission rates and evidence for increasing complex barrier shapes is presented. Recent data and interpretation suggest double and triple peaked fission barriers and multiple parallel paths in the saddle point region. These effects are generally understood in terms of modulations of a simple liquid drop fission barrier by energy deviations of ~1-3 MeV due to the extra stability of some deformed nuclear configurations (i.e., shell effects). The scission properties (mass and total kinetic energy distributions) for actinide nuclei are also reviewed, and it is demonstrated that nuclear shells in the nascent fragments near scission are also important. The most striking effect of this type is in the Fermium region where fission undergoes a sudden transition from asymmetric to symmetric mass division as the result of approaching the doubly magic configuration of two ^{132}Sn nuclei which have extraordinary binding energies. Various recent and proposed measurements to try to isolate shell and dynamic effects in the fragment distributions are also discussed.

THE PREPARATION OF PROTACTINIUM METAL AND COMPOUNDS

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Prior to the isolation of approximately 100 g of ^{231}Pa by U.K. scientists in 1960, the preparative chemistry of protactinium had been little investigated and few compounds were known. As a consequence of the availability of macro-quantities of a nuclide with a reasonably long half-life, world-wide interest was generated in the chemistry of protactinium. Much of this was directed at the preparation of the metal and a wide range of compounds, and investigations of their chemical and physical properties.

The currently available methods for the preparation of metallic protactinium are discussed together with publications dealing with its chemical properties. Details are provided of the preparative routes to all protactinium compounds, particular attention being given to those pentahalides and tetrahalides which are valuable starting materials for the preparation of other classes of compounds. Interesting structural aspects are highlighted and differences between the chemistry of protactinium (V) and that of uranium (V) are identified. Brief consideration is given to potentially interesting areas for future investigation.

DEFECT STRUCTURES IN ACTINIDE COMPOUNDS

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Many of the physical properties of actinide compounds, and in particular the transport properties (electrical and thermal conductivity, atomic diffusion) and the plastic properties, are controlled by defects in the crystal structure. Among these, the point defects responsible for thermal disorder and/or non-stoichiometry play the major role. The importance of the radiation-induced point defects on the behaviour of the nuclear fuels has of course not to be emphasized.

This paper will be first concerned with the atomic structure, electronic and thermodynamic properties of the point defects in two main actinide systems : the oxides with fluorite structure $MO_{2\pm x}$, and the carbides with rocksalt structure $MC_{1\pm x}$. Indeed, these two categories of compounds may be considered as "model compounds" for the treatment of non-stoichiometry, because of their simple crystal structure, and because we have a preliminary knowledge of their bonding. The two systems are very different, the first having a large ionic character and being semi-conductor, the second displaying a predominantly metallic character. In both systems, the defects responsible for thermal disorder and non-stoichiometry have been proved to be vacancies and interstitials of the metalloid sublattice ; but the electronic structure of the metal atoms near-neighbours of these point defects is largely modified compared to what it is in the pure compounds.

The understanding of the thermodynamic and physical properties of these compounds at high temperature or off-stoichiometry needs the knowledge of :
- the formation energies of the various possible point defects ;
- their interaction energies ; the latter may be separated into two contributions : an electronic contribution and a strain contribution, which includes the change in the average lattice parameter, and the atomic relaxations near the point defects.

We want to emphasize on the fact that, because of their large refractory character, it is difficult to obtain these compounds in true thermal equilibrium below 1000 °C. In particular, there is a temperature range in which the metalloid sublattice is in thermal equilibrium, but where the metal sublattice must be considered as "frozen".

1) Carbides.

Because of the complexity of their electronic structure, which displays altogether metallic, covalent and ionic character, no general model based on microscopic theories has yet been developped to calculate properties of the point defects and describe the non-stoichiometric carbides. On one hand, semi-empirical models have been used to describe phase diagrams such

as U-C, with pair interaction potentials fitted to the experimental data. On the other hand, preliminary experimental work has allowed to obtain data on :
- the high temperature phase diagrams,
- the short-range ordering of carbon vacancies, especially in ThC_{1-x},
- the atomic relaxations due to the size effect of vacancies,
- the formation energies of vacancies by quenching and diffusion experiments,
- the electronic structure of the largely non-stoichiometric ThC_{1-x} system .

The "lattice statics" approach of the lattice strains due to a carbon vacancy in UC, as developped by Lesueur [1] will be discussed.

2) Oxides.

The defect structure of UO_{2+x}, consisting of short-range order clustering of oxygen interstitials, has been studied in details by Willis [2], using neutron scattering techniques.

Because of the predominantly ionic character of UO_2, calculations of the formation and interaction energies of point defects in this compound have been performed in a purely ionic approximation, for example by Catlow [3]. These will be compared to the experimental data.

We shall recall our knowledge on the electronic structure of UO_{2+x}.

At last, the statistical thermodynamic models employed to describe the non-stoichiometric oxides at high temperature [4] will be discussed.

3) The paper will then treat more briefly various other aspects of point defects in actinide compounds :
- non-stoichiometry in mixed oxides such as $(U,Pu)O_{2\pm x}$ or $(U,Ce)O_{2-x}$,
- migration of the point defects (diffusion),
- radiation-induced point defects ; our lack of knowledge of basic data such as threshold displacement energies, and low temperature radiation damage, will be emphasized.

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THERMODYNAMIC PROPERTIES OF THE ACTINIDES : CURRENT PERSPECTIVES

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The chemical thermodynamic properties of the actinide elements and their compounds are being assessed by an international team of scientists under the auspices of the International Atomic Energy Agency (Vienna)[1] : This undertaking should result in the publication of fourteen distinct sections. Since 1976, *three parts, dealing with the elements, the aqueous ions* and miscellaneous compounds, have been published, the other parts being in various stages of preparation. That study is carried out in coordination with the U.S. National Bureau of Standards, which has issued since 1976 several reports in the field of actinide thermodynamics[2-4] supplementing a comprehensive critical review of thorium thermodynamics[5]. Tabulation of thermodynamic data based on these assessments will also be found in two forthcoming books[6,7]. Finally, an extensive list of the thermodynamic properties of the actinides and their compounds has been published by the USSR Academy of Sciences[8].

In view of these many efforts, the present paper will be limited in its scope to three aspects, namely :

1. The review and the evaluation of a number of important results in actinide thermochemistry that have appeared after the Fourth International Transplutonium Elements Symposium and the Fifth International Conference on Plutonium and Other Actinides (Baden Baden, September 1975). Vaporization studies on the metals, and enthalpies of formation of transplutonium aqueous ions, of halides and of binary oxides are only a few examples of such results.

2. The identification of areas in which experimental studies are definitely needed whether the existing data are unsatisfactory or simply lacking. This situation can be found even for compounds of the most studied elements of the series, but it is obvious that insufficient efforts have been directed towards the thermodynamics of compounds of actinium, protactinium and transcurium elements. In particular, acquisition of sound experimental data on a number of berkelium and californium species in their extreme oxidation states is essential as a key to our knowledge of heavier actinides unavailable in sufficient amounts.

3. A brief discussion of the usefulness and limitations of data analysis for the evaluation and the prediction of thermodynamic values. The establishment of a network of thermodynamic data involving the compounds of a given element is an extremely useful and straightforward method of identifying inconsistent data. The systematization of

properties throughout the actinide series is, however, a far more delicate matter because parameters such as atomic or molecular volume, metallic or ionic radii, electronic promotion energy, hydration energy ... which are used in such correlations either may not fully describe the complexity of the situation or may be lacking sufficient accuracy.

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SPECIFIC SEQUESTERING AGENTS FOR THE ACTINIDES

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Powerful complexing agents, such as diethylenetriaminepentaacetic acid (DTPA), are used in decontamination and decorporation applications for the actinides. While there are various chemical methods used for the separation, concentration, and purification of these elements, it has been true that there are no specific sequestering agents for the actinides. That is, the complexing agents such as DTPA form very strong complexes not only with the actinide(IV) ions, but also most other metal ions with a +2 or greater oxidation state. For some time we have concerned ourselves with the design and synthesis of compounds which would be specific for the actinide(IV) ions. Much of this work has been recently reviewed.[1-3] Our initial approach to this problem has been the recognition of the chemical and biological similarities of Fe(III) and Pu(IV). Our test of the degree to which we have an actinide-specific complexing agent has been based on studies in which Pu^{4+} is a biological contaminant. Under physiological conditions, plutonium exists primarily in the +4 oxidation state. The chemical similarities of Pu(IV) and Fe(III) extend from their similar charge per radius ratios, through their similar hydrolytic and hydroxide solubility properties, to their coordination behavior by the serum iron transport protein transferrin. Indeed, Pu^{4+} is transported in the blood plasma of mammals as a complex of transferrin and is bound at the same site that normally binds iron. It can thus be anticipated that coordinating groups or ligands which have a high affinity for high-spin ferric ion will show a similar affinity for Pu(IV) — and the design of multidentate specific sequestering agents based on such units can be envisaged.

Microorganisms have evolved low-molecular-weight chelating agents which use primarily hydroxamate or catecholate functional groups to solubilize ferric ion.[4] In particular, enterobactin, a tricatecholate compound, forms the most stable known Fe(III) complex, with an approximate formation constant of 10^{52}.[5] Using enterobactin as a prototype, but recognizing that a preferred coordination number for plutonium will be 8 rather than 6 [as for Fe(III)], we have synthesized a series of tetra catechoylamide (CAM) ligands which are specific for Pu(IV) and other actinide(IV) ions. These ligands have been designed to facilitate the formation of the D_{2d} trigonal-faced dodecahedral coordination environment we observed in structural studies of several $[An(catecholate)_4]^{4-}$ complexes.[6,7] In addition, the length and substitution pattern of the organic backbone has been varied to optimize the thermodynamic and biological properties of the ligands. A number of these tetra catechoylamides sequestering agents are shown in Figure 1.

An important consideration for metal ion decorporation therapy is the relative affinity of the ligand for the target metal ion as compared to its affinity for essential biological metal ions which are present in the body. A series of complexometric studies have examined the degree to which the newly synthesized compounds bind such biological ions. Neither Ca(II) nor Mg(II) are bound to any significant extent.[8] The strongest complex is formed with Cu(II), but even this complex is approximately 10^{16} times less stable than the corresponding ferric chelate under physiological conditions. The complexation of ferric ion is not considered a problem, since this occurs only for

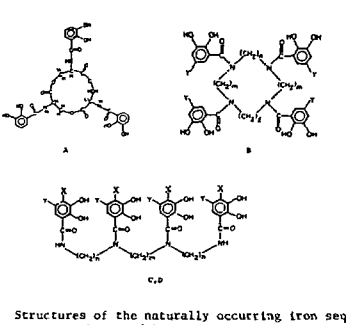

Fig. 1. Structures of the naturally occurring iron sequestering agent enterobactin (A) and the biomimetic synthetic tetracatechoylamide analogues 3,4,3,4-CYCAM, $\ell = 3$, $m = 4$, $n = 3$; 3,4,3-LICAMS (C), $m = 4$, $n = 3$, $X = H$, $Y = SO_3^-$; 3,4,3-LICAMC (D), $m = 4$, $n = 3$, $X = CO_2H$, $Y = H$.

the relatively small amount of labile, high-spin Fe(III) present in vivo. It is established then that these ligands demonstrate great specificity, particularly when compared to DTPA,[9] the ligand currently used to treat actinide contamination in humans.

Since plutonium does follow ferric ion metabolic pathways in the body,[10] we are concerned with its mode of coordination and binding by serum iron transport proteins. The similarity of the coordination chemistry of Th(IV) and U(IV) with that of Pu(IV) have made both uranium and thorium convenient models for plutonium binding in biological systems. In particular, because of its simple redox chemistry, thorium has been widely used. To test the degree to which it is in fact a good model for Pu(IV) in such systems, we have investigated the binding of Th(IV) to transferrin using difference ultraviolet spectroscopy. It has been found that Th(IV) is bound in each of the two sites of transferrin as a monohydroxo species. More important, the two sites differ in the manner in which the Th(IV) is bound. In the C-terminal site two tyrosines are bound to thorium, whereas there is only one tyrosine involved at the N-terminal site. This may be associated with the fact that the C-terminal site is slightly larger than the N-terminal site. Since Pu(IV) is smaller than Th(IV), it should fit easily into both sites and this may explain the difference that has been observed previously in the in vivo distribution between Th(IV) and Pu(IV).[12] The in vivo evaluation of CAM ligands in mice and dogs has shown that the CAM ligands are indeed effective sequestering agents for Pu(IV).[13,14] Chemical modifications of the catechol rings substantially increases the water solubility of the tetra catechoylamide compounds, increases the acidity of the catechoyl rings, and decreases the sensitivity of the ligand toward air oxidation. While sulfonation increased the effectiveness of the ligands for Pu(IV) removal, it was found to have some toxic side effects in test animals over prolonged periods of administration.[13] Incorporation of a carboxylate group instead of a sulfonate group accomplishes these same chemical modifications of the ligands described above, but has been

found to produce compounds which maintain their effectiveness without any observed side effects.[14] A summary of the actinide sequestering properties of tetrameric-catechoylamides is given in Table I.

Table I. Summary of actinide sequestering properties of tetrameric catechoylamides.

Cyclic		
3,3,3,3-CYCAM	Mobilizes Pu but deposits it in kidneys	
3,2,3,2-CYCAM-NO_2	Very toxic	
3,3,3,3-CYCAMS, 2,3,3,3-CYCAMS	Sulfonation increases acidity and solubility, prevents Pu deposition in kidneys	
Linear		
2,3,2-LICAMS	Least effective of linear compounds	
3,3,3-LICAMS, 4,3,3-LICAMS	Longer chain length, slight improvement, still not very effective	
4,4,4-LICAMS	Slightly toxic	Longer central bridge gives optimum geometry
3,4,3-LICAMS	Derivative of spermine (a natural product)	
3,4,3-LICAMC	Most effective agent to date, 73% Pu(IV) removal. Non-toxic.	

Less constrained linear structures are superior to corresponding cyclic compounds.

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CHEMICAL PROBLEMS ASSOCIATED WITH REPROCESSING

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After a general introduction giving an overview of the production of LWR fuels for the next decades and the programs of fast breeder reactors, the actual status of reprocessing plants in operation and in project is given. The chemical process is based on the Purex process whose main features are described.

Using as a reference thirty years of experience of reprocessing of natural uranium metallic fuels, one examines for LWR and FBR fuels what are the major changes and their consequences on the process chemistry.

For a same mass of uranium, the presence of larger quantities of plutonium, fission products, transuranium elements associated with a very high activity is the essential factor to be considered. One tries to evaluate the consequences through the main steps of the classical Purex process : dissolution, extraction cycles, effluent concentration and treatment etc ...

In conclusion, a large R and D program has to be pursued. It necessitates a large amount of work :

- to increase the efficiency of fissile products recovery and purification and also of gazeous and liquid effluents treatment,
- to gain a better knowledge of the chemistry of fission products : mainly Ru but also the minor ones : Tc, Pd, Mo etc ...,
- to obtain more data on the behaviour of solvent degradation products mainly with regards to plutonium compounds,
- to complete the kinetics studies of redox and extraction processes of plutonium systems when using short residence time contactors in liquid-liquid extraction,
- to extend studies on the adequate solid compounds which allow safe long term storage of the wastes.

CHEMICAL PROPERTIES OF THE HEAVIER ACTINIDES AND TRANSACTINIDES*

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The chemical properties of each of the elements 100 (Fm) through 105 will be reviewed and these properties will be correlated with the electronic structure expected for 5f and 6d elements. A major feature of the heavier actinides, which differentiates them from the comparable lanthanides, is the increasing stability of the divalent oxidation state with increasing atomic number. The divalent oxidation state first becomes observable in the anhydrous halides of californium and increases in stability through the elements to nobelium, where this valency becomes predominant in aqueous solution. In this range of elements, the II → III oxidation potentials decrease from ~+1.5 to -1.5 volts. These observations lead to the conclusion that, in comparison with the analogous 4f electrons, the 5f electrons in the latter part of the series are more tightly bound. Thus, there is a lowering of the 5f energy levels with respect to the Fermi level as the atomic number increases.

The metallic state of the heavier actinides has not been investigated except from the viewpoint of the relative volatility among members of the series. In aqueous solutions, ions of these elements behave as do "normal" trivalent actinides and lanthanides (expect for nobelium). Their ionic radii decrease with increasing nuclear charge which is moderated because of increased screening of the outer 6p electrons by the 5f electrons. These relative ionic radii have been obtained from comparisons of the elution position in chromatographic separations.

Completion of the actinide series of elements is expected with the element lawrencium (Lr) in which the electronic configuration is either $5f^{14}6d7s^2$ or $5f^{14}7s^27p$. From Mendelev's periodicity and Hartree-Fock calculations, the next group of element is expected to be a d-transition series corresponding to the elements Hf through Hg. Only the chemical properties of elements 104 and 105 have been studied and, indeed, they appear to show the properties expected of eka-Hf and eka-Ta. However, the nuclear lifetimes are so short and so few atoms can be produced that a rich variety of chemical information is probably unobtainable.

In addition to the extraordinary scientific effort required, there are other serious restrictions to obtaining extensive experimental data concerning elements beyond Fm in the Periodic Table. Experiments can be done with only a few atoms at a time; thereby excluding the measurement of many fundamental and important physical constants, atomic and molecular structures, magnetic properties, and other properties requiring macroscopic amounts of the element. Furthermore, there are some doubts about the deductions and conclusions drawn from observing the behavior of less than one hundred atoms. The question of whether this behavior is representative of the true chemical properties of an element will be discussed.

Because chemical research in this region of elements has progressed only with the development of techniques that are somewhat unique in the field of chemistry, a few of the unusual methods used in the past will be described.

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PREPARATION OF TRANSPLUTONIUM COMPOUNDS AND METALS*

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Studies of the transplutonium elements since their discovery 3-4 decades ago have progressed from tracer-level investigations to a status where weighable quantities of elements through einsteinium permit the preparation of both compounds and metals. At the present time, and for the foreseeable future, actinides beyond einsteinium in the series will only be available to the extent of 10^{10} atoms (4 pg) or less, which precludes the use of microchemical techniques that have been applied to the first five transplutonium elements

The preparation of transplutonium compounds and metals, and the subsequent research on these materials, require specialized techniques and facilities, and their inherent radioactivity and accompanying heat usually complicate the project involving them. Several ingeneous microchemical techniques have been developed for handling and investigating only a few μg of these elements, some of which are still employed today even though larger quantities of the elements are available. In some instances it has been possible to prepare samples and collect diffraction data on as little as 10 ng of material. One of the pioneers of actinide microchemical techniques was the late B. B. Cunningham. Among his contributions was development of the single ion-exchange resin bead technique for the concentration and manipulation of μg amounts of the actinides. The ability to quantitatively transport individual pieces of material containing μg amounts is often a prerequisite for carrying out the necessary chemical/physical operations. However, the bead technique is limited to ~10 μg or less, and has not been successful for the high specific activity encountered with ^{253}Es. Thus, it became apparent that another approach was required. A microprecipitation process using teflon molds was developed which allows the preparation of as little as 20 ug or up to multi-mg pieces of transplutonium oxide or fluoride.

The success and/or value of an experiment often depends on the quality and purity of the sample material being studied. In the United States the Department of Energy's program for transplutonium element production is carried out at the Oak Ridge National Laboratory and these elements in relatively pure form are available to researchers. Normally, the researcher must be concerned only with the additional purification necessary to attain the ultra-purity required for the particular research project, rather than recover and isolate these elements from reactor targets. However, as a result of the quantity of the material available and/or the in-growth of daughter products, the final purification and the sample preparation often become an integral part of a study. This is especially true with studies of ^{253}Es as the rate of daughter in-growth is approximately 3% per day.

The number, type and complexity of compounds that can be prepared is mainly limited by the ability and imagination of the researcher. Often the preparation of a compound on a μg or mg scale is carried out in the solid state but preparations have also been done in solutions, the vapor state and in molten salts. Some examples of these preparations will be discussed but the major emphasis will be placed on the preparation of oxides, halides and metals, since the majority of the work has been done on these substances

and they are also used as starting materials for other syntheses.

The oxides of the transplutonium elements were some of the first compounds to be investigated due both to the inherent interest in them and their relatively simple preparation. Although the sesquioxides and dioxides (except EsO_2) of the first five transplutonium elements have been well established, efforts are still being made to understand phase behavior, explain the trends observed in the melting points, and to investigate oxides with O/M ratios between 1.5 and 2.0. There is also interest in stabilizing higher oxidation states of the transplutonium elements by employing ternary oxide systems and using oxide samples to ascertain the effects of radioactive decay. Magnetic susceptibility measurements provide valuable information on these oxides and these data can serve as reference values for comparing susceptibilities in other transplutonium compounds. In all of these studies it is necessary to prepare and be able to transfer readily the oxide of interest. Some of the techniques that have been and are currently being used for preparing and handling these oxide samples will be discussed.

Although the anhydrous halides of the transplutonium elements can be prepared by several preparative methods, the treatment of an oxide with a hydrogen halide at elevated temperatures is often the preferred method. The iodides can not be directly synthesized in this manner; it is necessary to first prepare a lighter halide and treat it with hydrogen iodide. The iodides can also be conveniently prepared by reacting the elements directly and in the case of AmI_3 this is the best procedure to obtain its low-temperature crystal form. To assure the highest quality product, it is preferable to melt the halide being prepared under the hydrogen halide. Unfortunately, such melting often precludes the subsequent transfer of the halide product and additional synthesis with this material or the study of it then must often be done in situ. The preparation of fluorides involves treatment with HF, F_2, ClF_3, etc. which is carried out best in nickel or monel equipment. For many studies this necessitates the subsequent transfer of the product to other containers. The preparation and quantitative transfer of an oxygen-free fluoride is very important in one method used for preparing the transplutonium metals. The fluorides or ternary fluoride compounds are also attractive for preparing higher oxidation states of the transplutonium elements. Some of the recent investigations using anhydrous halides of these elements include studies on the structural and chemical consequences of radioactive decay and the determination of their magnetic susceptibility behavior. The preparation and handling of these transplutonium halides will be reviewed.

The preparation of transplutonium metals on a microscale is more difficult than for many other compounds due primarily to the reactivity of the products. Although in principal several preparative techniques could be used for making these metals, in practice only one of two different synthetic routes are normally considered. The first of these is a reduction of the transplutonium oxide by lanthanium or thorium metal followed by the volatilization and subsequent condensation of the actinide metal. The second method is the reduction of a transplutonium fluoride with lithium metal, followed by volatilization of the excess reductant and lithium fluoride. Each procedure has some advantages and some disadvantages. The method of choice depends on several factors, which include the volatility of the actinide metal being prepared, the quantity involved and the desired physical form of the product. The purity of the transplutonium metal is always of prime interest and importance. Their purity is probably more difficult to determine than for many other compounds due to the possible presence of hydrogen, nitrogen and oxygen. The small quantities of metal normally available, especially for the transcurium metals, preclude analyses for these three contaminants. Their presence

or absence in the product is often estimated from the appearance and physical properties of the metal, and the reported purity of the metal is normally based only on the total cations present as determined by mass spectrometry. The discussion of the transplutonium metals will address this question, the methods of preparation and the products that have been obtained, and some of the current research interests in these metals.

Acknowledgement

Many scientists have contributed to our knowledge of the transplutonium elements and the techriques that have been developed to carry out studies of them. Many other people have contributed to the production of these elements. Without this combined effort, our knowledge of the transplutonium elements could not have advanced to its present state.

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NEW ELEMENTS IN THE TRANSFERMIUM REGION

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The discovery and 40-year studies of the chemical and radioactive properties of actinide elements from Np to Md have greatly contributed to the development of natural sciences. During the last 25 years, main efforts in experiments to synthesize new elements have been concentrated on advance in the direction of transmendelevium and transactinide elements. While most of actinides can be accumulated in relatively large quantities in high-density neutron fluxes (powerful reactors, thermonuclear explosions, etc.), the transactinide region has been reached by the new means -- accelerated heavy ions.

Heavy ions have made it possible to extend the Mendeleev Periodic Table from element 91 to element 107, produce and investigate several dozens of new isotopes over the entire range of transuranium elements. Those studies have substantially added to the knowledge of the radioactive properties of the heaviest atomic nuclei and led to the very important conclusion that the stability of transactinide nuclei crucially depends on spontaneous fission. The studies of the chemical properties of element 104 (kurchatovium) have permitted the direct verification of one of the basic implications of the Periodic Law, following which the actinide series ends with element 103 and, as a result, a drastic change in chemical properties takes place as one goes to element 104. Finally, the development of knowledge about nuclear stability against fission has given rise to the hypothesis concerning the possible existence of superheavy elements in the region of magic numbers Z=114 and N=184 (Fig. 1). Subsequently, this hypothesis has obtained a fairly deep theoretical substantiation. The problem of the existence of superheavy elements radically influences the foundations of modern nuclear physics and nuclear chemistry, thus considerably enhancing the importance of further progress in the region of transactinide elements.

An analysis of cross sections for formation of known actinide and transactinide nuclei in different nuclear processes

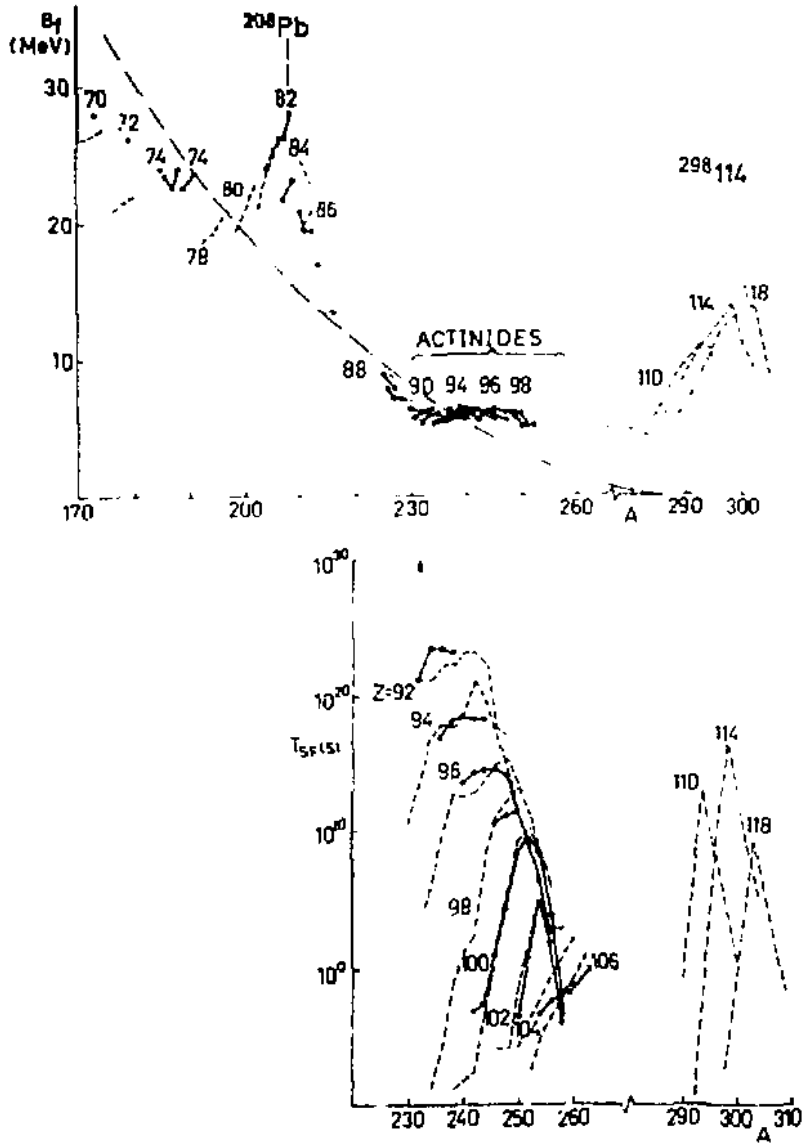

Fig. 1. Experimental (•) and theoretical (-----) values of the fission barrier height B_f (upper part) and spontaneous fission half-lives T_{sf} for heavy and superheavy nuclei. The classical liquid-drop predictions for B_f are shown by a dash-dotted line in the upper part.

involving heavy ions up to ^{238}U, as well as the direct considerations of the results of synthesis of elements through 107 show that fusion reactions are likely to remain the most efficient

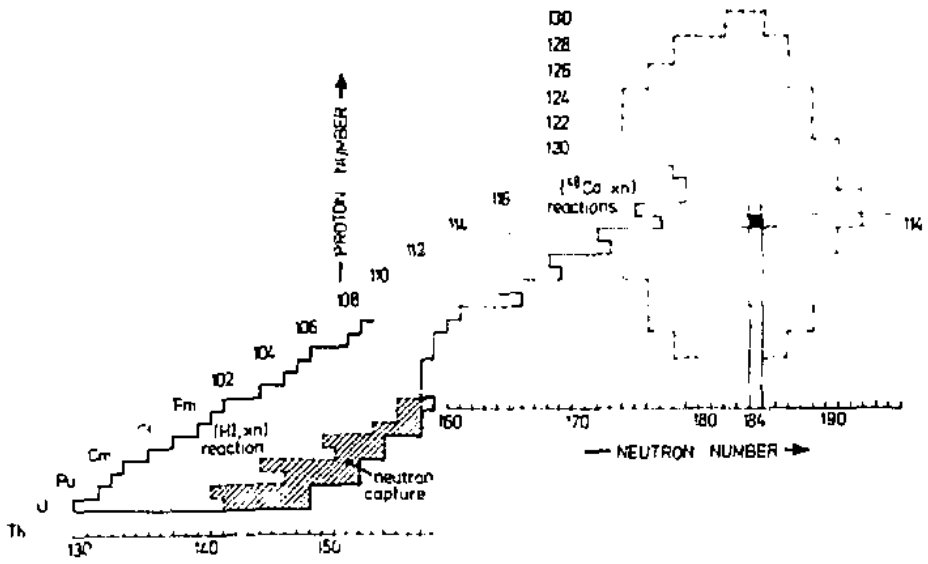

Fig. 2. Possibilities of synthesizing the isotopes of transuranium elements in various nuclear processes.

ones for the synthesis (Fig. 2). Among these reactions, of special interest are those induced by the ^{48}Ca, ^{50}Ti, ^{54}Cr and other ions, which allow one to produce moderately excited compound nuclei with a wide range of Z and N. In recent years, it has been ascertained experimentally that the use of heavy ions with mass A≳50-60, in combination with Pb-Bi targets, leads to formation of transactinide elements and isotopes with Z=104-107. There are sufficient grounds to assume that just this type of fusion reactions, in somewhat different target-projectile systems, is most promising for producing the heavier transactinides with Z up to 114-116. The advent of a new generation of high-current heavy-ion accelerators, such as SUPERHILAC, UNILAC and U-400 allows one, in our view, to substantially extend research into this field.

ISOTOPE IDENTIFICATION IN THE TRANSFERMIUM REGION BY α-α CORRELATION AFTER IN-FLIGHT-SEPARATION

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The investigation of the heaviest nuclei formed in fusion reactions does not only require more and more sensitive detection methods but also demands the extension of the explorable halflife range especially to short halflives. Up to now reaction products are mostly stopped in catchers and gases and transported out of the active target region to the detector positions. These experimental methods are limited to seconds or milliseconds and have the disadvantage of being sensitive also to nuclei formed in other reactions than fusion.

Separation of the unslowed fusion products, taking advantage of reaction kinematics, extends the explorable halflife region to the microsecond region and provides a separation of the nuclei to be investigated from background. The results from this experimental technique, obtained in the transfermium region, will be presented and discussed in the frame of the currently used methods.

Nuclei formed in fusion reactions have the full momentum transfer from the projectile. They recoil in beam direction with a well defined velocity which is considerably lower than that of the projectiles and differs substantially from that of other nuclear reaction products. This velocity is changed only slightly by neutron evaporation during the de-excitation of the compound system or by energy loss in the target. Hence, fusion products can be separated efficiently in-flight with a velocity filter[1].

The separated nuclei are implanted into a surface barrier detector which is sensitive to α decay and spontaneous fission. We use an array of 7 position sensitive detectors: All decays of a certain nucleus implanted in the detector have to be observed at the same position[2]. The time distances between the signal from the evaporation residue impinging the detector and subsequent decays allow to evaluate the halflives of the evaporation residue and eventual daughter decays[3]. A time-of-flight measurement in combination with the energy signal from the nucleus stopped in the surface barrier detector allows to check its velocity and to estimate its mass roughly. Decays of the implanted nuclei are observed in anticoincidence to the time-of-flight or during the 15 ms intervals between the 5 ms beam bursts of the accelerator.

New isotopes can be identified by α decay chains ending in known α-transitions. As few characteristic correlations are sufficient for an identification, this method is sensitive to evaporation residues from fusion reactions formed with cross sections even below nanobarns. The in-flight-separation allows to investigate nuclei with lifetimes down to microseconds.

We investigated fusion reactions of ^{40}Ar, ^{50}Ti, and ^{54}Cr with targets of $^{206-208}$Pb and ^{209}Bi.

With ^{40}Ar on ^{208}Pb we observed all known deexcitation channels of 2n to 4n evaporation leading to $^{246-244}Fm$ reported by various authors. With ^{40}Ar on ^{206}Pb we found the new isotopes ^{243}Fm and ^{239}Cf, for ^{209}Bi irradiations we observed firstly ^{247}Md. In these experiments, where most of the observed isotopes are well known, formation cross sections range from 1.5 nb to 15 nb, halflives range from ms to s and nuclei undergo either α decay or spontaneous fission, we could prove the sensitivity of our experimental technique and the high background suppression of the velocity filter especially with respect to α-active transfer products near Pb.

For ^{50}Ti on ^{208}Pb the isotope $^{256}104$ is formed, which due to results from Oganessian[4] et al. undergoes spontaneous fission with a halflife of about 5 ms. This result indicates a change of the spontaneous fission halflife systematics valid in the actinide region and hence has been questioned. We irradiated at various energies and observed the well known α decay of $^{257}104$[5] indicating the 1n channel and at increasing projectile energy a spontaneous fission activity with $(8.1^{+1}_{0}:^{3}_{8})$ ms halflife and an excitation function of less than 10 MeV width, indicating the formation of $^{256}104$ via 2 neutron evaporation. The observed formation cross section of (6^{+6}_{3}) nb also agrees well with the results from Oganessian.

In an irradiation of ^{207}Pb with ^{50}Ti we found the expected α decay branch of $^{255}104$ discovered in Dubna by its spontaneous fission, and also spontaneous fission of corresponding halflife.

In the fusion reaction of ^{209}Bi and ^{50}Ti we intended to investigate the α decay of the isotope $^{257}105$ to which a spontaneous fission activity of 5 s has been attributed. This isotope plays an important part in the assignment of $^{261}107$ by Oganessian et al. In irradiations at various specific energies between 4.65 MeV/u and 4.95 MeV/u we observed α decays of $^{257}105$ and $^{258}105$, identified by α-α correlations and also spontaneous fission. The exact halflives and decay energies of ^{254},^{253}Lr have been determined and will be presented.

By fusion of ^{54}Cr with ^{209}Bi element 107 could be produced. We observed five α decays of (10376±35) keV energy and $(4.7^{+2}_{1}:^{3}_{5})$ ms halflife and one decay of (9704±50) keV and (115^{+23}_{-15}) ms, partly correlated to decays of $^{258}105$ and ^{254}Lr, observed in the ^{50}Ti on ^{209}Bi irradiations. Some of the chains ended in known transitions of ^{250}Md and ^{250}Fm. We assigned these decays to the isotope $^{262}107$. The spontaneous fission activity observed by Oganessian et al. in the same reaction and assigned to $^{261}107$ was not investigated in our experiment, which was performed to collect as much information as possible on the α decay of $^{262}107$.

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SOLUTION CHEMISTRY OF THE TRANSPLUTONIUM ELEMENTS

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Discovery of the possibility of existence of some transplutonium elements (TPE) in unusual oxidation states is the greatest achievement in the study of chemical properties of transplutonium elements in aqueous solutions. During the time since the International symposium on chemistry of TPE in Baden-Baden (1975) Am(VII) /1/, Cm(VI) /2/, Cf(IV) /3/ were obtained for the first time. At the same time stabilization conditions of Am(IV,V,VI), Cm(IV) and Bk(IV) were found, new methods of their preparation were suggested and their stability was studied. These remarkable achievements are associated with the use of such compounds for the stabilization of TPE in unusual oxidation states as unsaturated heteropolytungstates, phosphoric acid, alkaline and carbonate solutions.

The use of phosphortungstate ions $/PW_{11}O_{39}/^{-7}$ and $/P_2W_{17}O_{61}/^{-10}$ /4/ in the presence of which oxidation-reduction potentials of M(IV)/Me(III) couples are shifted for Pu, Am, Bk and Ce by 0.9-1.0 V into a more negative region /5/ has permitted to obtain rather stable solutions of Am(IV), Cm(IV), Tb(IV), Pr(IV) and for the first time - solution of Cf(IV). The stability of these ions was investigated and the reduction of Am(IV) was shown to take place mainly under the action of radiolysis products, whereas Cm(IV) and Cf(IV) are reduced by water.

In the presence of $K_{10}P_2W_{17}O_{61}$ americium may be quantitatively oxidized to Am(IV) or Am(VI) depending upon existing conditions, even in 3-6 M HNO_3 /6/.

Various methods were developed for the preparation of Am(IV), Am(V) and Am(VI) in phosphoric acid solution under the action of various oxidants including electrochemical oxidation /7/. Pure Am(IV) is formed on the anode in 10-15 M H_3PO_4 and is later reduced to Am(III) and is disproportioning with the Am(III) and Am(VI) formations under the decreasing of H_3PO_4 concentration. The speed of Am(IV) disproportion strongly increases under the decreasing of the solution acidity and because of this during the electrochemical oxidation only Am(VI) is being formed under the concentration of $H_3PO_4 \leq 2$ M.

The reaction involving four americium ions in different states of oxidation: $Am(IV)+Am(V) \rightleftharpoons Am(III)+Am(VI)$ was the first to have been studied experimentally. The reaction of Am(IV) with water was established to be the main cause of its reduction in concentrated H_3PO_4 solutions.

Am(VII) was initially obtained in 3-4 M alkaline solutions in the course of oxidation of Am(VI) at 0°C under the action of ozone or O^- ion radicals formed during γ-irradiation of the solution saturated with N_2O /1/. It can be also produced by disproportioning Am(VI) in 12-18 M NaOH.

The utilization of concentrated carbonate solutions in which oxidation-reduction potentials are shifted into a more negative region by 1.7 V seems to be very promising for the stabilization of the highest oxidation states of TPE. Pr(IV) and Tb(IV) have been recently produced in a 5.5 M potassium carbonate solution /8/.

The method of the impulse radiolysis with a rapid spectrophotometric recording of short-lived products is used very extensively nowadays along with the utilization of chemical oxidants and reductants and electrochemical methods for the preparation of the TPE in unusual oxidation states. This method was used for the preparation of Am(II) and Cm(II) as well as for the preparation of Am(IV) and Cm(IV) in perchlorate solutions /9,10/.

β-Decay can also be used as an oxidation process, thus permitting to obtain an experimental evidence of the existence of hexavalent curium /2/.

The investigation of the oxidation and stabilization conditions of TPE in highest oxidation states has permitted to develop efficient methods for isolation, separation and determination these elements. In the report behaviour of Bk(IV), Am(V) and Am(VI) during extraction using organophosphorous extractants, primary, secondary and tertiary amines as well as quaternary ammonium bases; in ion exchange using organic ion exchangers and inorganic sorbents; in extraction chromatography and during precipitation by various precipitates will be discussed.

The investigations of TPE reduction to a lower oxidation states are still in progress. The results obtained through the use of radiopolarographic and radiocoulometric methods are summarized in the report /11/. The oxidation potential of Fm(II)/Fm(III) couple (found to be close to analogous Yb potential) was determined experimentally through the use of the co-crystallization method /12/. The investigations to prepare Md(I) in various conditions were being continued. The possibility of Md(I) existence in the solutions was indicated in 1972 in the co-crystallization experiments of Mikheev and coworkers /13/. However, possible existence of Md(I) was not confirmed in subsequent work /4,5/. In a new series of the Mikheev and coworkers experiments it was shown that mendelevium is reduced to a monovalent state and co-crystallized with NaCl and KCl in the presence of Eu(II) /16/. On this basis an efficient method was developed for the separation of Md from Fm and Es by co-crystallization of Md(I) with NaCl in water-ethanol solutions. Separation time is 5-7 min and factor of separation of Md- 10^5 /17/. The solubility of MdCl as well as interaction

distances were shown to lie between the appropriate values of NaCl and KCl /18/. Thus, monovalent Md is analogous to the ions of alkaline metals (Na, K) by its properties as also No(II) is similar to Sr and Ca /19, 20/.

In conclusion, some methods of chemical and radiochemical determination of Am in presence of Cm and Bk are discussed.

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SOLUBILITIES OF ACTINIDES IN NEUTRAL OR BASIC SOLUTIONS

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Long-lived actinides and their daughter products would be among the radionuclides that would dominate the biological hazards from the nuclear fuel cycle. It is of prime importance that the chemical behaviour and mobility of these elements in the environment are well understood in order to allow predictions of path ways and doses to man from actinides released in nature. Thus, there is a renewed interest in the solution chemistry of actinides in natural waters, which are essentially neutral or slightly basic solutions. The speciation and solubility of actinides in neutral or basic aqueous solution with particular emphasis on environmental waters, are discussed in this paper.

There are many recent compilations and critical reviews of formation constants for actinide complexes with anions in natural waters (e.g. hydroxide, fluoride, sulphate, phosphate),[1-7] and work on the important carbonate system,[8] and on macromolecular acids (e.g. humic and fulvic acids)[9] are in progress. Considering known or estimated actinide complex formation constants for these anions and their expected concentration ranges in natural waters,[10] it can be concluded that the speciations and solubilities of actinides in undisturbed natural waters are almost entirely related to [11]
- hydrolysis, including formation of polynuclear complexes
- complex formation with carbonate, and possibly
- complex formation with organic macromolecules.[9]

Of prime importance is naturally also the redoxpotential of the water, determining the valence state.

In a geologic system the total analytical concentration is also related to the properties of solids present, since particularly hydrolyzed cationic actinide species in solution tend to be strongly adsorbed on exposed oxide and silicate surfaces.[12-14] Also the presence of strongly complexing anions in the lattice of water exposed solids (e.g. phosphates) will lead to an increased surface adsorption, thus influencing the analytical concentration in solution.

A probable set of complex formation constants and solubility products are suggested, based on measured, or in some cases estimated data, and expected actinide speciations and solubilities are calculated for various waters. The distribution of actinide species between aqueous solution and exposed solid surfaces is discussed. Calculated data are compared with experimental solubility data available in the literature. Some examples of the effects of e.g. chelating agents on the total actinide solubility are briefly mentioned.

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ORGANOACTINIDE CHEMISTRY*

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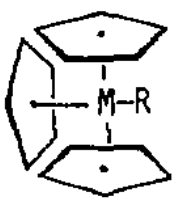
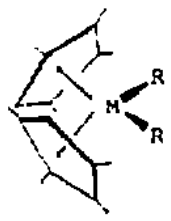
The organometallic chemistry of the actinide elements has been the subject of increasingly intense research activity during the past several years.[1-3] This activity reflects a realization that these important elements have been largely overlooked during the flowering of contemporary organotransition metal chemistry, and that exciting new vistas in structure, bonding, and stoichiometric/catalytic chemical reactivity await exploration.

The purpose of this lecture is to review recent developments in the organometallic chemistry of the 5f elements. Our effort at Northwestern has focused largely on the chemical and physicochemical properties of metal-to-carbon and metal-to-hydrogen sigma bonds (fundamental building blocks of synthetic and catalytic organometallic chemistry),[1-3] while thrusts elsewhere have dealt with other ligand systems (e.g., cyclopentadienyl, cyclooctatetraene, dialkylamide, etc.). The research at Northwestern has been conceptually motivated by the properties of actinide ions which we consider to be unique: large ionic radii, 5f valence orbitals, high oxophilicity, and high kinetic lability. It is seen that if the actinide ion coordination sphere is properly "tuned," it is possible to capitalize upon the aforementioned properties and to develop organometallic compounds with rather extraordinary reactivity.

The cyclopentadienyl, pentamethylcyclopentadienyl, and homoleptic organoactinide hydrocarbyls A-D



A



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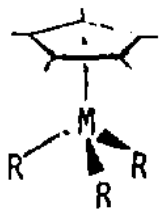

C

MR_4

D

M = Th, U
R = alkyl, aryl, alkenyl, or alkynyl group

range from thermally stable but relatively unreactive triscyclopentadienyls (A), to thermally unstable tetraalkyls (D). The chemistry of the pentamethylcyclopentadienyl derivatives B and C is by far the most diverse. Unusual and instructive reaction patterns include vigorous C-H, H-H, CO, olefin, acetylene, and CO_2 activation. Much can be deduced about the bonding in these compounds from X-ray and neutron diffraction, infrared, Raman, NMR, and optical spectroscopy, magnetic susceptibility, and He-I/He-I photoelectron spectroscopy.

* This work was supported by the National Science Foundation under grant CHE8009060.

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STATUS OF SUPERHEAVY ELEMENT RESEARCH

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A review is given on the search for superheavy elements in nature and on recent attempts to produce them by nuclear reactions. Most of the searches in nature produced negative results but there are at least two observations which might give evidence for the existence of superheavy elements in nature: i) the detection of a spontaneously fissioning activity in the water of the hot springs of the Cheleken peninsula and ii) the determination of weak spontaneous fission activities and of an excess of neutron-rich xenon isotopes in meteorites of the type of carbonaceous chondrites.

For the synthesis of superheavy elements in the laboratory mainly two processes have been attempted: fusion and deep-inelastic reactions. A number of fusion reactions have been studied among them the reaction between ^{248}Cm and ^{48}Ca which provides the closest approach to the predicted island of relatively stable nuclei around atomic number 114 and neutron number 184. All these experiments have failed, delivering upper limits for production cross sections between 4×10^{-32} and 2×10^{-35} cm^2 in a half-life range of 10^{-9} s to 10 yr.

A search was made for superheavy elements in damped collisions of two uranium nuclei using different techniques. No spontaneous fission activity that could be attributed to the decay of superheavy elements was found at upper cross section limits of 10^{-32}, 10^{-33} and 10^{-35} cm^2 for half-lives from 1 to 100 ms, 100 ms to 1 d and 1 d to 1 yr, respectively. The status of the most recent experiments where targets of ^{248}Cm metal were bombarded with ^{238}U-ions is discussed.

PREPARATION OF ACTINIDE METALS

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The actinide elements form a unique series of elements with properties changing from those of the transition elements to those typical of the localised partially filled shell. In the first part of the series (from Pa to Pu) the 5f electrons are similar to the d electrons in the transition metals, in particular they hybridize with the 6d and 7s electrons and participate in the chemical bond. Lanthanide behaviour appears at americium with well localised 5f electrons.

This situation complicates the work of the metallurgist who has to diversify his efforts into different preparation, refining and crystal growth techniques mastering those typical of transition elements as well as those typical of the lanthanides to produce a sufficently large spectrum of samples of the different elements.

Thorium and protactinium metals are obtained by a van Arkel process starting from the carbides. The van Arkel process allows an excellent refining of the metal and small single crystals (up to 5o mm^3) are produced. Uranium, neptunium and plutonium are prepared by the calciothermic reduction of the fluorides and refined by electrolysis in molten salts. Starting with americium, the typical lanthanide metal preparation processes are used. (metallothermic reduction of the oxide by lanthanum (Am, Cf) or thorium (Pu, Cm) or of the carbide by tantalum (Pu,Cm) followed by the evaporation of the metal in vacuum). The metals are refined by evaporation in high vacuum and large single crystals are obtained by physical vapour transport.

ELECTRONIC STRUCTURE I

EFFECT OF PRESSURE ON THE FERMI SURFACE OF UIr_3

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The effect of pressure on the two smallest cross sections of the Fermi surface of UIr_3 (branches α and γ in Fig. 1) has been determined from de Haas-van Alphen measurements in solid He to ~ 4 kbar. In this measurement[1] the position in field, or the phase of a single oscillation, is measured as the pressure is varied and is related to the derivative of the cross sectional area by the simple relation

$$d\ln F/dP = B^{-1}\Delta H/\Delta P$$

where F is the frequency in Gauss and P is pressure.

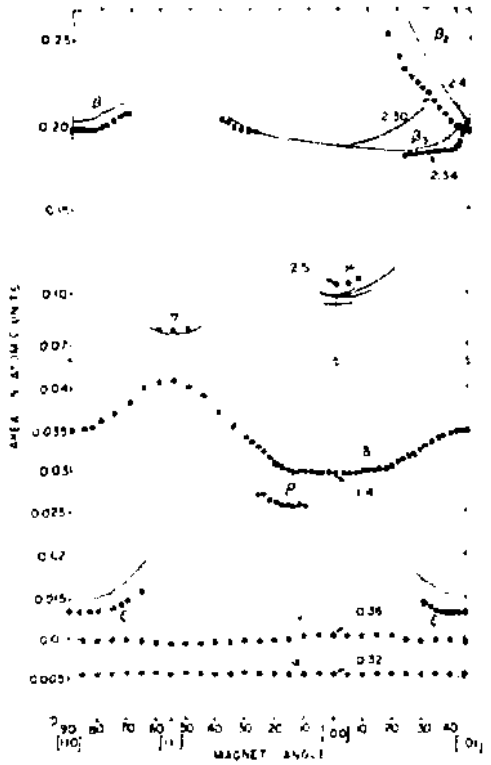

Fig. 1.

We find that the α frequency (2.14 x 10^6G or 0.0057 atomic units) decreases rapidly with pressure: $d\ln \alpha/dP = -1.9\ (\pm 0.2) \times 10^{-3}$ kbar^{-1}. The larger γ frequency also decreases but at the lesser rate: $d\ln \alpha/dP = -1.8\ (\pm 0.4) \times 10^{-4}$ kbar^{-1}. Such a decrease would be consistent with the cursory observation that the comparable frequencies in isostructural and isoelectronic URh_3 (lattice constant = 3.991 A vs 4.023 in UIr_3) are much smaller so that the effect of pressure is to decrease these surfaces. However, in addition to quantitative differences between the two materials, there are also some qualitative differences in the Fermi surfaces. Direct comparisons may not be possible.

The band structure calculation for UIr_3 (shown in Fig. 2) has been extremely successful[2] in mapping out the large M-centered pieces of Fermi surface (frequencies β_i in Fig. 1). The solid lines in Fig. 1 in fact are a result of a theoretical calculation and they are within a few percent of

experiment. The calculation has been less successful for the δ-frequency, while the α and γ frequencies are not found in the present calculation at all. Since the band structure calculation is not self-consistent it is not surprising that it fails to satisfy all parts of the Fermi surface. Relative shifts in the bands can be obtained by slightly changing the electronic potential. It is known[3] that by assigning some s-electron character to Ir (~ 0.2 electrons/atom) the Γ- and (or) R-centered d-bands can cross E_F. In all likelihood, the α and γ frequencies are due to hole pockets arising from these bands. Our present pressure derivatives should be able to distinguish between the two sets of hole pockets in more detailed calculation.

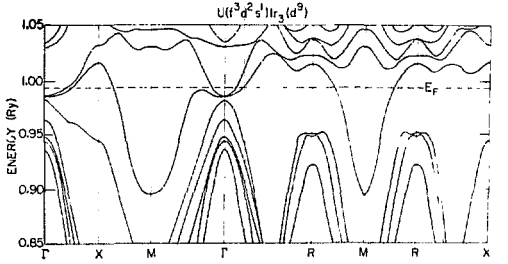

Fig. 2.

We were unable to shift the bellies of the large multiply-connected electron surface β_1 because of their sensitivity to orientation. Nor were we able to separate the ζ or δ frequencies from the strong harmonics of δ sufficiently to obtain pressure derivatives. Clearly these would be useful in any future calcualtions as a function of atomic spacing. We believe however that enough data already exists to make clear identifications.

*Work supported by the U.S. Department of Energy under contract AT(29-1)-789.
**Work supported by the U.S. Department of Energy.

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ANGLE RESOLVED PHOTOEMISSION IN UPd_3*

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We have made angle resolved photoemission measurements in UPd_3 (using 16.8, 21.2, and 40.8 eV incident photon radiation and a standard Vacuum Generators ADES-400 spectrometer) in order to verify the expected non-dispersive nature of the localized f-level, versus the dispersion of the filled d-bands.

Neutron scattering experiments of Murray et al.[1] have shown that hexagonal UPd_3 exhibits well-defined magnetic excitations which are consistent with crystal field transitions in a $5f^2$ configuration. In addition, specific heat measurements of Andres et al.[2] show that the γ-value of UPd_3 can be no larger than 5mJmole^{-1}K^{-2} indicating a low density of states at E_F. All this points to a localized f-level near E_F which apparently has been observed by Baer and Ott[3] in their XPS measurements (feature A in bottom spectrum of Fig. 1). Their identification of the f-level was based on a comparison with isostructural $ThPd_3$ which contains all features in the XPS spectrum except feature A.

Single cry were prepared by an rf heated floating zone technique and (0001) face was cut from the ingot and mechanically poli , of the surface was accomplished in situ by argon ion sputter annealed at ≈ 600°C. Auger spectroscopy and LEED were used to characterize the surface and orient the sample in situ along the $(10\bar{1}0)$ and $(11\bar{2}0)$ azimuths.

Our UV photoemission spectra from the (0001) face of UPd_3 at normal emission are shown in Fig. 1 (curves 2-4) for 3 photon energies in the $[11\bar{2}0]$ azimuth. Shoulder A is clearly observed in the 40.8 ev spectrum but not at lower energies. This is consistent with previously observed[4] energy dependence for f-electron photoabsorption cross-sections and can be identified unambiguously as an f-level. Peaks H and J in the 16.8 eV spectrum (curve 5) are seen only at low photon energies and $k_{||} \neq 0$, and are likely due to uranium 7s levels.

Peak positions (relative to E_F) are plotted versus the parallel component of momentum ($k_{||}$) in Fig. 2. Note that shoulder A at -0.7 eV is totally non-dispersive within experimental error. This total lack of dispersion is consistent with a localized f-level and indeed may prove useful in future measurements to determine the degree of localization.

There is small but definite dispersion in the d-band spectra (-2 to -5 eV). We have connected the peak positions with lines which we believe are a reasonable representation of the band structure. However, without a band structure calculation we cannot be certain that we have connected the data points properly.

There is almost complete correspondence in peak positions between the 21.2 eV and the 40.8 eV spectra for peaks A-E. Indeed, even the 16.8 eV peak positions correspond except that additional peaks F, G, H and J are

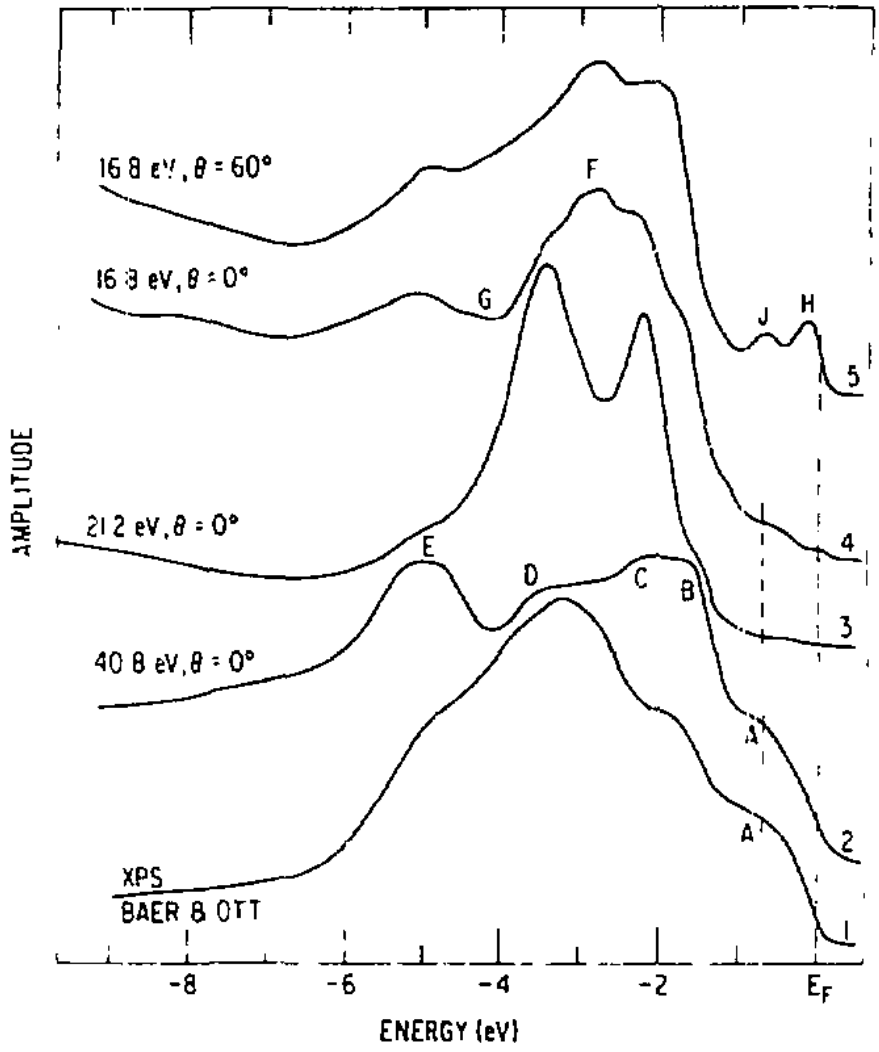

Figure 1.

observed. Thus, we believe that peaks in the spectra correspond to peaks in the one-dimensional densities of states. A band structure calculation would prove most useful. A first glance might indicate that peak J closely corresponds to the localized f-level observed with 40.8 eV light, but the clear dispersion of this branch (J) rules out the correspondence. It does however raise interesting questions as to why there is no hybridization.

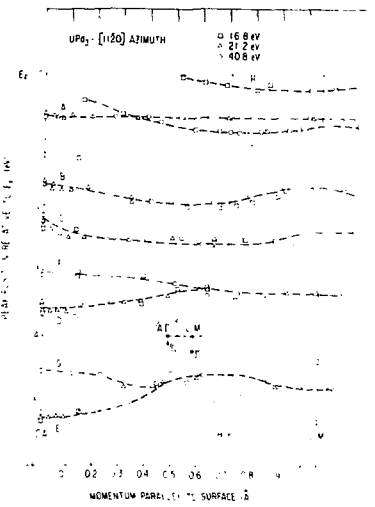

Figure 2.

*Work supported by the U.S. Department of Energy.

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PHOTOEMISSION SPECTROSCOPIC STUDY OF THE URANIUM INTERMETALLIC COMPOUNDS USi_3, UGe_3, UAl_2 and UFe_2*

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This study examines the electronic band structure in the valence band region of the cubic Laves phase compounds UAl_2 and UFe_2, and the Cu_3Au-type compounds USi_3 and UGe_3, using both x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). This combination of techniques enables us to observe the valence band features using a significant range of photon energies, 21.2 and 40.8 eV from a He discharge UV source and 1486.6 eV from an Al anode x-ray source. This can aid in peak identification because initial states of different orbital angular momentum character have photoemission cross-sections which exhibit different dependences on excitation energy.[1]

The measurements were taken on a Physical Electronics model 548 spectrometer equipped with an auxiliary rare-gas discharge lamp. Bar shaped samples were prepared which could be fractured in ultra high vacuum ($\sim 10^{-10}$ torr) to expose a fresh clean surface for examination.

UPS spectra on UAl_2 have been previously taken and discussed by Naegele et al.[2] We have extended the data to include an XPS valence band spectrum (Fig. 1). (All spectra are presented with arbitrary relative scaling.) The spectra show a narrow peak at E_F which grows relative to the other features with increasing photon energy indicating probable 5f character. A partially filled narrow 5f band at E_F would also account for the very high γ value of 142.[3]

Figure 2 shows valence band spectra of UFe_2 taken at three different photon energies. The He(I) and He(II) spectra show a prominent peak about 1 eV below E_F together with a narrow shoulder at E_F. Features at similar positions were seen by Naegele et al. in UCo_2,[2] however, in UCo_2 the narrow peak at E_F grows substantially upon going from He(I) to He(II) whereas in UFe_2 the height of the shoulder remains about half that of the peak at 1 eV in both spectra.

Figure 3 shows XPS valence band data on UGe_3 and USi_3. The overall similarity is striking. Both reveal a narrow strong peak at E_F with a shoulder on the high binding energy side. The peaks at E_F are almost certainly 5f in character becoming progressively more prominent in going from He(I) to He(II) to Al K_α photoemission spectra (UPS data not shown). The presence of 5f states at E_F is also consistent with the rather high γ values of 20.4 in UGe_3 and 14.0 in USi_3.[4] The only noteable difference between the UGe_3 and USi_3 spectra is the more prominent shoulder in UGe_3.

These photoemission spectra will be analyzed in terms of the known physical properties and electronic structures of these compounds.

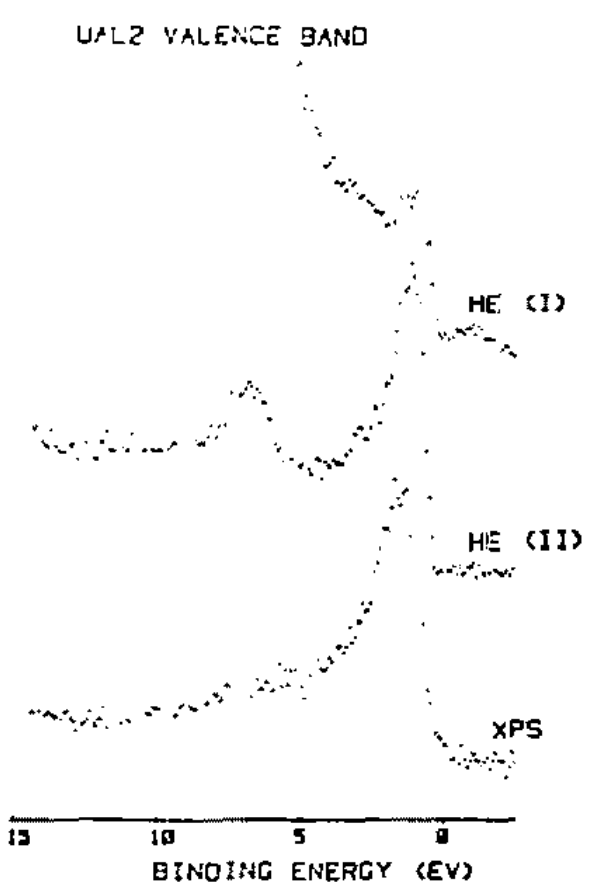
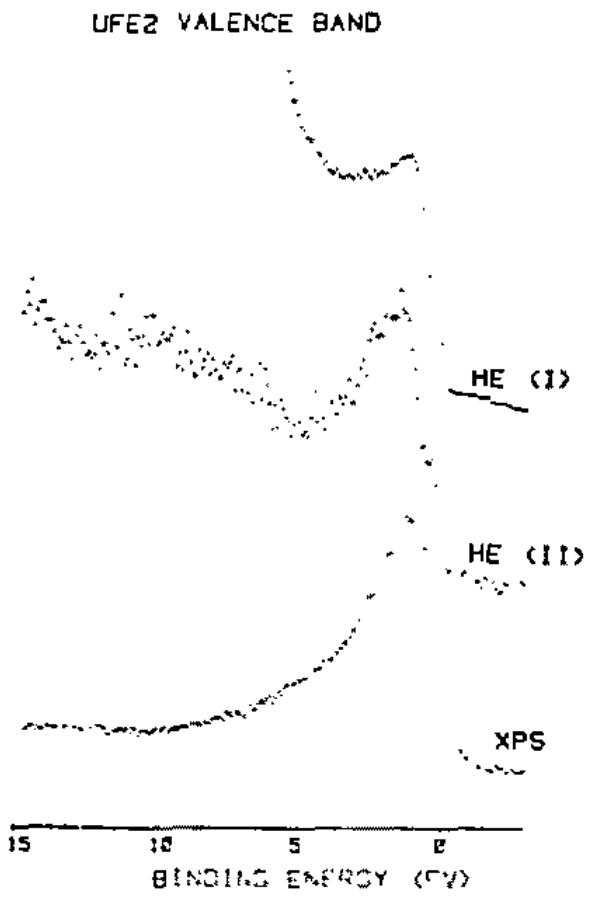

UAL2 VALENCE BAND
HE (I)
HE (II)
XPS
15
10
5
0
BINDING ENERGY (EV)

Fig. 1.


UFE2 VALENCE BAND
HE (I)
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BINDING ENERGY (EV)

Fig. 2.

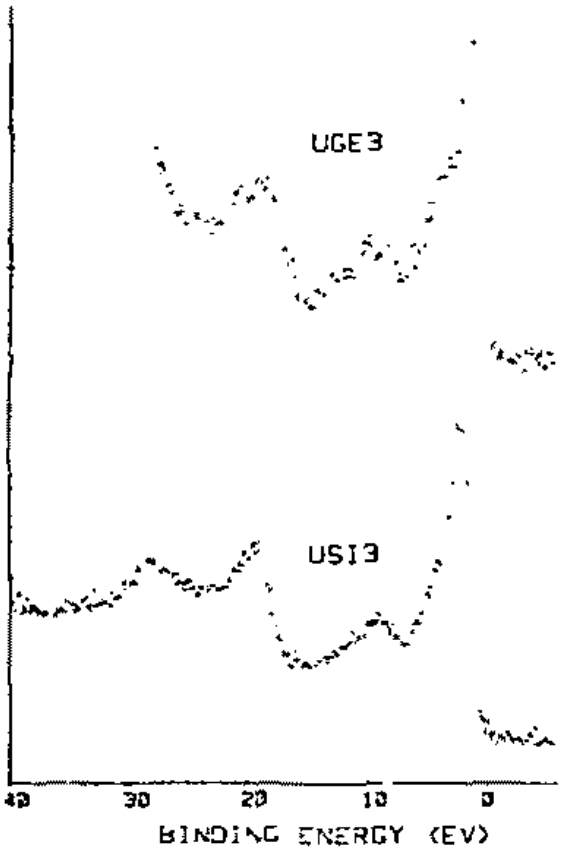

Fig. 3.

*Work supported by the U.S. Department of Energy.

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ITINERANT 5f-ELECTRON BEHAVIOUR IN USn_3 and $U_{0.15}Ce_{0.85}Sn_3$

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Many uranium-halogenides, -chalcogenides, and -pnictides as well as -intermetallic III-group compounds show typical 7 eV-satellite structures in the photoemission spectra. Recently it has been shown that these satellites are due to two hole final states in the photoemission process and that their presence is an indication for a 5f-localization in these compounds[1]. The reason for the increased 5f-localization as compared to α-U and to uranium-transition-metal-compounds was mainly ascribed (aside from increased interactinide spacings and therefore reduced 5f-5f overlap) to a decrease of the f-d hybridization in these compounds.

In this context the compounds USn_3 and $U_{0.15}Ce_{0.85}Sn_3$ have been investigated by means of X-ray photoelectron spectroscopy (XPS). These compounds crystallize in the Cu_3Au structure with lattice constants a=4.626 Å and a=4.720 Å, respectively. The samples have been prepared separately in an arc furnace under reduced Argon atmosphere, have been mixed appropriately, remelted several times and annealed for one week at 800°C. An X-ray structure analysis yields reflexes which are in accordance with the literature for USn_3 and pure $CeSn_3$.

The XPS-measurements were performed with a VG-ESCA-3 electron spectrometer with a resolution of about 1 eV mainly due to the inherent $AlK\alpha_{1,2}$ X-ray linewidth. The base pressure in the spectrometer chamber was about 4×10^{-10} Torr.

Fig. 1 shows the XPS-valence band spectrum of USn_3. Formally it can be described by a superposition of the valence band spectra of α-U and Sn where the sharp structure in the vicinity of E_F can be ascribed to the 5f-electrons, the shoulder at approximately 3 eV to the U6d and Sn3p and the hump at about 7 eV to the Sn5s electrons. Fig. 2 shows the U4f region of the two compounds USn_3 and $U_{0.15}Ce_{0.85}Sn_3$. The energetic line positions at 377.4±0.2 and 388.4±0.2 eV show that uranium (and Ce) have a valency of 3+ in these compounds. Both spectra show a satellite structure 15.2 eV below the main lines which by comparison with the Sn 3d spectra (not shown) can be attributed to 2 plasmon losses.

Both core-level spectra show no sign of a 7 eV satellite indicating a predominantly itinerant character of the 5f electrons in these compounds. Since a direct 5f-5f overlap due to the large interatomic U-U spacings (4.6 Å and 6.5 Å mean separation, respectively) can be excluded, a strong hybridization of the 5f states with conduction electron states is concluded[2] to take place. Bandstructure calculations of Arko and Koelling

on the isoelectronic and isostructural compound UGe_3 predict a strong 5f-4p hybridization caused by the contribution of the 5f electrons to π-bonding with the Ge 4p orbitals. Thus the present measurements seem to confirm this model: In analogy to the f-d hybridization in uranium-transition-metal-compounds an f-p hybridization in USn_3 and $U_{0.15}Ce_{0.85}Sn_3$ leads to itinerant 5f electron behaviour.

+ This work was supported by the Deutsche Forschungsgemeinschaft, Sfb-161.

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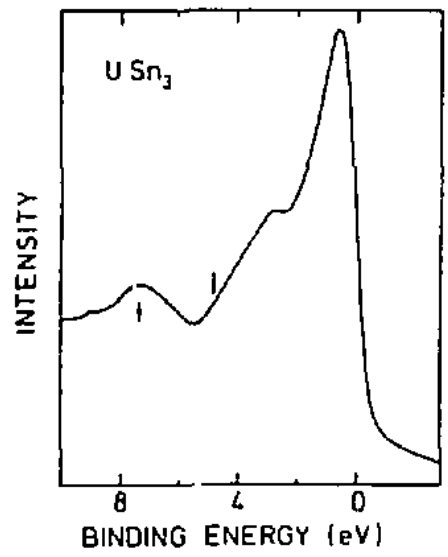

Fig. 1

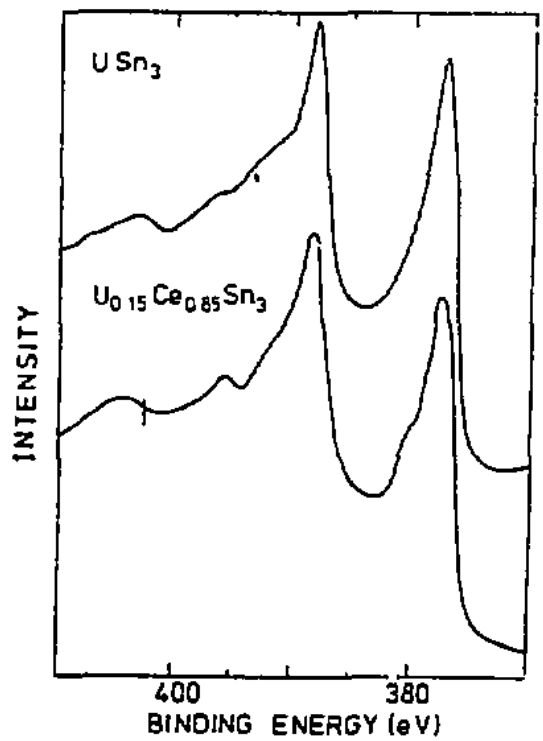

Fig. 2

X.P.S. STUDIES ON BINARY AND TERNARY URANIUM COMPOUNDS IN THE SOLID STATE

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The contribution of X-ray photoelectron spectroscopy to the knowledge of electronic structure and chemical bonding with uranium is analyzed, mainly from unpublished results obtained with monochromatized Al Kα radiation.

The compounds studied are oxides, halides and oxyhalides ; also chalcogenides and pnictides. Samples (often difficult to prepare) were obtained from various sources[1], and had to be handled under inert conditions. In spite of this, surface oxidation remains a major difficulty of this research.

The results will be analyzed in a threefold way, taking into account all aspects of the experimental data which make X.P.S. a powerful technique : simultaneous observation of core levels - with their satellites - and valence levels ; surface selectivity.

1. An approach to defining ionicity as a function of U 5f electronic populations, using different degrees of oxidation and different halides.

2. A discussion of bonding in the uranium - oxygen system, as a function of the proportion of oxygen : degrees of oxidation, role of uranyl groups.

3. A summary of contamination problems, and some conclusions as to their interest for the understanding of solid state chemical properties.

+ Holder of a fellowship of I.R.S.I.A.(Belgium) from 1975 to 1978.
1. We gratefully acknowledge in particular the cooperation with Drs.H.NOEL and J.C.LEVET, Université de Rennes, Laboratoire de Chimie Minérale B (France), and Dr. R.TROC, Institute of Low Temperature and Structural Research of the Polish Academy of Sciences, Wrocław (Poland).

ANGLE RESOLVED PHOTOEMISSION OF UO_2*

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Angle resolved photoemission spectroscopy (ARPES) taken with 21.2 (HeI) and 40.8 eV (HeII) exciting radiation were obtained on single crystal samples of UO_2.[1] Spectra were taken on lightly sputtered samples that showed a simple LEED pattern characteristic of a cubic surface.

The dotted line of Fig. 1 shows a smoothed energy distribution curve (EDC) for $h\nu$ = 40.8 eV taken at 18° from the (100) sample normal. The solid curve is the (smoothed) second derivative. The sharp peak at 1.5 eV (dots) is a localized 5f electron peak. The broad band centered near 5 eV binding energy contains electrons that predominately originate from O 2p orbitals. Features in the normal spectrum (dots) are weak but they are adequately enhanced in the second derivative.

Second derivative minima (arrows in Fig. 1) are monitored as a function of electron emission angle to establish the region of the Brillouin zone from which the electrons were excited.[2] The plane $\Gamma X \Gamma' X'$ in Fig. 2 shows the region of the Brillouin zone examined in this study. For a given θ (which defines $k_{||}$, the crystal momentum parallel to the sample surface) the spectrum monitors those electron states along a line parallel to the ΓX line.

Figure 3 shows a composite of the second derivative minima, taken at various electron emission angles, plotted versus $k_{||}$. Data for both HeI (squares) and HeII (dots) radiation are included. A significant amount of dispersion occurs in the "O 2p" bands. Symmetry should occur about the X' point shown as the dotted line in Fig. 3.

The nondispersive 5f maximum is located at 1.5 eV (solid line). A prominent shoulder appears in the second derivative EDC's at 2.3 eV. This nondispersive feature may be associated with the $^2F_{7/2}$ final state multiplet of the localized 5f level; the strong peak at E = 1.5 eV being associated with the $^2F_{5/2}$ multiplet.

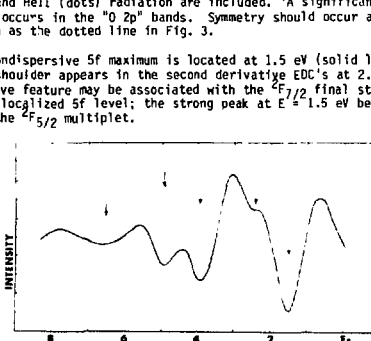

Fig. 1.

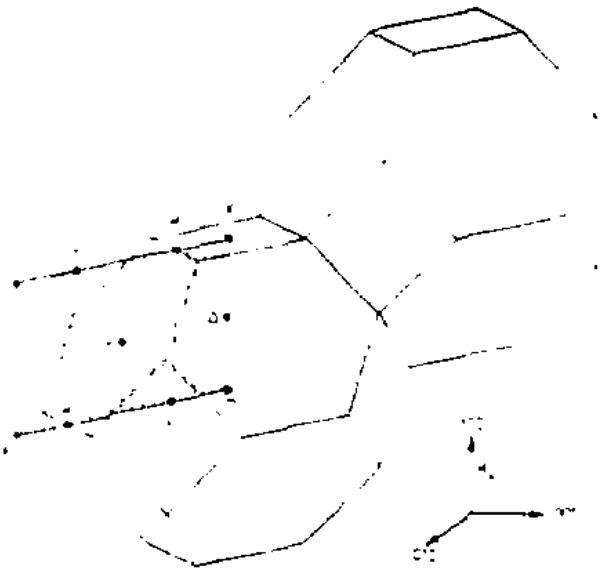

Fig. 2.

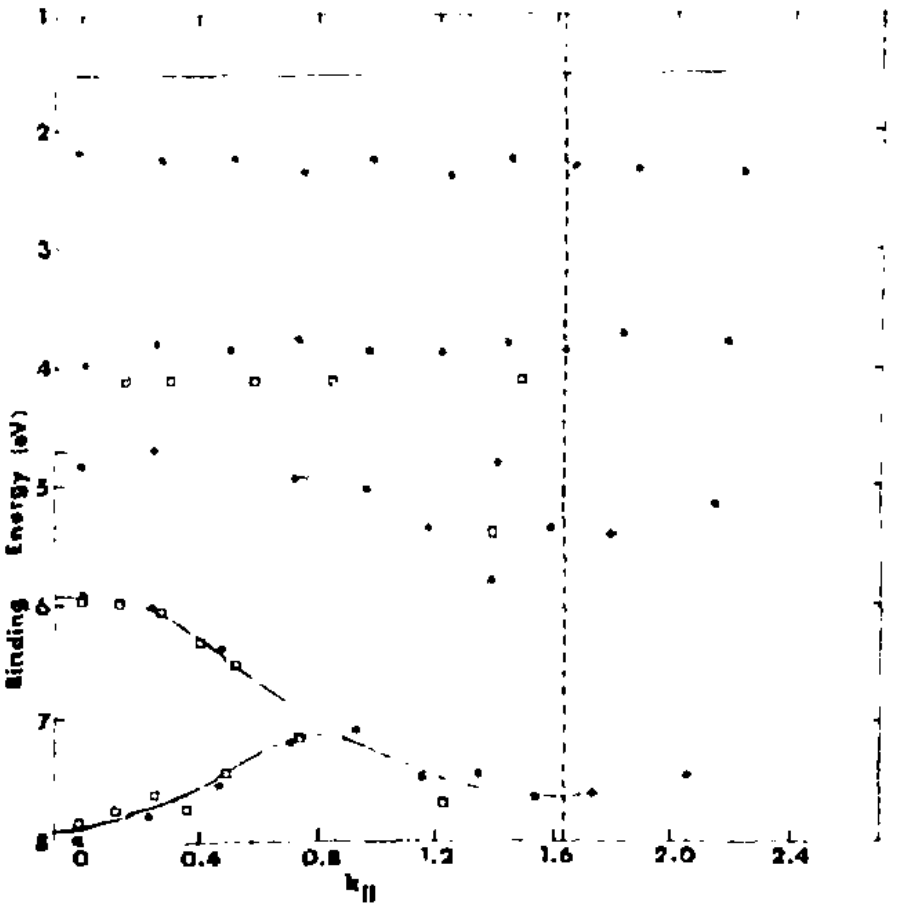

Fig. 3.

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ENERGY DEPENDENT PHOTOEMISSION OF UO_2, NpO_2 AND PuO_2:O2p AND An5f CONTRIBUTION TO THE VALENCE BAND

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Energy dependent photoemission measurements of the valence band region (UPX, XPS) have been published only for UO_2[1,2,3,4]. To the best of our knowledge, only one XPS study has been published[5] for the oxides of the transuranium elements. These data are interpreted mostly on the basis of the final-state multiplet structure of the f^{n-1} configuration. Due to the much higher photoemission cross section of f than p electrons for X-ray excitation the contribution of bonding electrons (mainly O2p) to the observed spectrum is thought to be small for oxides higher than UO_2.

The main aim of this study was therefore to separate the different contributions of the bonding electrons from the localized f electrons by using different photoemission excitation energies: 21.2eV(HeI), 40.8eV(HeII) and 48.4eV(HeII*). The photoemission spectra were obtained by using a Leybold spectrometer with a modified UHV preparation chamber (base pressure $5 \cdot 10^{-9}$Pa) for work under glove box conditions. The energy resolution was 1.0eV for MgKα excitation, 45 meV for HeI and 85 meV for HeII excitation. The base pressure in the analysis chamber was $8 \cdot 10^{-9}$Pa. Polycrystalline samples of NpO_2 and PuO_2 (ion sputter deposited layers+, molten bulk samples++) and single crystals of UO_2 were used. The samples surfaces were cleaned in situ by different methods like Ar^+ and O_2^+ sputtering, annealing at different O pressures and temperatures, and mechanical scraping with an Al_2O_3 file.

The UPS valence band spectra varied strongly with the surface preparation whereas the XPS valence band spectrum was not influenced and gave the published results[5,6]. Especially for PuO_2 the valence band emission varied seriously with a surface contamination from adsorbed oxygen[7].

Figure 1 shows the valence band for the cleanest An-oxides. These spectra show for the first time clearly a separation of the "2p" valence band and the An5f level. The spectrum for 21.2eV excitation for which the 2p cross-section is much larger that that for 4f electrons is dominated by 2p emission as seen in Fig.1. Only weak structures occur at about 2eV and 6 to 7eV. For higher excitation energies these structures become stronger. Especially the 2eV peak is dominant at 48.4eV excitation, showing the effect of the increasing cross-section for 5f electrons. Thus the f-character of this peak is clearly identified.

Due to localization of the An5f electrons in the oxides a final-state multiplet structure is expected. Theoretical calculation[8], predict 2, 4 and 6 emission lines for UO_2, NpO_2 and PuO_2 respectively which are not observed in the spectra. Only for PuO_2 the HeII* spectrum shows a second strong line at the bottom of the valence band, in addition to the O2p and Pu5f peaks. This indicates a 5f emission. Assuming the final state multiplet theory to be valid, this peak may be attributed to the ^4F state whereas the ^4G state could be

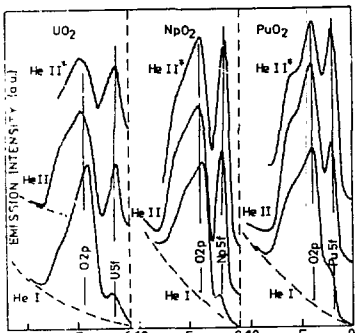

Fig.1

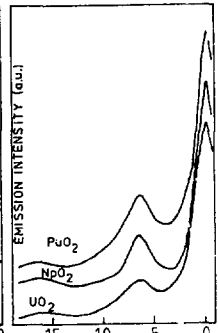

Fig. 2

hidden in the 2p emission. Multiplet components are presumably not resolved due to strong phonon broadening. A more detailed comparison with multiplet intensity calculation[5,8] will be given; covalent contribution by 5f electrons to the bonding will be discussed as well.

Figure 2 shows the actinide 4f core levels and its satellites. The main satellite for all oxides is separated by 6.9eV from the An4f$_{5/2}$ peak on the high binding energy side. The intensity of this line varied with the surface conditions for PuO_2: the higher the O1s to Pu4f intensity ratio the higher is the 6.9eV peak. This gives further evidence that the 6.9eV peak has to be assigned to an excitation from the p valence band to an unoccupied localized An5f level[6,7](shake-up). The second satellite (16.0-17.0eV) is assigned to an energy loss process. The close similarity of the spectra for UO_2, NpO_2 and PuO_2 supports the assumption that the valence band is essentially the same for the three oxide.

+ We are thankful to Dr. J. Kwinta, Paris, for providing the NpO_2 and PuO_2 films.

++We are thankful to Dr. K. Richter and Dr. C. Sari for providing bulk samples of PuO_2.

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ELECTRONIC STRUCTURE OF UO_2

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We have calculated the electronic structure of UO_2 using several different techniques in order to interpret and correlate XPS, UPS and BIS data on this compound.

First a self-consistent-field (SCF) energy band calculations was performed using the LAPW (non-muffin tin) method.[1] Next a SCF Multiple Scattering X_α cluster[2] calculation (UO_6^{8-}) was performed. Both calculations were relativistic.[3,4] Transition state energies[5] were calculated in the cluster to obtain some estimate of relaxation energies. The results of these calculations were compared with previous band[6] and cluster[7] calculations on this system.

Using our calculational results we have tried to interpret and correlate the following experimental data:

(1) The optical gap[8] and the density of states of the unoccupied levels as seen in the BIS experiments.[9]

(2) The structure in the valence band (oxygen-2p) as seen in the UPS data[10a] and the 5f peak.[10b]

(3) The XPS peaks below the valence band (6p and 2s).[11]

(4) The XPS data in the 5p and 5s region (atomic origin).[12]

(5) The XPS data in the 4f energy region (bulk effects).[13]

Using all this information, we can comment on the role of the 5f electrons in this system (localized-vs-nonlocalized).

*Work supported by the US DOE.

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SIGNIFICANCE OF 6d VS. 5f ELECTRONS IN ACTINIDE SYSTEMS

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Similar to the 4f electrons in the rare-earth series, the actinides and their compounds are believed to be determined by the 5f electrons.[1,2] In contrast to this belief, we have found in a systematic study of single crystal U and Th pnictides and chalcogenides using high resolution ($\Delta E \leq 150$ meV) photoemission with synchrotron radiation ($10\ eV \leq h\nu \geq 130\ eV$) that the 6d electrons also play a significant role and can strongly influence the electronic properties near E_F. Furthermore, they are crucial in understanding the complex magnetic behavior in these compounds. Our results in particular are:

a) We can distinguish 5f and 6d emission and have determined their energetic positions via hν-dependent photoemission measurements including resonant 5f photoemission at the 5d → 5f threshold.

b) For the first time we observe different photoemission density of states for U-pnictides and -chalcogenides (see e.g. Fig. 1). We find that U has a quasi-localized $5f^{1-\delta}$ configuration (features B and C) in resonance with itinerant 6d states (e.g. feature A) that become increasingly filled in going from USb to UTe.

c) We find a similar filling of 6d electrons at E_F with increasing Th concentration in $U_xTh_{1-x}Sb$. Assuming that the 6d-moment is polarized antiparallel[4] to the 5f-moment, we can explain the decreasing ordered moment M for $1.0 \geq x \geq 0.3$. In particular, we see no evidence for a valence change towards an $U\text{-}f^2$ configuration as proposed by Cooper et al.[5] to explain this decrease of M.

* Work supported in part by the Air Force Office of Scientific Research under Contract No. FY9620-80-C0025.
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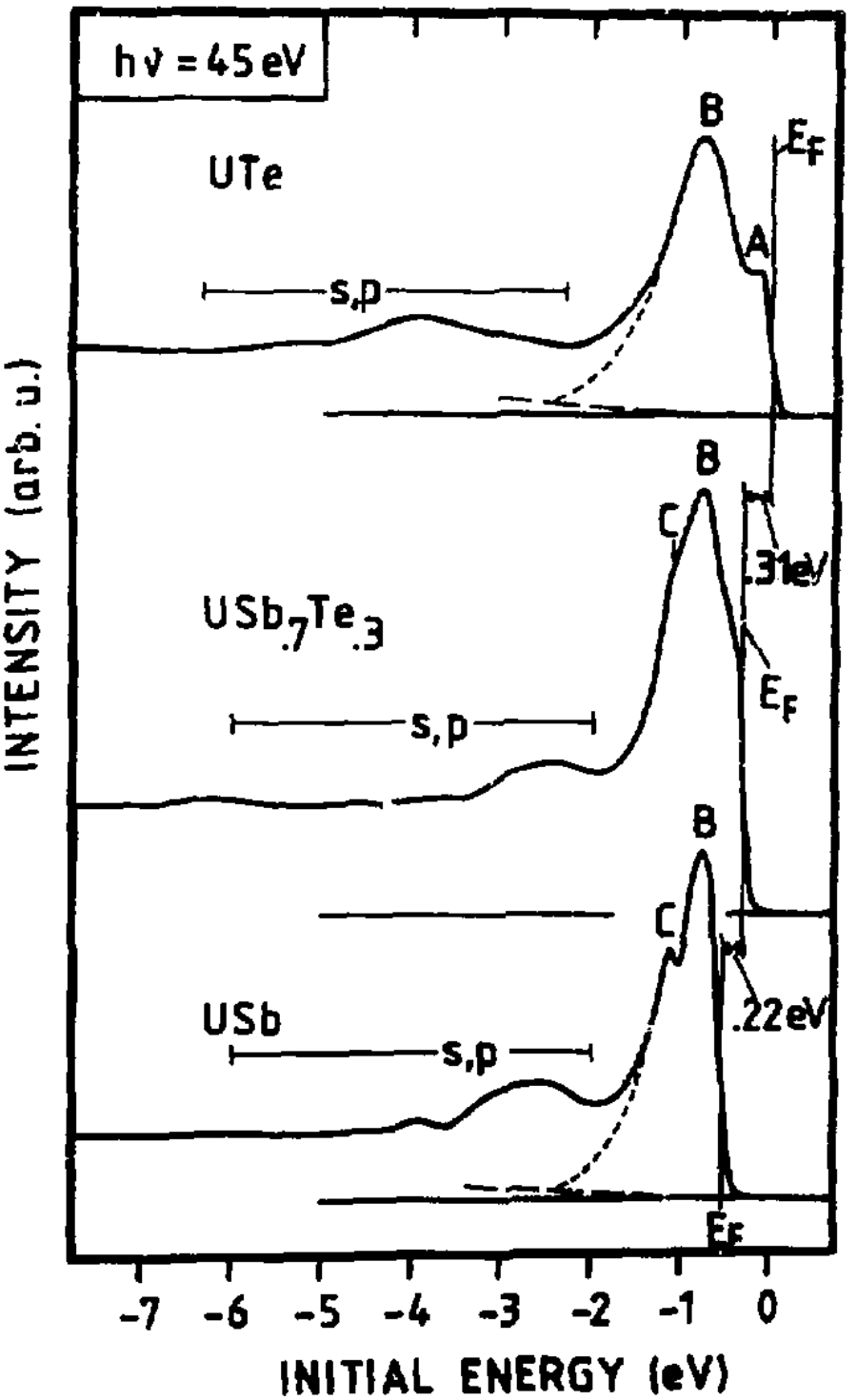

Fig. 1 Energy distribution curves at hν = 45 eV for USb, $USb_{.7}Te_{.3}$, and UTe at room temperature. The curves are not normalized. Zero energy corresponds to the Fermi level of UTe. The spectra are aligned so that peaks (B) coincide. The resulting shifts of E_F for $USb_{.7}Te_{.3}$ and USb are -0.31 eV and -0.53 eV, respectively (from Ref. 6).

IMPORTANCE OF FINAL STATE COUPLING IN THE 5f·6d EXCITATION OF UO_2

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High field Faraday-rotation and magnetic circular dichroism D measurements (up to 100 kOe) of UO_2 in the photon energy range between 1.4 and 5.4 eV are reported for different temperatures below and above the Néel temperature T_N = 30.6 K. The measurements have been performed on thin films prepared by evaporation of UO_2-single crystals from a Knudsen cell onto heated fused quartz substrates.

The absorptive part of the off-diagonal conductivity tensor element

$$\mathrm{Re}\ \sigma_{xy} = \frac{c}{2\pi}\ (n_+ - n_-)$$

has been derived using the measured magneto-optical and optical data. [1] The results for an external magnetic field of 40 kOe and a temperature of 33 K are shown in Fig. 1. The inserted vertical

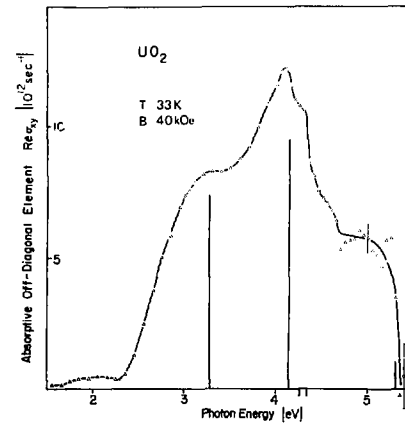

Fig. 1

bars represent the calculated relative magneto-optical oscillator strenghts which will be discussed below.

It has been shown that in the energy range of our experiments transitions from the $5f^2$ ground state into 6d states predominate [1]. Only at the high energy side at about 5 eV an onset of p-d transitions is expected [1,2].

Due to the lack of results for the coupling mechanism in the 5f6d final state, we have used in our calculation both possible approximations, namely LS- and jj-coupling. Fig. 2 displays the energy level scheme of the $5f^16d^1$ multiplet for both treatments in a second order perturbation calculation. The spin-orbit parameters ζ_{5f} = 2173 cm^{-1}, ζ_{6d} = 3200 cm^{-1} and the Slater-Condon parameters G^k and F^k have been derived from U^{4+} ... ie ion spectroscopic measurements [3,4]. The LS-coupling treatment shows no agreement with the experiment. The magneto-optical oscillator strenghts displayed in Fig. 1 by the vertical bars represent the jj-coupling calculation which reproduces very well the two domi-

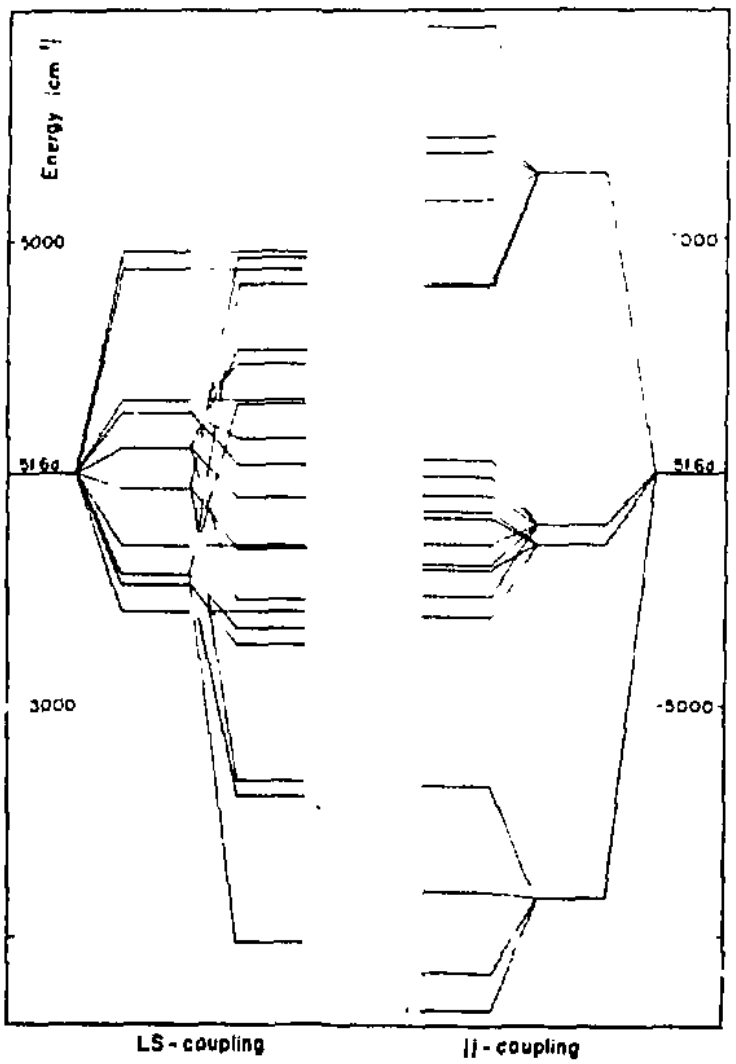

Fig. 2

nant structures at 3.25 and 4.15 eV. The peak at 5.1 eV cannot be explained in terms of a $5f^2 \rightarrow 5f^1 6d^1$ transition but has to be assigned to p→d transitions in agreement with optical spectroscopy [1] and XPS-BIS measurements [2].

Thus our magneto-optical study shows the importance of the coupling between the excited and the remaining 5f electron in the final state and it evidences that this coupling is of the jj-type.

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OPTICAL STUDY OF THE ELECTRONIC STRUCTURE OF UPd_3 AND $ThPd_3$

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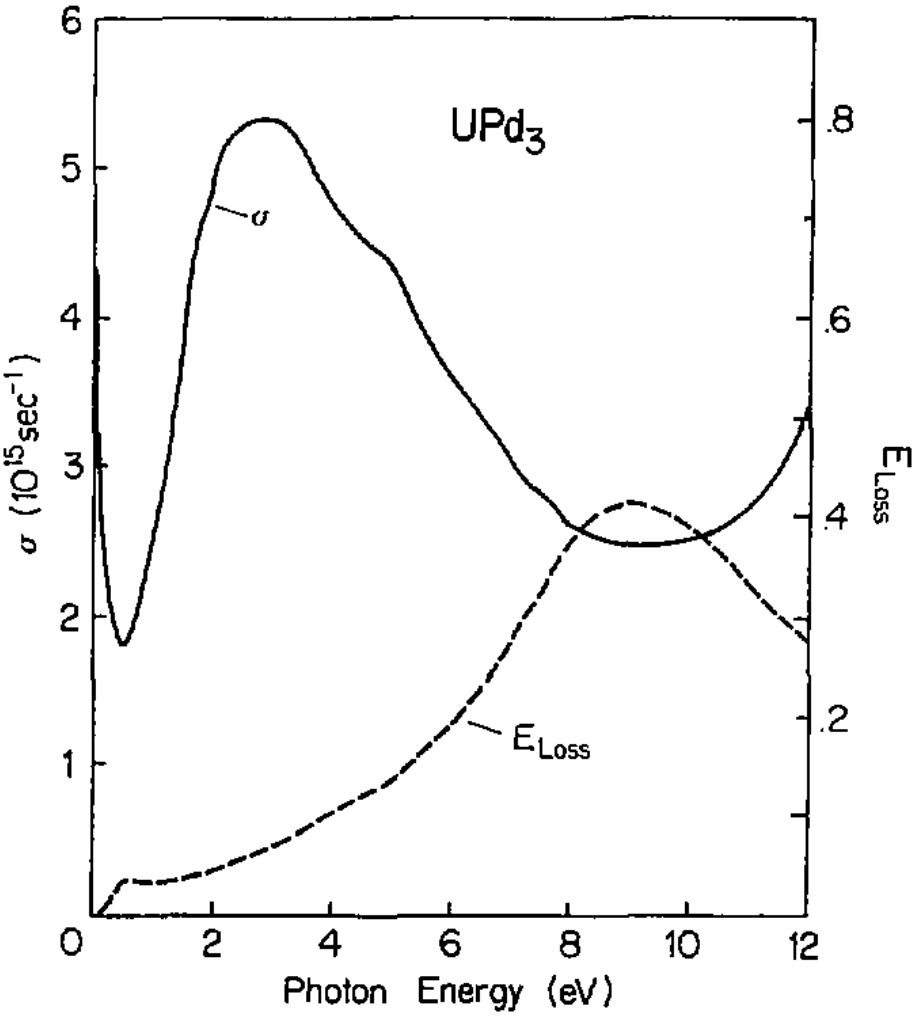
The intermetallic compound UPd_3 has attracted considerable interest the last few years due to: i) the observation of non magnetic phase transitions at low temperatures [1,2], and ii) evidence for a localized $5f^2$ ground state provided by inelastic neutron scattering [3,4] and electron spectroscopy [5] experiments.

We present the first optical investigation of UPd_3 together with the isostructural $ThPd_3$. From the former material both a single crystal oriented perpendicular to the hexagonal c-axis and a polycrystalline sample have been studied. $ThPd_3$ was only available in polycrystalline form.

The near normal incidence reflectivity has been measured at room temperature from 0.03 to 12 eV. The reflectivity spectra have been Kramers-Kronig transformed to obtain the complex dielectric function, the optical conductivity, the energy loss and the number of electrons contributing to optical transitions as functions of the photon energy.

Fig. 1 displays the real part of the optical conductivity (full line) and the energy loss function (dashed line) for the UPd_3 single crystal. The optical conductivity shows extremely weak intraband transitions at low energies but strong interband transitions with structures at 1.8, 2.8, 4.5, (6.5) and 7.5 eV. For $ThPd_3$ the same structures are found with the exception of the weak structure at 6.5 eV which is not resolved. Subtracting the optical conductivity spectrum of $ThPd_3$ from the one of UPd_3 one finds a further peak near 1 eV for UPd_3 whose presence is also evident if one compares directly the reflectivity spectra of the two materials. The peak at 1 eV is attributed to transitions from the $5f^2$ state of uranium to empty 6d states forming the conduction band. The other structures present in both compounds are assigned to transitions between the occupied 4d valence bands and empty p,s conduction bands derived from Pd.

It is noteworthy that the optical conductivity and the XPS [5] spectra of UPd_3 are nearly identical in respect to the shape as well as to the energies of the structures. This indicates that the final states play a minor role for the observed excitations



in agreement with our assignment of rather free electron like p- and s- character to these states. In addition it follows that the final states of the optical excitations are very close to E_F. The small intraband contributions to the optical conductivity of UPd_3 compared to the one of pure Pd [6] evidences the filling of the Pd 4d band in UPd_3 in agreement with XPS and BIS [5]. The four electrons per formula unit in excess of the $[Kr]4d^{10}$ configuration of Pd^0 and the $[Rn]5f^2$ configuration of U^{4+} give rise to a plasma excitation as shown by the maximum at 9 eV in the energy loss function (Fig. 1).

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CALCULATED ENERGY POSITIONS OF THE 5f LEVELS FOR THE HEAVIER ACTINIDES

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The recently growing interest in applying photoelectron spectroscopic methods to actinide materials has mainly been concentrated on Th- and U-compounds. In the near future, however, these methods might be expected to become more extensively applied also to the heavier actinide systems. Thus, for example, it becomes of considerable interest to calculate the position of the 5f level for the transplutonium metals. Such a calculation is performed in the present contribution, where a similar method is applied as was earlier used successfully for the calculation of the position of the 4f level in the lanthanide metals.[1] Also the positions of the 5f levels for surface atoms relative to bulk atoms (so-called surface shifts) are considered.

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COHESION AND ELECTRONIC STRUCTURE OF THE ACTINIDE METALS

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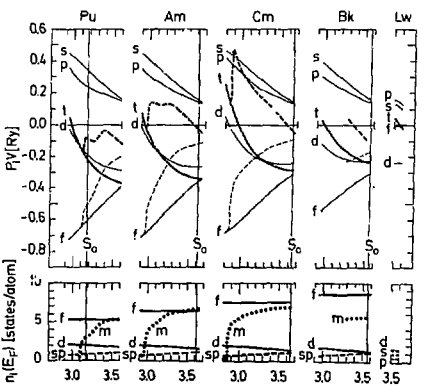
We have applied the local spin density (LSD) formalism in calculations[1] of ground state properties for the series of actinide metals Fr-Cf, Lw. The self-consistent energy band problem resulting from the LSD formalism was solved by the relativistic LMTO method. This allows us to interpret the cohesive properties as functions of atomic volume in terms of a few physically significant quantities. The figure shows partial and total pressures, s-, p-, d-, and f-occupation numbers, and the spin polarization m as functions of atomic radius for those actinide metals which are close to the point where the 5f-electrons have their localization-delocalization transition.



We present the calculated band structures in terms of plots of band edges as functions of atomic radius. We show occupation numbers, state densities at the Fermi level, 5f-bandwidths, and total and projected state densities as functions of atomic number.

The fundamental question of localized versus itinerant behaviour of the 5f-electrons is discussed in terms of the effect of spin-polarization on the partial pressures. We find that the elements beyond Pu have a spin-polarized ground state, and that they will undergo first order phase transitions under pressure (100 kbar for Am[2] and 400 kbar for Cm) which will take them from high volume spin-polarized phases to low volume non-polarized phases. The results may be interpreted in a Stoner type picture in analogy with the case of itinerant magnetism in the 3d-transition metals.

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THE ELECTRONIC STRUCTURE OF ACTINIDE CARBIDES

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The fully relativistic Korringa-Kohn-Rostoker method, with double group symmetrisation, has been used to obtain the electronic band structures of the actinide monocarbides that crystallize in the rock salt structure. These computations, which employed the X_α exchange approximation, are self-consistent, within the usual muffin-tin partitioning of the solid.

The chemical bonding in these compounds is discussed in terms of charge transfer between the scattering regions by decomposing the crystal wave functions and charge densities into their atomic partial wave components. This procedure allows a discussion, for a particular non-metal constituent, of the trends in electronic structure and f-electron localisation across the early members of the actinide series, and complements earlier computations on UC and UN.[1,2] Finally, the use of single-site scattering properties, such as the resonant differential Friedel sums, to give a qualitative picture of the electronic structure is also illustrated, as earlier work has indicated that such properties can give a surprisingly accurate characterisation of the electronic structure.[1,2,3]

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ELECTRONIC STRUCTURE, ELECTRICAL AND MAGNETIC PROPERTIES FOR THE PLUTONIUM-HYDROGEN SYSTEM*

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The plutonium hydrides represent the first actinide-hydrogen system with apparent heavy rare-earth properties. The effects of progressive electron localization are first seen in the high-temperature phases of Pu metal and also in some compounds. A number of studies have been reported for the Pu-hydrogen system in the past,[1-3] and results for the P-C-T relationships, phase diagram and crystal structures are in general agreement. More recent work has been concerned with some of the physicochemical properties of the system, including NMR studies[4] and magnetic behavior.[5]

Sample characterization is extremely important in these more sophisticated studies, and unfortunately all the work has been performed on small powdered samples, often sealed in containers and "heat-treated" to a hoped-for composition. The extreme reactivity of these powdered samples and the strong tendency toward decomposition can make the identity of the sample somewhat questionable.

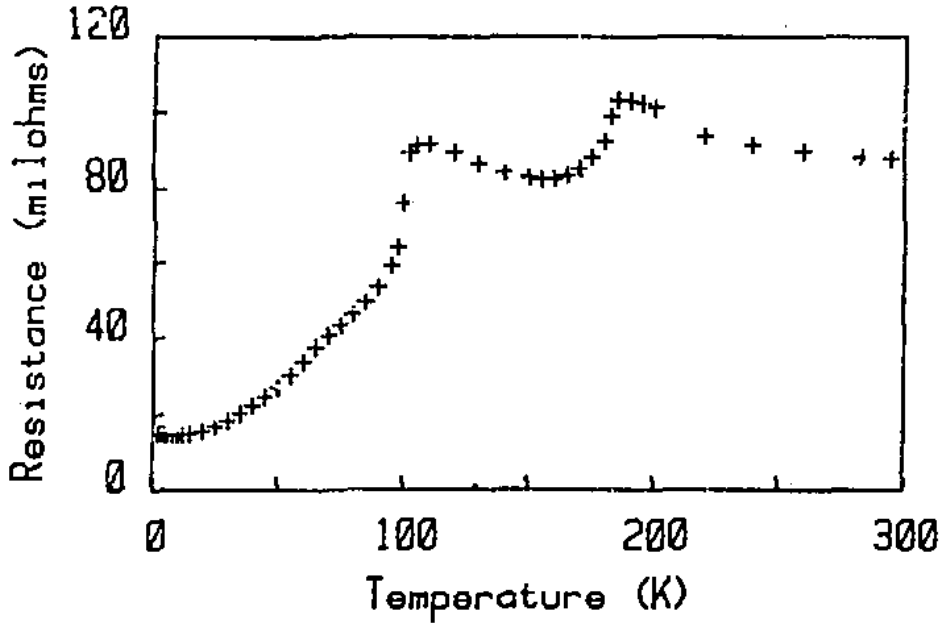
In the present study, bulk plutonium hydride samples were prepared to precise compositions, using the techniques developed by Haschke and coworkers.[6,7] Approximately 15 g sample rods of high-purity α-plutonium were hydrided in the plastic region (350-450°C) at high pressure, and then equilibrated under controlled conditions of time, temperature and hydrogen pressure to give a series of five known compositions, which were checked by chemical analysis and x-ray diffraction. Upon cooling the initially large specimens broke into smaller fragments due to internal strain, but many pieces were large enough to perform the measurements discussed below. The compositions obtained were $PuH_{1.93}$, $PuH_{2.10}$, $PuH_{2.42}$, $PuH_{2.53}$, and $PuH_{2.65}$. Handling operations were carried out in an argon-inert glovebox. For compositions below $PuH_{2.75}$ there is no detectable hydrogen loss from bulk samples at room temperature, even over a considerable period of time. The two lower compositions had metallic luster and did not easily shed contamination, whereas the higher compositions were progressively more friable.

Electrical resistivity

Resistivity studies were carried out on these samples with a 4-terminal DC method, using spring-loaded gold contacts. This technique was used in an earlier study on the uranium-deuterium system.[8] The metallic-appearing $PuH_{1.93}$ sample produced a curve falling smoothly from ~500 μΩ-cm at room temperature to a value of ~70 μΩ-cm at 4 K; α-Pu metal exhibits a resistivity of about 20 μΩ-cm at 4 K. This behavior is in marked contrast to the rare-earth dihydrides, where the resistivity is considerably lower than in the parent metals.

The higher H/Pu hydrides exhibited resistivities that did not correlate monotonically with composition; these hydrides showed numerous microcracks under metallographic examination, and thus the variability in absolute resistivities is not surprising. However, the observed transitions were well-

defined, reproducible, and increasingly complex at the higher H/Pu ratios. The $d\rho/dT$ value became positive near room temperature for the two higher compositions, possibly indicative of the onset of semi-conductor behavior. Data for the $PuH_{2.65}$ composition are shown in the first figure, as an example. Transitions were observed in varying degrees at 46-67 K, 107 K and 190 K; only the first two involve concomitant magnetic effects.

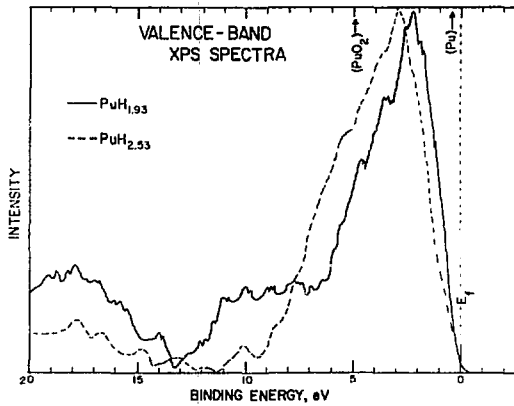


Magnetic effects

Magnetic susceptibility studies were also performed on all compositions from 1.4 to 230 K, using the vibrating-sample magnetometer method. Sharp ferromagnetic transitions were noted for all samples, starting at 46 K for $PuH_{1.93}$, and reaching 67 K for $PuH_{2.65}$. The sharp transition in resistivity at 107 K showed only a small magnetic inflection, and no magnetic change was seen in the region of 190 K. This latter reproducible transition could be structural, or perhaps due to the "freezing out" of the more mobile octahedral hydrogens. The Curie-Weiss effective moments were 0.86-0.87 μ_B for all samples.

ESCA results

Two compositions, $PuH_{1.93}$ and $PuH_{2.53}$ were examined by x-ray photoelectron spectroscopy, using a Physical Electronics ESCA-SAM instrument. Samples were mounted in the fracture stage and spectra taken in the valence band and 4f core-level regions immediately after fracture. Vacuums before fracture were in the mid-10^{-10} torr region. In contrast to the behavior for α-plutonium,[9] the hydrides seem quite stable toward oxidation. The valence-band spectra are shown in the second figure; comparative binding-energy values for the 5f peaks are indicated for PuO_2 and α-Pu. The 5f peak is noticeably broadened, especially for the higher H/Pu ratio, and the location for the more metallic composition is slightly closer to the Fermi level. The hydrogen bonding band, assuming plutonium behaves somewhat like zirconium or the rare-earths, should be in the range 5-7 eV, i.e., under the tail of the 5f peak. This results in a total spectrum that is somewhat featureless, and probably represents the sum of several peaks.



In summary, although the chemistry of the plutonium-hydrogen system is quite like the heavy rare-earths, the electrical properties are decidedly different. The presence of the dominant f-band in the vicinity of the Fermi energy must cause several effects in the valence band. Strong electron scattering should increase the resistivity markedly, and the interactions between f-orbitals and the hydrogens should increase as more hydrogen is incorporated into the lattice. Since f-electrons bond poorly in cubic lattices, a lower heat of formation might be anticipated; this seems to be true in the actinide hydrides, as compared to the rare-earths (e.g. ΔH_f (PuH_2) = 37.0 kcal/mol vs about 50 for most rare-earths).

* This work is performed under the auspices of the U. S. Department of Energy.

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THE $5f^1$ CONFIGURATION IN CRYSTAL FIELDS OF DODECAHEDRAL SYMMETRY

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The $5f^2$ configuration of highly coordinated uranium (IV) exposed to effective crystal fields (= CF) of D_{2d} symmetry has been the subject of several studies [1-5]. In spite of comparable coordination polyhedra around the U^{IV} central ion in UCl_4, $ThBr_4:U^{4+}$ and $ZrSiO_4:U^{4+}$ the derived CF parameters were not only widely different in magnitude but also different in sign [6,7]. Moreover, three attempts of interpreting the optical spectra of UCl_4 have resulted in three very different parameter sets [1,3,6]. Insertion of none of these parameter sets into the energy matrices of the isomorphous f^1 system $PaCl_4$ reproduces successfully its zero-phonon absorption spectrum. In contrast to this finding, the CF parameters of UCl_6^- and $PaCl_6^-$, respectively, are of comparable magnitude [7].

In a CF of D_{2d} symmetry, the f^2 configuration splits into as much as 70 CF states. The absorption spectra of dodecahedrally coordinated f^2 systems exhibit not only numerous bands of zero-phonon transitions, but also many additional signals of vibronic nature. An identification and correct assignment of all observed bands is often very complicated and is (besides possibly incorrect energy matrices [4]) suggested to be the main reason for strongly different parameter sets of UCl_4 [1,3,6] or $ZrSiO_4:U^{4+}$ [2,4], respectively, in the literature.

The f^1 configuration offers, if exposed to a dodecahedral CF, the advantage of producing only seven Kramers pairs, the misassignment of which is somewhat reduced. On the other hand they give rise to only six linearly independent energy differences to extract the five CF parameters and the spin orbit coupling parameter respectively. Absorption spectra taken by commercial spectrometers usually start at $\leq$ 3000 nm so that the first and second excited CF states of dodecahedrally coordinated protactinium (IV) compounds cannot be observed.

In contrast to this situation, five non-phonon transitions of dodecahedral uranium (V) compounds should become observable owing to increased CF parameters. As the spin orbit parameters of U^V compounds do not vary very much, these five linearly independent energy differences should offer enough information to evaluate here the five CF parameters of interest.

Appropriate systems for CF studies of $5f^1$ systems exposed to a CF of D_{2d} symmetry are the compounds AUF_6 (A= K, Rb, NH_4) which crystallize in the $RbPaF_6$-type structure [8,9]. Unlike in $PaCl_4$ where all eight ligands are bridging, only four are bridging in AUF_6; the coordination polyhedra around the central ions of both compounds are however comparable. For this reason the CF parameters of $RbUF_6$ and $PaCl_4$ should be comparable too, if an appropriate scaling factor is accounted for, owing to the larger CF strength of the F ligands and to the higher

oxidation state of U^V.

It had been our aim to derive, by interpreting the zero-phonon low temperature absorption spectrum of $RbUF_6$, a versatile master CF parameter set for dodecahedrally coordinated f^1 systems. We hoped that this reduced parameter set will, together with $\zeta_{5f} = 1523\ cm^{-1}$, roughly reproduce the experimental CF splitting of $PaCl_4$ with satisfactory accuracy. By a better fit of the absorption spectrum reported by Brown et al. [10], we also hoped to evaluate a more refined parameter set. It is further intended to test the adequacy of this parameter set for other $AnCl_4$ compounds (An = U, Np) by inserting the derived parameters of $PaCl_4$ into the energy matrices of UCl_4 and $NpCl_4$, respectively, and to compare the calculated optical and magnetochemical properties with the experimental results.

The room temperature absorption spectrum of $RbUF_6$ gives rise to essentially five relatively broad bands that envelope both the purely electronic and some associated vibronic transitions. After cooling with liquid helium a rich vibronic fine structure appears in addition to the considerably more intense purely electronic peaks. Simple model calculations on the basis of the angular overlap model indicate that B_2^0 and B_6^0, respectively, should have negative and B_4^0 positive signs; B_4^4 and B_6^4 should be different in sign. With a e_π/e_σ ratio of 0.413 and $e_\sigma = 4340\ cm^{-1}$ (as found in the case of the octahedral compound $CsUF_6$) and by damping the influence of the more distant ligands by a factor of 0.4 as well as by increasing the CF parameter B_4^4 and reducing B_6^4 (as compared with the predicted values on the basis of the angular overlap model) we arrived at the following sequence of CF states:

$$E(\Gamma_6) < E(\Gamma_7) < E(\Gamma_8) < E(\Gamma_6) < E(\Gamma_7) < E(\Gamma_8) < E(\Gamma_7)$$

This sequence agrees well with a proposal by Mackey and Vance for $ZrSiO_4:U^{5+}$ [11]. Accepting the sequence $E(\Gamma_6) < E(\Gamma_8) < E(\Gamma_7) < E(\Gamma_6) < E(\Gamma_7)$ for the observed zero-phonon transitions of $RbUF_6$ in the region above $4000\ cm^{-1}$, we have been able to fit the observed partial crystal field splitting pattern by means of the following parameter set:

$$\zeta_{5f} = 1965,\ B_2^0 = -2500,\ B_4^0 = 715,\ B_4^4 = \pm 11000,\ B_6^0 = -270,\ B_6^4 = \mp 850$$

To test the quality of this parameter set, the Γ_7 state predicted at $1549\ cm^{-1}$ was searched in the low temperature IR spectrum. The corresponding zero-phonon peak was indeed found at $1555\ cm^{-1}$ accompanied by some vibronic side bands.

Multiplying each component of the CF parameter set of $RbUF_6$ by a factor of 0.35 and adopting $\zeta_{5f} = 1523\ cm^{-1}$, the partial crystal field splitting pattern of $PaCl_4$ could be satisfactorily reproduced. Better agreement between experimental and calculated values was achieved by the slightly modified set:

$$B_2^0 = -825,\ B_4^0 = 250,\ B_4^4 = \pm 2300,\ B_6^0 = 250,\ B_6^4 = \pm 180\ cm^{-1}$$

With this parameter set, a non-magnetic ground state followed by a close lying first excited CF-doublet is predicted for UCl_4. Between both states second order Zeeman effects are expected, which is in agreement with the observed TIP between 4.2 and 30 K and the Curie-Weiss behaviour above 80 K. The applicability of the CF parameters of $PaCl_4$ on the absorption spectra of UCl_4 and $NpCl_4$ is presently

tested by Kanellakopulos and his group.

Experimental and Calculated CF Splitting Patterns of $RbUF_6$ and $PaCl_4$

	$RbUF_6$		$PaCl_4$	
	exp.	calc.	exp.	calc.
Γ_7	12500	12494	6790	6790
Γ_6	11001	11007	6271	6271
Γ_7	7952	7951	ca. 5550	5573
Γ_6	7087	7121	5320	5316
Γ_6	4599	4598	-	1270
Γ_7	1555	1549	-	339
Γ_6	0	0	0	0

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SPECTROSCOPICALLY PURE BIS(PHTHALOCYANINATO) COMPLEXES OF TH(IV), PA(IV) AND U(IV), THE INTERPRETATION OF THEIR ELECTRONIC SPECTRA AND THE PREPARATION OF A MONO(PHTHALOCYANINATO) COMPLEX OF TH(IV)*

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As the first phthalocyaninato compounds of the actinoids, the bis(phthalocyaninato)actinoid(IV) complexes $AnPc_2$ (An = Th, Pa, U, Np, Pu, Am) were prepared in our laboratory some years ago [1-4]. For subsequent syntheses of the thorium and uranium compounds by other authors see Ref. [4,5].

The synthesis of $ThPc_2$ and UPc_2 has been reinvestigated in order to find the optimal conditions for a new preparation of $PaPc_2$. With the modified method the compounds are obtained with a reproducible yield of at least 60 %. Two essential points were the use of $AnI_4 \cdot 4CH_3CN$ as starting material (previously AnI_4)

$$AnI_4 \cdot 4CH_3CN \xrightarrow[\text{1-chloronaphthalene, 250 °C, 1h}]{\text{16 PDN}} AnPc_2 + 2\ I_2 + \text{side products}$$

PDN = o-phthalic acid dinitrile

and the application of an improved sublimation procedure for the purification of the complexes. It was essential to remove free phthalocyanine (H_2Pc) as completely as possible since this compound disturbs an exact investigation of the $AnPc_2$ spectra.

The three types of phthalocyanines have characteristic bands between 600 and 700 nm [4]: H_2Pc two main absorption bands (two *mab*), mono(phthalocyaninato) complexes one *mab*, bis(phthalocyaninato) complexes one *mab* and one satellite band (*sat*) on the long wave length side of the *mab*. In the range of this *sat* there lies one of the two *mab* of H_2Pc.

The purification was performed by sublimation at 10^{-3} Pa in a temperature profile with three clearly defined zones (520 °C/350 °C/room temperature). In the spectra of the resulting $AnPc_2$ samples, the *mab* of H_2Pc can be detected only in the 4th derivative. We call such samples "spectroscopically pure".

Using the new methods of preparation and purification, 112 mg spectroscopically pure $PaPc_2$ have been prepared [6]. X-ray powder diffraction shows the compound to be isostructural with $ThPc_2$ and UPc_2 [7]. The ligand spectrum is typical of $AnPc_2$ complexes.

MO schemes have been described for H_2Pc and for mono(phthalocyaninato) complexes [8]. The existence of *mab* and *sat* in the spectra of bis(phthalocyaninato)lanthanoid complexes was explained in one publication by the theory of molecular excitons [9].

In order to interpret the electronic spectra of $AnPc_2$ (An = Th, Pa, U), we applied in a first step symmetry considerations. According to single crystal X-ray analyses, the mono(phthalocyaninato) complexes (of the d-elements) have the symmetry D_{4h} [10], $ThPc_2$ and UPc_2 the symmetry D_4 and nearly the same structural data[11-13]. The latter complexes are of the sandwich type, the two ligands are rotated by 38° and 37°, respectively. $PaPc_2$ is isostructural with

them, as already mentioned. On account of D_{4h}-D_4 the one *mab* in the spectra of mono(phthalocyaninato) complexes is splitted into one *mab* and one *aat* in the $AnPc_2$ spectra. Considering the structural data of $ThPc_2$, $PaPc_2$ and UPc_2 one has to expect that the degree of splitting for the three compounds should be nearly the same. In the room temperature spectrum of UPc_2, however, the *aat* seems to have a longer wave length (+20 nm) than the *aat* in the spectra of $ThPc_2$ and of $PaPc_2$; the three *mab* have nearly the same position (see table).

Positions of the characteristic bands in the spectra of $AnPc_2$
Spectroscopically pure compounds, 1-chlornaphthalene, 293 K

	Main absorption band	Satellite band
$ThPc_2$	645.5 nm	682 nm
$PaPc_2$	641.5 nm	680 nm
UPc_2	642.5 nm	708 nm

In the low temperature spectrum (80 K, 2-methyltetrahydrofuran) of UPc_2 one can see a shoulder on the short wave length side of that band which has been called so far the *aat* of UPc_2 (see figure 1). The 4th. derivative of the spectrum [1] shows that this shoulder has nearly the same position as the *aat* of $ThPc_2$ (+3 nm). Obviously, the band in the UPc_2 spectrum which has been regarded so far as *aat* consists of two bands at least. One of them is the shoulder appearing in the low temperature spectrum, which, on account of its position, can be designated as the real *aat* of UPc_2. The other band (or bands) could be assigned to unresolved strong 5f transitions (see figure 1).

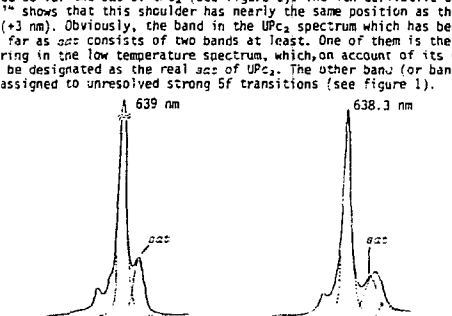

Figure 1. $ThPc_2$ UPc_2

In a second step the results of the low temperature measurements have been interpreted by the theory of molecular excitons. The values of the intensity ratios *mab/aat* calculated from the angles of rotation of the two ligands agree satisfactorily with the experimental ones.

Of the mono(phthalocyaninato)actinoid complexes there has been so far only reported the spectroscopic indication of a thorium compound [3], but no details of its isolation have been given. We have prepared $ThPcI_2(py)_2$ by reaction of ThI_4 with the stoicheiometric amount of PDN (Th:PDN = 1:4) in a melt of o-terphenyl at 230 °C for 9 h, followed by extraction of the crude material with pyridine and vacuum drying (10^{-3} Pa) of the substance precipitated in the extraction flask. The yield of analytically pure compound was 41 %. The complex is extremely sensitive to moisture. Its electronic spectrum is typical of mono(phthalocyaninato) complexes (see figure 2).

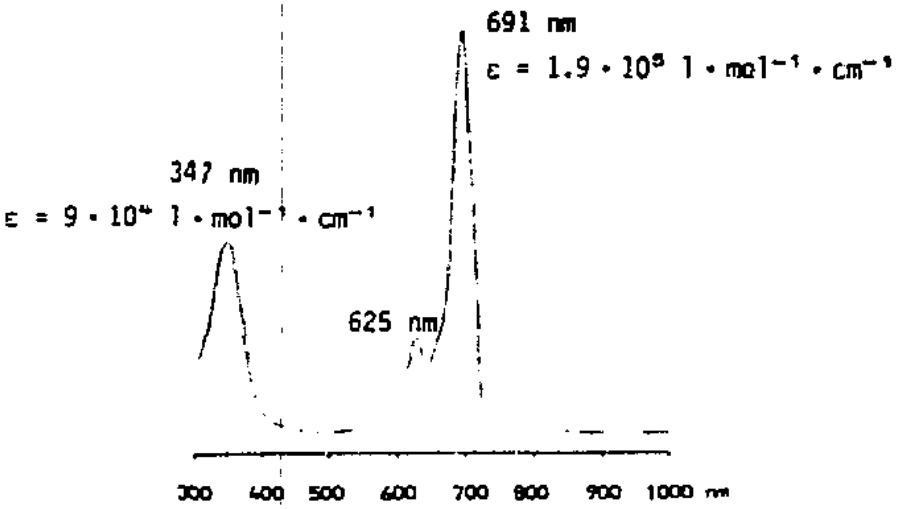

Figure 2. $ThPcI_2(py)_2$ in pyridine

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AN ANALYSIS OF THE INTENSITIES OF TRANSITIONS OBSERVED FOR THE HEAVIER ACTINIDE AQUO IONS*

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The Judd-Ofelt theory for calculating intensities of transitions within the f^N-configuration has been shown to be in excellent accord with the aqueous solution spectra of the lanthanides.[1,2] However, little progress has been made in developing a systematic treatment of the comparable spectra for trivalent actinides. Recently, we were able to measure fluorescence lifetimes for transitions observed in $Cm^{3+}(aquo)$,[3] $Bk^{3+}(aquo)$ and $Es^{3+}(aquo)$. This led us to reexamine the interpretation of the solution spectra of these elements to determine whether in light of both our present understanding of the energy level schemes,[4] and recent additional studies of the solution spectra of Bk^{3+} and Cf^{3+} with much larger samples than were previously available, a systematic interpretation of heavy actinide transition intensities could be developed. The effort was successful, and the results will be communicated in this paper.

Consistent analyses of the atomic energy level parameters for $Bk^{3+}(aquo)$ and $Cf^{3+}(aquo)$ were carried out using a method of successive approximation based on intensity calculations.[5] These results together with a previously published analysis of $Cm^{3+}(aquo)$,[5] were used to improve the estimate of the atomic parameters for $Es^{3+}(aquo)$,[6] and complete a systematic intensity analysis for the heavy actinides. The resulting calculations of total radiative transition rates, $A_T(\Psi J)$, for the observed fluorescing states have been used as one basis for interpreting the relative rates of non-radiative relaxation, $W_T(\Psi J)$, since the total fluorescence lifetime of a state $(\tau_T)^{-1} = A_T(\Psi J) + W_T(\Psi J)$.[2]

In addition to the intensity analysis of the f → f transitions, new insights into the structure and intensity relationships in $5f^{N-1}ud$-configurations were obtained; $f^N \rightarrow f^{N-1}d$ transitions could be clearly identified in both $Bk^{3+}(aquo)$ and $Cf^{3+}(aquo)$. The lowest state (spin-forbidden, ^9D) in $Bk^{3+}(aquo)$, has a factor of 20 greater intensity than its analogue in $Tb^{3+}(aquo)$. This is approximately the same factor obtained by comparing the relative intensities of f → f transitions in $Bk^{3+}(aquo)$ and $Tb^{3+}(aquo)$.

*This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Nuclear Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38.

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URANYL NITRATE PHOTOCHEMISTRY AND APPLICATIONS TO A PHOTOGALVANIC EFFECT

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The uranyl ion UO_2^{2+} is well known for the characteristic luminescence and the power to oxidize a wide range of molecules or ions of its excited state(1). On the other hand, there is a considerable interest in the visible light redox photoreactions.

We have demonstrated that in aqueous solution the fluorescence is quenched by NO_3^- anion and that UO_2^{2+} excited is able to oxidize the NO_3^- in $NO_3\cdot$. The nature of the excited species is discuted. In acetonitril solution $NO_3\cdot$ radicals have been detected by EPR spectroscopy.

An application of the uranyl photo chemistry to solar energy conversion has been found(2) : a photogalvanic cell comprising a solution of uranyl nitrate in acetonitril with a platinum and graphit electrodes. This cell produces a voltage of 0.6V in open circuit and a power of 100µW by square cm of irradiated electrode. This effect is stable for hundred hours and depends on wave lenght, H_2O concentration of the solution, cell geometry.

The suggest mechanism relies on the NO_3^- oxydation and H_2O_2 production in the liquid layer in the neighbourhood of the platinum electrode.

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OBSERVATION OF ELECTRON PARAMAGNETIC RESONANCE OF TRIVALENT URANIUM IN AN ORGANOMETALLIC COMPOUND

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A broad resonance signal on a frozen solution of $(C_5H_5)_3$ U(thf) has been observed at very low temperature (7K) with g = 3.5. This compound was prepared[1] by photolysis of $(C_5H_5)_3$ $U(CH_3)$ dissolved in tetrahydrofuran. An analogous spectrum has also been obtained at 7K with a fluoride of zirconium and uranium, $UZrF_7$[2], in which the trivalency of uranium is well established.

Since there are no EPR transitions, neither for uranium (VI), nor for uranium (IV) except in very exceptional cases[3], and since the g-factor of electronic resonance of pentavalent uranium is always lower than 1.4, and generally lower than 1, observation of a resonance signal of uranium around g = 3.5 or 4 appears as characteristic of the trivalent state. Contrary to electronic absorption spectroscopy, EPR thus allows unambiguous assignment of the valence three to uranium in $(C_5H_5)_3$ U(thf). The only other absolute proof of valency is by electrochemistry but this requires a pure compound. Thus EPR is the only method which permits the identification of the valency of uranium when the compound under study can not be isolated. This is the case with the product obtained through reduction of $(C_5H_5)_3$ $U(CH_3)$ by $LiCH_3$ in tetrahydrofuran[5] ; proton magnetic resonance enables to suggest the formula $[(C_5H_5)_3\ U(CH_3)]^-\ Li^+$ (thf) for the latter.

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OXIDATION AND HYDRIDING OF URANIUM STUDIED BY POSITRON ANNIHILATION*

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Positron annihilation analysis has been used to explore the interstitial/vacancy complexes[1,2,3,4] that control electrical conduction in uranium oxides, and should also be present during the oxidation of uranium metal under different environmental conditions. Because uranium hydride may play a role in the oxidation of uranium in water vapor, we have also studied this compound. Clean uranium powder samples were exposed to dry oxygen, dry hydrogen, water vapor in a static mode, and water vapor in flowing nitrogen gas.

Both the positron lifetime and positron doppler broadening profile were measured in each of the samples. Distinct annihilation lifetimes in the positron lifetime spectrum were associated with samples treated in dry oxygen, water vapor in a flow system, and hydrogen. The strength of the lifetime component associated with oxygen and water vapor in a flow system grew to saturation as a function of the exposure of the uranium sample. A much longer-lived component was measured for samples hydrided in dry hydrogen or hydrogen in the presence of water vapor ($H_2O(v)$ in a static system). Individual, distinct features could not be identified for each of the annihilation conditions in the doppler measurements. However, the overall behavior of the doppler profiles has the same general features as those found in the lifetime measurements.

The results of this study indicate that positron annihilation analysis is specific to the charged species associated with oxidation or hydriding conditions for uranium. The close similarity of the lifetimes, identified with oxidation of the metal in dry oxygen and water vapor in a flow system, suggests that the positrons are annihilating at a common species in the uranium oxide. One feature of these samples is that they were all prepared in an environmental regime, i.e., reactant type [O_2, $H_2O(v)$] and pressure, where a single defect complex has been postulated to control the oxidation.[5] Our results indicate that a common defect or defect complex is involved in the oxidation process, and that this complex is identified as the annihilation site of the positrons.

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ABSORPTION OF SYNCHROTRON RADIATION BY URANIUM COMPOUNDS

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Photoabsorption measurements of metallic uranium and some uranium compounds have been performed with synchrotron radiation as an intense and continuous photon source.

The X-rays generated in the SOR-ring at the Institute for Nuclear Study, University of Tokyo, are made monoenergetic by a Vodar type monochromator with a concave 2400 lines/mm grating. The radius of Rowland circle is 2 m and the resolution is about 15 meV. Transmitted photon is counted by a windowless Be-Cu photoelectron multiplier with CsI coating at the first stage. The counting is recorded for a fixed count of monitor electron beam.

Film samples have been prepared by the following procedure. Carbon is evaporated on the sodium chloride film previously evaporated on a glass plate. The plate is immersed in water and the floating carbon film in a thickness of 100-150 nm is picked up on a sample holder with a hole of 7 mm in diameter in the center. Metallic uranium, uranium dioxide or tetrachloride is then evaporated on the carbon film. The thickness was 24, 95 and 65 nm for U, UO_2 and UCl_4, respectively.

In the case of uranyl nitrate, the solution in PVA is doped on the polystyrene film on a glass plate and the solidified nitrate film is then transferred on a sample holder as in the case for other samples.

Fig. 1 shows the absorption spectra for these samples. The general structure characterized by two distinguished peaks is common to all spectra and has also been observed for metallic uranium [1] and uranium tetrafluoride [2]. The spectrum of UO_2 shows a close similarity particularly with that of UCl_4, suggesting that valency of uranium plays an important role upon the detailed structure.

Since the threshold energy of the smaller peak (peak A), about 98 eV, nearly coincides with the binding energy of $5d_{5/2}$ measured by the ESCA for UO_2 (96.4 eV), this peak is attributed to the $5d_{5/2} \rightarrow 5f$ transition. The absorption due to $5d_{3/2} \rightarrow 5f$ transition is then estimated to be found at about 8 eV higher than the peak A, because the binding energy of $5d_{3/2}$ is 104.8 eV. The peak is expected to be smaller than the peak A owing to smaller multiplicity for j=3/2 than for j=5/2. Shoulders appearing at about 107 eV in the spectra of UO_2, UCl_4 and uranyl are considered to indicate this absorption.

Atomic spectra calculation for the transition $5d \rightarrow 5f$ has been made on tetravalent uranium. As the dominant transitions are $5f^2(^3H_4) \rightarrow 5d^9 5f^3(^3G_3, {}^3H_4, {}^3I_5)$, we have calculated energies of levels included in these terms and intensities for the transitions. Tentatively it is assumed that $F_2 = 200\ cm^{-1}$, hydrogenic values for F_4 and F_6 and $\zeta = 9.5\ F_2$ in the intermediate coupling scheme. Interactions between 5d and 5f are neglected and the spin-orbit splitting of 5d is assumed to be 8.0 eV.

The calculated spectrum, neglecting minor peaks, is shown in Fig. 2. Major peaks denoted as a, b, c in Fig. 2 are, respectively, $^4I_{9/2}$, $^4I_{11/2}$, $^2K_{13/2}$ terms appearing in $5f^3$ configuration each coupled with $^2D_{5/2}$ in $5d^9$. Thus these peaks correspond to transitions from $5d_{5/2}$ to levels in $5f^3$. The peak d is due to coupling of $^4I_{9/2}$ with $^2D_{3/2}$. The shape of the peak A with high-energy tail for UO_2 and UCl_4 seen in Fig.1 would be explained by this transition scheme.

As for the peak B, though it involves the absorption due to $5d_{3/2} \rightarrow 5f$ transitions, the main part remains unexplained at present. Transitions $5d \rightarrow 7p$, 8p and 6f would contribute to the peak.

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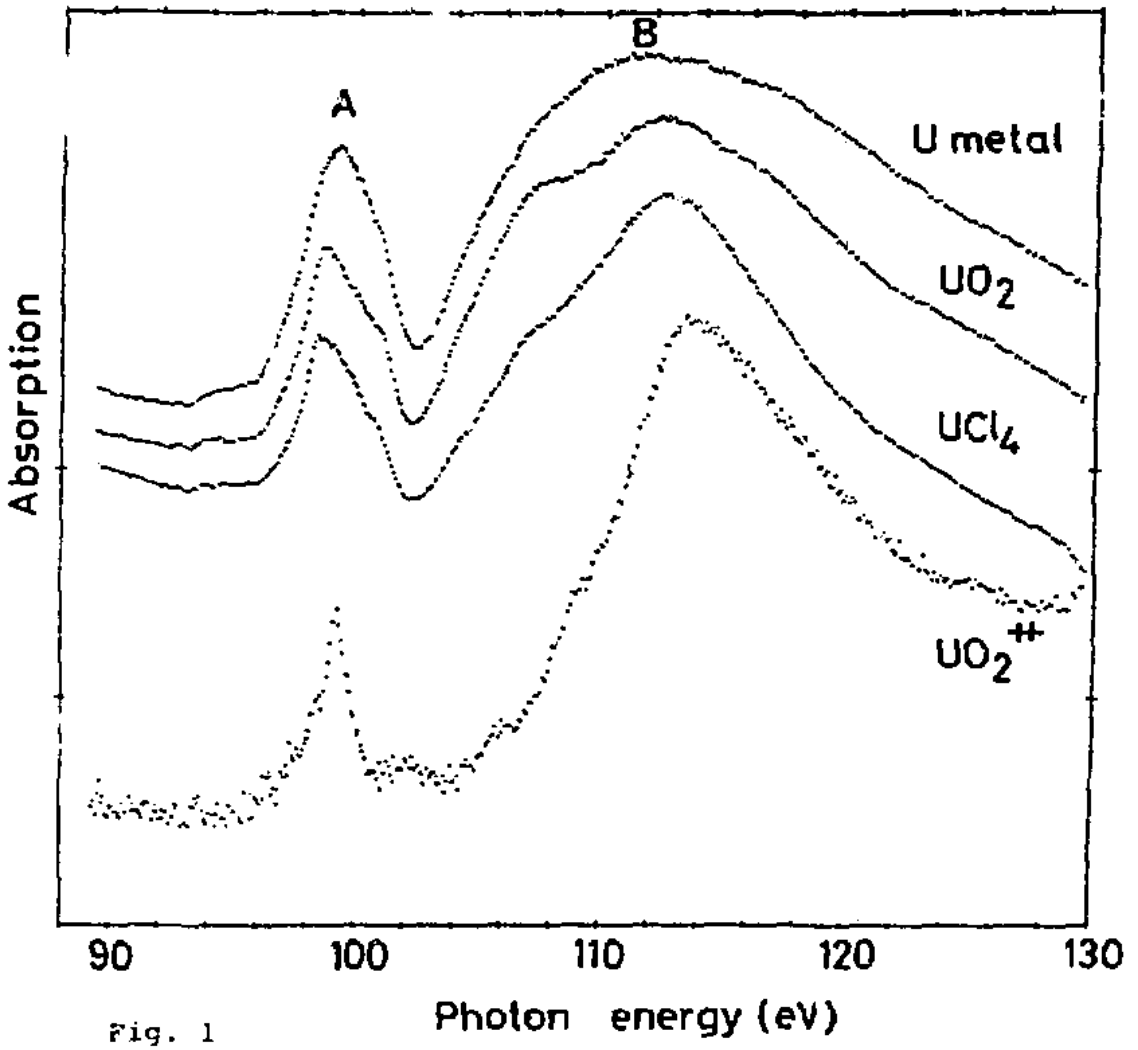
A
B
U metal
UO_2
UCl_4
UO_2^{++}
Absorption
90
100
110
120
130
Photon energy (eV)

Fig. 1

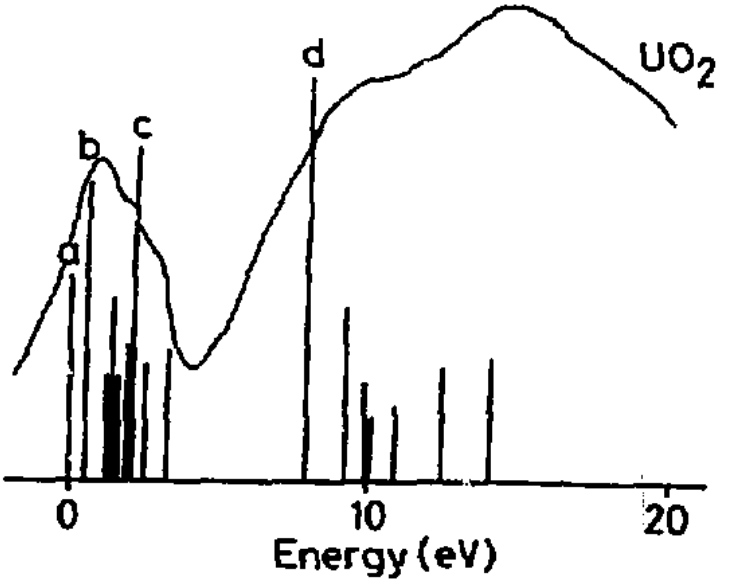
a
b
c
d
UO_2
0
10
20
Energy (eV)

Fig. 2

RAMAN SPECTROMETRIC STUDIES OF "CATION-CATION" COMPLEXES OF PENTAVALENT ACTINIDES IN AQUEOUS PERCHLORIC SOLUTIONS*

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The initial report about the existence of complexes of pentavalent actinides, AnO_2^+, with other multiply charged cations (cation-cation complexes) was made by Sullivan et al.[1] in 1961. Several different techniques have been used to study these complexes,[1-9] such as proton spin relaxation and potentiometric titrations[1], electron paramagnetic resonance[8], infrared spectroscopy[4], and Mössbauer spectroscopy.[9] To a large extent, absorption spectrophotometry has been used to measure the strengths of the complexes, with shifts in the wavelengths of electronic transitions taken to be evidence for complexation.[1-3,8] The nature of these complexes, however, is still not clear.[5-7]

Raman spectrometry can often be used to detect the formation of complexes in solution from changes in vibrational spectra. Although the Raman scattering of actinides (in oxidation states V, VI, and VII) in solution has been reported, no Raman studies have previously been made of cation-cation complexes. We have used this technique to study the formation of such complexes of NpO_2^+ in acidic aqueous solutions.

To obtain quantitative Raman analyses, the non-complexing perchlorate ion was used as an internal standard in our solutions, with the ν_4 band at 627 cm^{-1} being chosen as the reference. In a given series of spectral determinations, the perchlorate ion was maintained at constant concentration. The acid concentration and ionic strength were also kept constant. By normalizing the neptunyl bands to this internal standard, the effects of such experimental factors as sample cell variations, cell position, laser power fluctuations, and absorptivity of the sample were eliminated.

As seen in Fig. 1, in dilute solutions containing neptunium, ~ 0.2M in NpO_2^+, only the symmetrical stretching vibration, ν_1, of NpO_2^+ at 767 cm^{-1} is Raman active. At higher NpO_2^+ concentrations, from 0.3M to 1.2M, two new bands appeared at 180 and 738 cm^{-1}. The band at 180 cm^{-1} can be assigned to ν_2, the bending vibration of the linear triatomic $(O=Np=O)^+$ ion. We attribute the band at 738 cm^{-1} to an associated neptunyl-neptunyl species. A further increase in neptunium concentration, above 1.5M, leads to a fairly complicated spectrum in the range 650-850 cm^{-1}. At least six overlappin peaks can be distinguished, approximately centered at 685, 712, 738, 767, 783 and 820 cm^{-1}.

A plot of the logarithm of the relative intensity (normalized to the 627 cm^{-1} peak) of the peak at 738 cm^{-1} versus that of the NpO_2^+ peak at 767 cm^{-1} is shown in Fig. 2. The results indicate formation of a previously unknown neptunyl species. The points obtained in the range 0.1-1.0 M Np(V) lie on a straight line with a slope close to 2, indicating that two neptunyl groups are involved in the reaction (i.e., dimer formation). The systematic deviation above the line of the points with log $R_2>0$ is interpreted as indicating that higher polymers than the dimer are formed at large NpO_2^+ concentrations. This conclusion is consistent with the observation (Fig. 1) that above 1.5M concentration, additional peaks appear in the vicinity of the ν_1 band of NpO_2^+. From these data, we derive a value of the formation constant, $K_2/\Gamma = 0.69 \pm 0.27$, where Γ is the activity coefficient ratio.

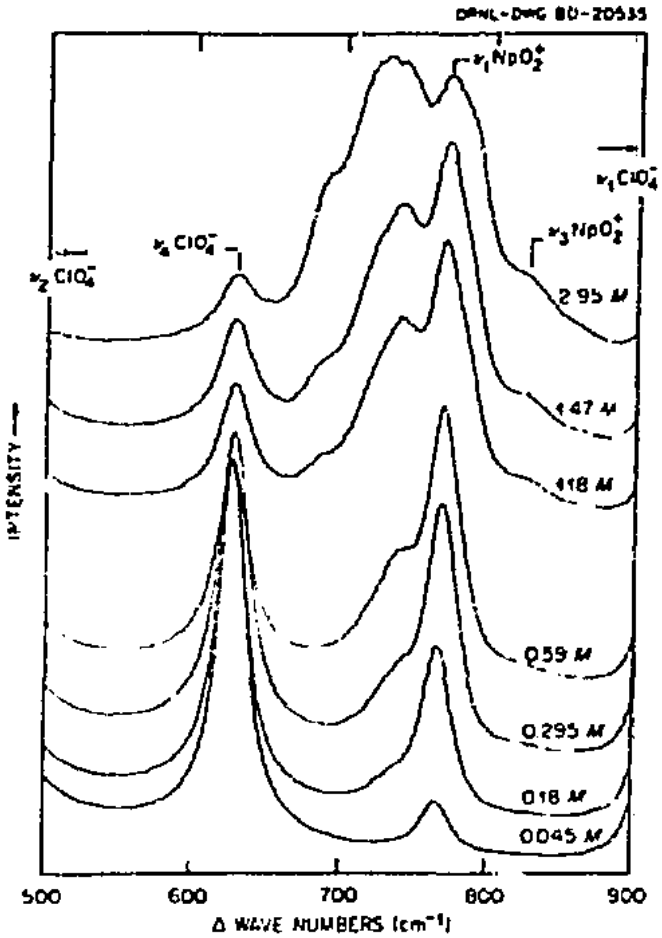

FIGURE 1

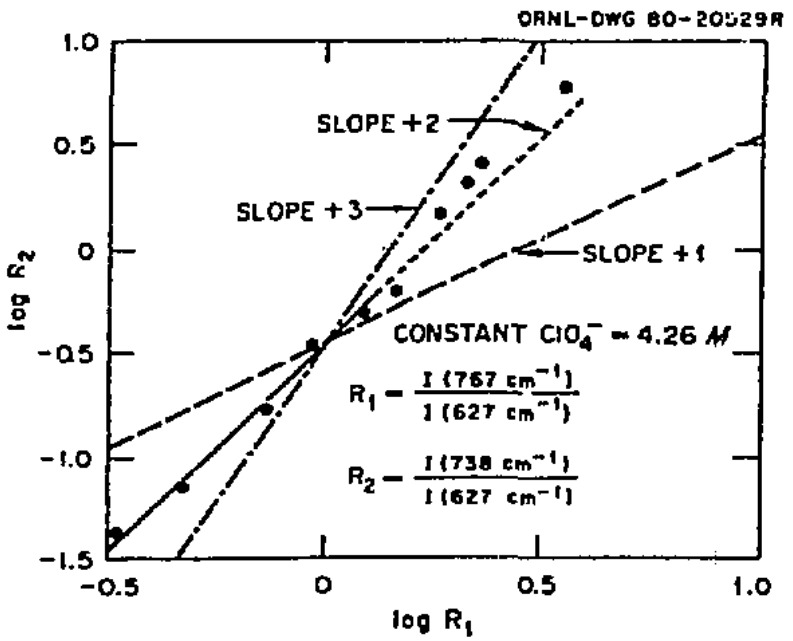

FIGURE 2

The effect of acidity on the neptunyl dimerization was also studied. At most, there is a variation of ~20% in the intensity ratio of the dimer to monomer peaks for a change in acidity from 0.1 M to 2.65 M, indicating that protons are not strongly involved in this association reaction. This result is markedly different from that found for polymerization of Pu^{4+} and UO_2^{2+} at higher pH values, where polymerization proceeds by hydrolysis and so depends sensitively on $[H^+]$.

The Raman spectra of dilute neptunium(V) perchlorate solutions are also markedly modified by the addition of uranium(VI), at Np(V) concentrations below those where dimerization is observed. Upon addition of 2M UO_2^{2+}, the ν_1 band of NpO_2^+ at 767 cm^{-1} decreases in intensity and a new band centered at 741 cm^{-1} appears. This result is strong confirmatory evidence for the claimed formation[1,8] of a complex of Np(V)-U(VI). The values of K/Γ obtained for this complex, by taking either the Raman data or absorption spectrophotometric data for the same solutions, are in excellent agreement with each other. The value for this constant, extrapolated to [U(VI)] = 0, is $K = 2.1 \pm 0.6$.

In summary, the present work demonstrates that Raman spectroscopy is a powerful additional technique for investigations of complexes of pentavalent actinyl ions with other multiply charged cations. We have confirmed the existence of the Np(V)-U(VI) complex, and have found evidence for the formation of Np(V)-Np(V) dimers and even higher polymers. We are also investigating the applicability of Raman spectroscopy and other techniques[10] to the question of the structure of such complexes.

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INVESTIGATION OF "CATION-CATION" COMPLEXES OF NpO_2^+ SOLUTIONS BY LARGE-ANGLE X-RAY SCATTERING

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As part of the study of cation-cation complexes[1] of neptunium(V), NpO_2^+, we have used the technique of wide-angle X-ray scattering[2] to determine the pair distribution functions of the ions in solution. Our aim in this work was to learn if a well defined distance could be formed for nearest neighbor actinide atoms in the solution. Finding such a characteristic distance would provide strong evidence for a chemical association between the actinide ions, and serve as verification of the existence of cation-cation complexes of NpO_2^+.

Five different solutions containing either NpO_2ClO_4, $UO_2(ClO_4)_2$ or both of these compounds, were prepared. ClO_4^- ion was used because of its weak complexing ability. All of the solutions were acidic, with $HClO_4$ concentrations varying from 0.07 to 0.2 M. A special sample holder was constructed so that a minimum volume of solution, ~1ml, could be used (to minimize the hazard of radioactive contamination) while exposing a surface area >2 cm^2 to the Mo K-X radiation.

Details of the X-ray scattering apparatus and data analysis are given in Ref. 3. The angular distributions of the scattered radiation were analyzed to give structure factors, S(k), where $k = 4\pi \sin\theta/\lambda$. These were then Fourier transformed to give the radial pair distribution functions, G(r), where G(r) is related to the probability that if one atom is at r=0, a second atom will be found at a distance between r and r+dr.

The resulting radial distributions so obtained were found to contain several peaks, including those that were attributable to the Cl-O (1.5Å) and O-O (2.3Å) distances in the ClO_4^- ion.[4] It was also noted that the usual structure[5] found for liquid water, with a peak at 2.8Å, was severely perturbed by the presence of the large actinyl and ClO_4^- ions. The radial distributions, from which the known contributions due to ClO_4^- have been subtracted, are shown in the figure. The peak at 1.8Å is the actinyl-oxygen distance in the linear NpO_2^+ and UO_2^{2+} ions; this value agrees with the distances determined for solid neptunyl(V) compounds[6] and for solids and solutions containing the uranyl(VI) ion.[7]

The feature in the radial distributions that we wish to draw attention to is the peak at 4.2Å that is found for solutions 1 to 3, which contain either concentrated Np(V) or both Np(V) and U(VI). Solution 4, which contains 0.5M NpO_2^+, has a small peak at this distance, while solution 5, containing UO_2^{2+} only, does not. There is some indication, for solutions 1 to 3, that the intensity of the peak at 4.2Å increases with increasing actinide ion concentration. However, the intensities of these peaks are so low that a quantitative dependence upon concentration cannot be established.

We interpret the peak at 4.2Å as representing the nearest neighbor distance between actinide atoms in the cation-cation complexes. The fact that the peak also appears in the 1.7M solution of Np(V), in the absence of U(VI), indicates that self-association of NpO_2^+ ions occurs at high concentrations. This result supports the conclusion derived independently from

Raman scattering[1] that a dimer of Np(V) is formed in such solutions.

It is noteworthy that the actinide-actinide distance that we find, 4.2Å, is comparable to the value of 3.9Å reported as the U-U distance for solutions containing polymers of hydrolyzed uranyl(VI) species.[7,8] A point of distinction between the two sets of results is that the uranium atoms in the polymers are joined by OH^- bridges, while the cation-cation complexes are formed in strongly acidic media, where hydrolysis is not possible.

* *Work sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation and by the Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France.*

- Guest Scientist on assignment from Centre d'Etudes Nucléaires, Departement de Génie Radioactif, Fontenay-aux-Roses, France.

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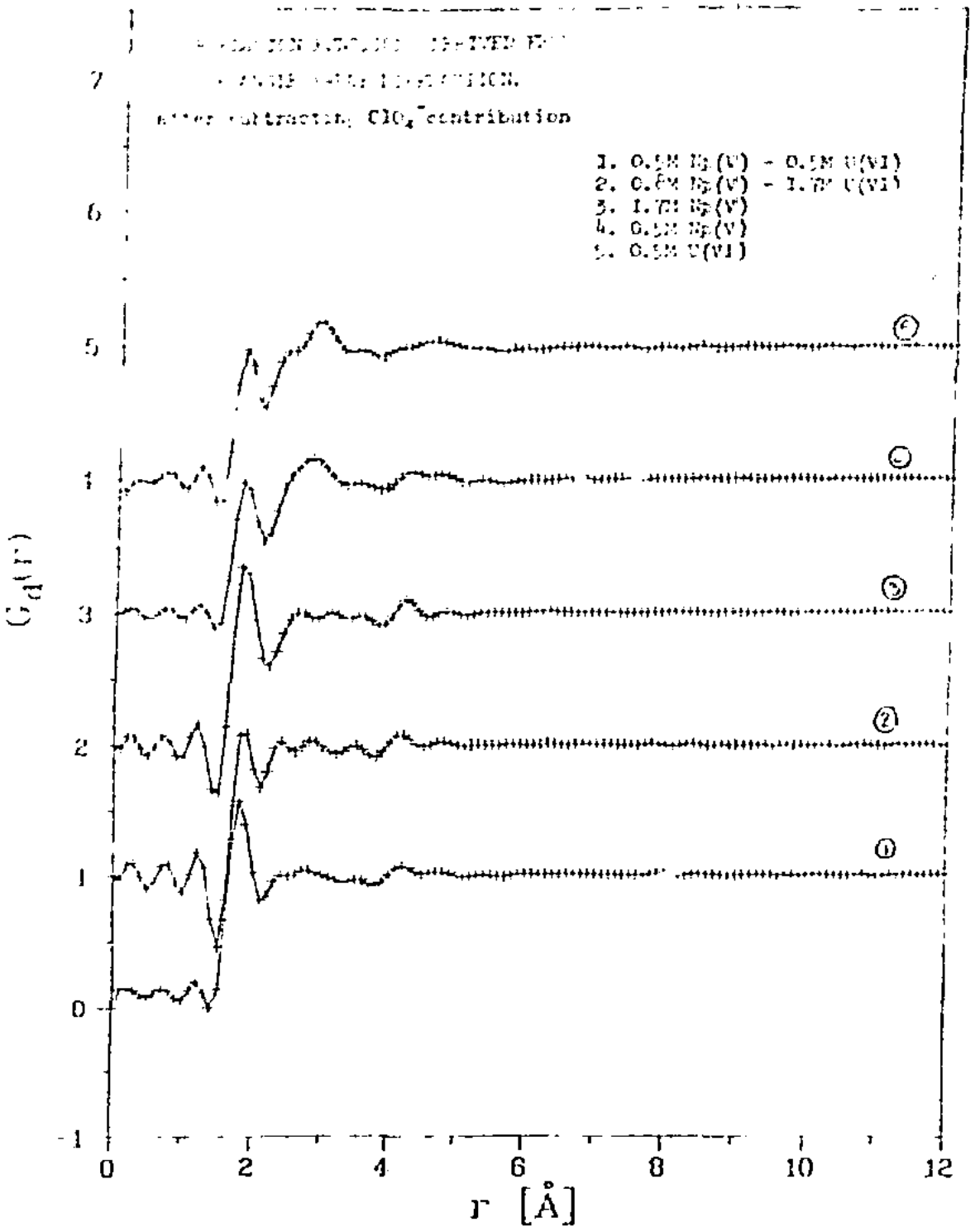
after subtraction ClO_4^- contribution
1. 0.5M Np(V) - 0.5M U(VI)
2. 0.5M Np(V) - 1.7M U(VI)
3. 1.7M Np(V)
4. 0.5M Np(V)
5. 0.5M U(VI)
$G_d(r)$
r [Å]

FIGURE 1

FLUORESCENCE STUDIES OF AQUO TRANSURANIC IONS*

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We have begun a systematic study of aquo An^{3+} ion fluorescence in H_2O and D_2O solutions based on our pioneering work concerning aquo Cm^{3+} fluorescence.[1] In this study we seek to define the parameters which determine the fluorescence properties of actinide ions in aqueous solution. This work is providing a basis for assessing fluorescence detection of transuranic ions in aqueous solution and impacts on efforts to understand non-radiative decay of excited electronic states. Based on previous studies of aquo Ln^{3+} ion fluorescence[2] we might expect that solvent deuteration (lowering vibrational mode frequencies) and the energy gap between the emitting electronic state to next lower electronic state would also be key factors in determining the magnitude of non-radiative decay rates of aquo An^{3+} ions.

Using selective laser excitation techniques similar to those used to study aquo Cm^{3+} fluorescence,[1] we have measured the fluorescence emission spectra and lifetimes of aquo Es^{3+} and aquo Bk^{3+}. An important feature of this technique is the use of laser excitation at a wavelength much shorter than that at which the actinide ion fluoresces. Both directly scattered laser light and Raman scattered laser light from solvent modes were therefore easily blocked from reaching the photomultiplier. The nitrogen laser or Nd:YAG laser pumped dye laser excitation pulse was of a few nanoseconds duration. The dye laser was tuned to an optical absorption maxima of the actinide ion of interest and passed through the high purity quartz cell containing the sample solution. Fluorescence at 90° to the laser beam path was collected by a lens system, bandpass filtered with glass filters (lifetime measurements) or a scanning monochromator (emission spectra measurements) and imaged onto the photocathode of a cooled photomultiplier. A boxcar integrator and chart recorder were used to acquire fluorescence emission spectra. A digital transient recorder-signal averager system (10 ns resolution) was used to measure fluorescence lifetimes.

The results obtained for Bk^{3+} and Es^{3+} are collected in Table I along with our earlier work on Cm^{3+}. The optical properties, including free ion energy levels, of these and other An^{3+} and Ln^{3+} species have recently been reviewed.[3] Except for aquo Cm^{3+} in D_2O, the purely radiative lifetimes for the emitting transitions of the species shown in Table I are sufficiently long that the observed fluorescence lifetimes are simply the inverse of the non-radiative transition rates. The non-radiative decay rate for aquo Cm^{3+} in D_2O is $5.1 \times 10^2\ s^{-1}$ based on a radiative decay time of 1.8 ms.[1] It is apparent from the results shown in Table I that solvent deuteration substantially diminishes the non-radiative decay rate of Cm^{3+} and Es^{3+}. Undoubtedly the same is true of Bk^{3+} but improvements in instrument time response will be necessary to study the fluorescence lifetime of aquo Bk^{3+} in H_2O.

From the data in Table I we see that the aquo An^{3+} non-radiative decay rate depends nearly exponentially on the energy gap of the particular actinide ion. The same factors, solvent vibrational mode frequencies and energy gap, identified as important in determining non-radiative decay rates for aquo Ln^{3+} ions are also important in determining aquo An^{3+} non-radiative decay rates.

TABLE I. Fluorescence Properties of Aquo Transuranic Ions

An^{3+}	Emission Band (nm) Peak	FWHM	Observed Fluorescence Lifetime[b] (μs)	Non-Radiative Decay Rate (s^{-1})	Estimated Energy Gap (kJ/mole)
$^{248}Cm^{3+}$[a]	593	8	940±20 (D_2O)	5.1×10^2	203
			65±2 (H_2O)	1.5×10^4	
$^{249}Bk^{3+}$	647	22	0.10±0.01 (D_2O)	1.0×10^7	66
$^{253}Es^{3+}$	1070	125	2.8±0.1 (D_2O)	3.6×10^5	108
			0.105±0.08 (H_2O)	9.5×10^6	

[a]Data from Ref. 1.

[b]Solvent indicated in parenthesis. Typically 0.5 M HCl or 0.5 M DCl was used to prevent hydrolysis.

Comparison of aquo Ln^{3+} and aquo An^{3+} non-radiative decay rates at comparable energy gaps is instructive. Stein and Wurzberg's measurements[4] for Tb^{3+} and Dy^{3+} and Heller's measurements[5] for Nd^{3+} provide aquo Ln^{3+} ion data at roughly comparable energy gaps to those of Cm^{3+}, Es^{3+}, and Bk^{3+}, respectively. Using these Ln^{3+} data, the An^{3+}/Ln^{3+} non-radiative decay rate ratios vary from 2.8 to 22. Even larger ratios result if the Ln^{3+} non-radiative decay rate versus energy gap data are extrapolated to the exact An^{3+} energy gaps. We conclude that while the key factors influencing non-radiative decay rates for aquo Ln^{3+} and aquo An^{3+} ions are similar, the An^{3+} species interact more strongly with their immediate environment, possibly reflecting the greater radial extent of the 5f An^{3+} electron wave functions as compared to the Ln^{3+} 4f electron wave functions.

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Nuclear Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38.

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EPR INVESTIGATIONS OF ^{243}Cm, ^{244}Cm, AND ^{238}U IN $LuPO_4$ SINGLE CRYSTALS*

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The natural mineral monazite is characterized by an established long-term stability under a variety of geological conditions. Additionally, many monazites contain appreciable amounts of uranium and thorium, and this material is apparently relatively resistant to α-particle and nuclear recoil radiation damage. Accordingly, lanthanide orthophosphates that are synthetic analogs of monazite could well represent ideal hosts for the immobilizaton of α-active actinide wastes. These phosphates may be divided into two classes: The compounds $LaPO_4$ through $GdPO_4$ which have the monoclinic "monazite" structure, and the orthophosphates of the second half of the rare-earth series ($TbPO_4$ through $LuPO_4$) plus $ScPO_4$ and YPO_4, which have the tetragonal "zircon" structure.

A flux technique has been used to grow single crystals of every lanthanide orthophosphate (except $PmPO_4$), as well as $ScPO_4$ and YPO_4 and extensive studies of the chemical and physical properties of mixed host-impurity systems are underway. These investigations include examinations of iron-group, rare-earth, and actinide impurities in order to obtain information regarding their valence states, crystalline site symmetries, and other solid state properties.

Electron paramagnetic resonance (EPR) spectroscopy has been used in characterizing orthophosphate-impurity systems since the number of observed EPR transitions and their position as a function of the strength and relative orientation of the magnetic field can be used to determine the valence state of the paramagnetic impurity, the site occupied by the impurity, and can provide information regarding the local crystal structure. Previous EPR studies of Gd^{3+} ($4f^7$) in the orthophosphate hosts have established that while the impurity ion is located in the substitutional rare-earth site, the crystal field interaction, which splits the S=7/2 ground state, is positive for the monoclinic hosts[1] and negative for the tetragonal hosts.[2] In the present work, the actinide analog of Gd^{3+} (i.e., Cm^{3+}, $5f^7$) has been incorporated in the tetragonal host $LuPO_4$ and the EPR spectra of both ^{243}Cm and ^{244}Cm were observed. The I=5/2 nuclear spin of the 243-Cm isotope allows a positive identification to be made,[3] and Fig. 1 shows the spectrum observed at T = 4.2 K with the magnetic field applied parallel to the crystal tetragonal c axis. The g value in this parallel orientation is 7.98(1) while the corresponding value in the perpendicular orientation is 4.096(4). These values cannot be fit to the doublet wave function $\alpha|\pm 7/2> + \beta|\mp 1/2>$ to give a consistent Landé g-factor but can be fit to the doublet wave function $\alpha|\pm 5/2> + \beta|\mp 3/2>$ yielding a Landé g-factor of 1.92. Further verification of this doublet identification comes from the observation that lowering the temperature to ~ 1.5 K reduces the intensity of the EPR signals, clearly indicating that this is an excited doublet. Therefore, the sign of the crystal field interaction for the $5f^7$ ion in the tetragonal $LuPO_4$ host is negative and is the same as that found previously for the $4f^7$ ion.

The EPR spectrum of U^{3+} in $LuPO_4$ has also been observed and was found to be very similar to the previously reported[4] spectrum of its $4f^3$ analog Nd^{3+}.

Figure 2 shows a graph of g^2 plotted versus $\cos^2\theta$ where θ is the angle between the applied magnetic field and the tetragonal crystal field axis. This plot was used to determine a value of 0.98(8) for $g_\perp$ and a value of 3.14(2) for $g_\parallel$.

Additional investigations of Np and other actinide impurities are in progress.

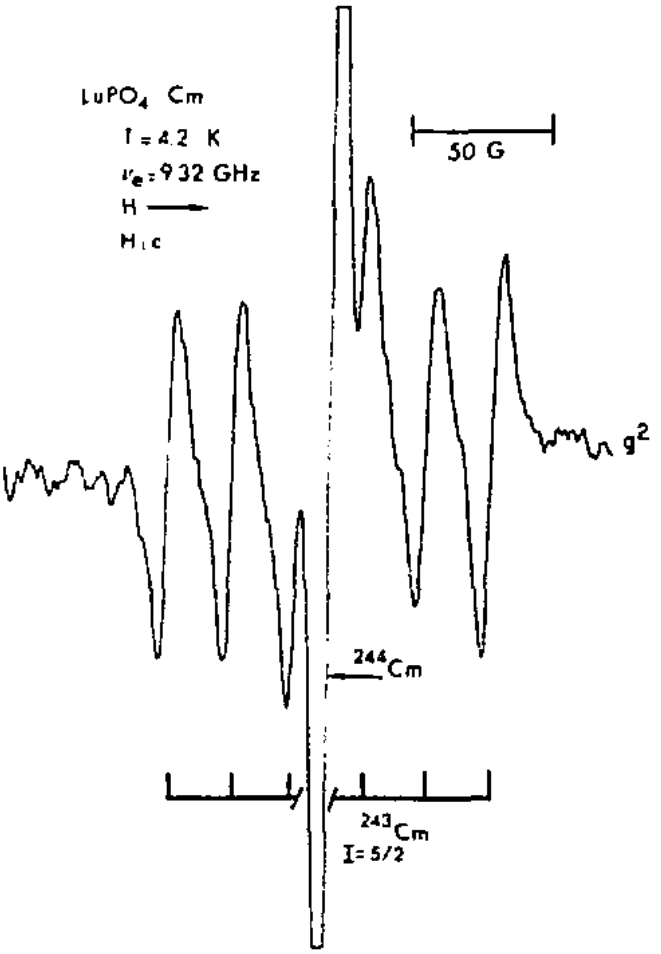

Fig. 1

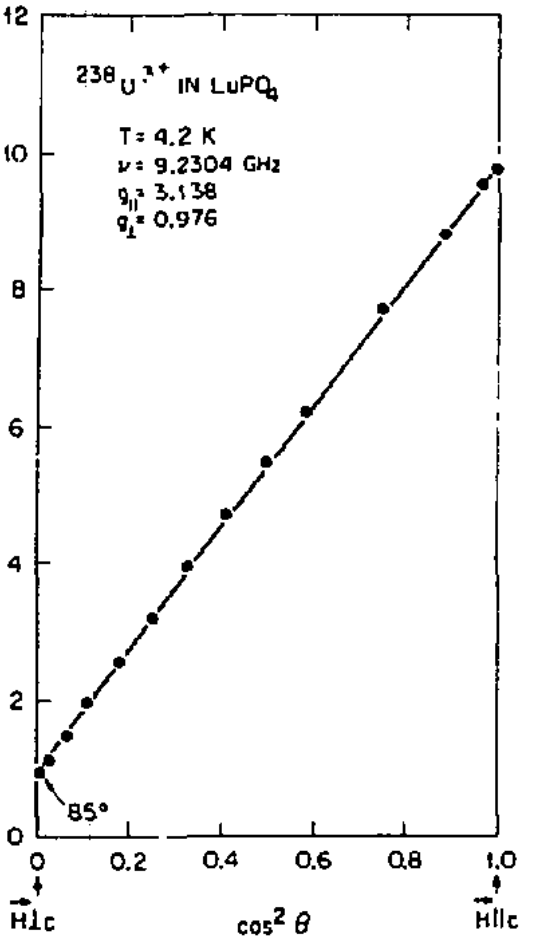

Fig. 2

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UP CONVERSION AND ABSOLUTE OSCILLATOR STRENGTHS OF U^{4+} IN $ThBr_4$ SINGLE CRYSTALS

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We have recently found that infra red excitation of $ThBr_4$ and $ThCl_4$ single crystals doped with U^{4+} or Np^{4+} give strong emissions in the visible range even when ions were unintentionally introduced as traces. This not so common anti-stokes fluorescence called "up conversion" or APTE effect (Addition de Photons par Transport d'Energie) has been discovered fifteen years ago using 4f elements (1) (2) and to the best of our knowledge is mentioned here for the first time in connection with 5f elements.

Results given in this paper are only dealing with $ThBr_4 : U^{4+}$ (~ 0.1 %) crystals. Tetravalent uranium in single crystal as well as in microcrystalline powder form of $ThBr_4$ acts as an up converter. Absorption of two (or more) IR photons by one or two consecutive U^{4+} ions is involved in reaching an excited state which by spontaneous decay gives rise to a visible fluorescence. In the case of $ThBr_4 : U^{4+}$, IR excitation with $\lambda > 8200$ Å at room temperature gives an emission band between 6700 A to 7200 Å. The intensity variation of this red emission with respect to IR excitation intensity is found to be quadratic. According to theoretical considerations (2) this indicates that excitation is obtained by a two photon mechanism. Experiments are in progress with various U^{4+} concentration in $ThBr_4$ crystals to determine whether this absorption takes place on one or several uranium ions.

With $ThBr_4 : U^{4+}$ crystals, the same red fluorescence is readily observed using a classical UV excitation (3). Whatever the excitation UV or IR, a weak green emission is also observed ($\sim$ 5200 Å) at 77 K, probably connected with the phase transition of the matrix which appeared below 92 K. Evidence of up-conversion at very low concentration levels could be an indication of strong oscillator strengths : in a dipole-dipole interaction model, the energy transfert probability is proportionnal to the product of oscillator strengths of the involved transition (2). This consideration induced us in meaning oscillator strengths of U^{4+} in $ThBr_4$ (4). Calculations of absolute oscillator strengths of U^{4+} have been obtained by graphical integration of absorption spectra at room temperature recorded with a double beam CARY 17 spectrometer. The considered spectral range lies between 1.3 μ and 0.45 μ. The uranium concentration in $ThBr_4$ crystal were done by α-counting activity of uranium chemically separated from thorium by anion exchange technique. Application of Judd theory leads to the determination of the $T\lambda$ parameters and to the theoretical values of Table I where unresolved terms are taken together. One can note that f numbers are large for $5f^2$ being of order 10^{-4} instead of 10^{-5} for U^{3+} (5) and 10^{-6} for Pr^{3+} (6).

Table I

Observed and calculated oscillator strengths of U^{4+} transitions in $ThBr_4$

Level assignment	Energy region (cm^{-1})	Center of band energy (cm^{-1})	$f \times 10^4$	
			exp.	cal.
		Cryst.	Cryst.	Cryst.
$^3F_3$, $^3F_4$	7810-10100	8547	2.80	2.84
$^3H_6$	10100-13330	1111	1.05	0.83
$^3P_0$, $^1D_2$, $^1G_4$	13330-16500	14724	2.93	2.87
$^3P_1$	16500-18700	17391	0.99	1.47
$^1I_6$	18700-22200	19342	2.84	2.64
$^3P_2$	22200-25000			0.06
$^1S_0$				0.095
rms deviation x 10^4				0.40
T_λ ($\times 10^{18}$ s^{-1})	$T_2 = 5.6$; $T_4 = 2.2$; $T_6 \simeq 0$			

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ABSORPTION AND EMISSION SPECTRA OF Pa^{4+} IN $ThCl_4$

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The problem of interpreting optical data on ions in the solid state can be facilited by the proper choice of the host material. In the case of Pa^{4+} ($5f^1$) the use of thorium tetrachloride as a crystal matrix was enhanced because of the following favorable factors :

1 - $ThCl_4$ is optically inert from the cut off of the crystal near 0.3 μm to more than 2.5 μm and chemically inactive towards the oxidation state of Pa^{IV}.

2 - $ThCl_4$ can be prepared in large optically clear single crystal (1). The crystalline structure is tetragonal allowing the observation of polarized spectra.

3 - The thorium ion - which presents an ionic radius little bit larger in size than that of Pa^{4+} - is at a site of relatively high symmetry, D_{2d}. The absence of inversion centre allows electronic transitions to be intense compared with vibronic transitions.

The absorption and emission spectra were recorded at a number of temperaturesbetween 4.2 K and 300 K in the infra-red region (1 μm - 2.5 μm). At 4.2 K, four main absorption bands were observed with accompanying vibronic lines which have been assigned. The band structures are not yet well explained. Some extra lines can be due to the phase transition which occurs at 70 K in $ThCl_4$ (2) and be interpreted as different sites of the same symmetry. According to the selection rules associated with the D_{2d} symmetry for electric dipolar transitions, we expect two transitions clearly σ polarized ($\Gamma_6 \rightarrow \Gamma_6$ and $\Gamma_7 \rightarrow \Gamma_7$) and two common transitions, σ and π ($\Gamma_6 \leftrightarrows \Gamma_7$).

One of the most important fact is the observation of a strong fluorescence line, at 4 912 cm^{-1}, which appears at low temperature and becomes more and more intense as the temperature is decreasing. A second weaker emission line, at 4 076 cm^{-1}, completes the fluorescence spectrum. These two lines were used in the identification of the low-lying states. Selective excitation of the four main absorption bands (using a 1 kw tungsten lamp as IR generator and a monochromator for the wavelength selection) shows that all the four $^2F_{7/2}$ states give the same fluorescence lines which are originated from the lowest $^2F_{7/2}$ state.

The electronic states resulting from a $5f^1$ configuration restricted to D_{2d} symmetry can be described by considering the spin orbit and the crystal field interactions. The hamiltonians are :

$$H_{S.O.} = \zeta \vec{l} \cdot \vec{s}$$

$$H_{C.F.} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6 + B_4^4 (C_4^4 + C_{-4}^4) + B_4^6 (C_4^6 + C_{-4}^6)$$

A priliminary calculation, starting from an initial estimate of the crystal field parameters found for U^{4+} in $ThCl_4$ leads to a satisfactory agreement between experimental and calculated level energy values. The seven crystal-field-split levels have been assigned and a least square fit gives a mean energy deviation of 62 cm^{-1}. The values in cm^{-1} of the parameters obtained from the fit are listed in the following table :

$$F_0 = 3651.71$$
$$B_0^2 = -1135.00$$
$$B_0^4 = 1742.14$$
$$B_0^6 = -2360.00$$
$$B_4^4 = -2557.74$$
$$B_4^6 = 75.00$$
$$\zeta = 1518.00$$

Further experiments are in progress on $ThBr_4 : Pa^{4+}$. These new results will help us to confirm the first indexation given in this paper.

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U^{4+} ABSORPTION AND EMISSION SPECTRA IN THE INCOMMENSURATE PHASE OF $ThBr_4$

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β-$ThBr_4$ (D_{4h}^{19} at RT) is used as host substance for high resolution spectroscopic studies of tetravalent actinide ions substitued for Th^{4+}. The crystal symmetry site of the Th^{4+} ion is D_{2d}. At T_0 = 94 K, β-$ThBr_4$ undergoes a structural phase transition (1). Single crystal neutron diffraction experiments have subsequently revealed the existence, below T_0 of satellite reflexions at $h\,k\,\ell \pm \frac{1}{3}(1-\delta)$ with δ = 0.063, independant of temperature. No lock in phase is observed down to 4.2 K (2). The low temperature structure is then incommensurate with a modulation along the four-fold axis.

The existence of a modulate phase was first suspected on the basis of the optical emission and absorption spectra of U^{4+}. Absorption spectra of U^{4+} over the 4 000-2 000 cm^{-1} range were measured at temperature down to 4.2 K. The spectra obtained consisted of many more lines that could be reasonably expected from splitting of J states of 5 f^2 configuration by D_{2d} crystal field. In addition anomalous absorption line shapes were observed suggesting the presence of a continuum of U^{4+} sites (fig. 1A). A dye laser has been used for fluorescence experiments by resonant excitation of U^{4+} ions in $ThBr_4$. Scanning the excitation radiation through the absorption line width while fluorescence was observed (Fig. 1B) has put into evidence two sets of lines. One set can be described as many broad continuum of sharp lines limited by two edge singularities whose line shapes can be quantitatively described by taking into account a sinusoïda' modulation of the U^{4+} site along the $\vec{c}$ axis. The other set corresponds to lines belonging to U^{4+} in a Γ_{2d} symmetry. A new crystal field calculation has been made for these energy levels (3).

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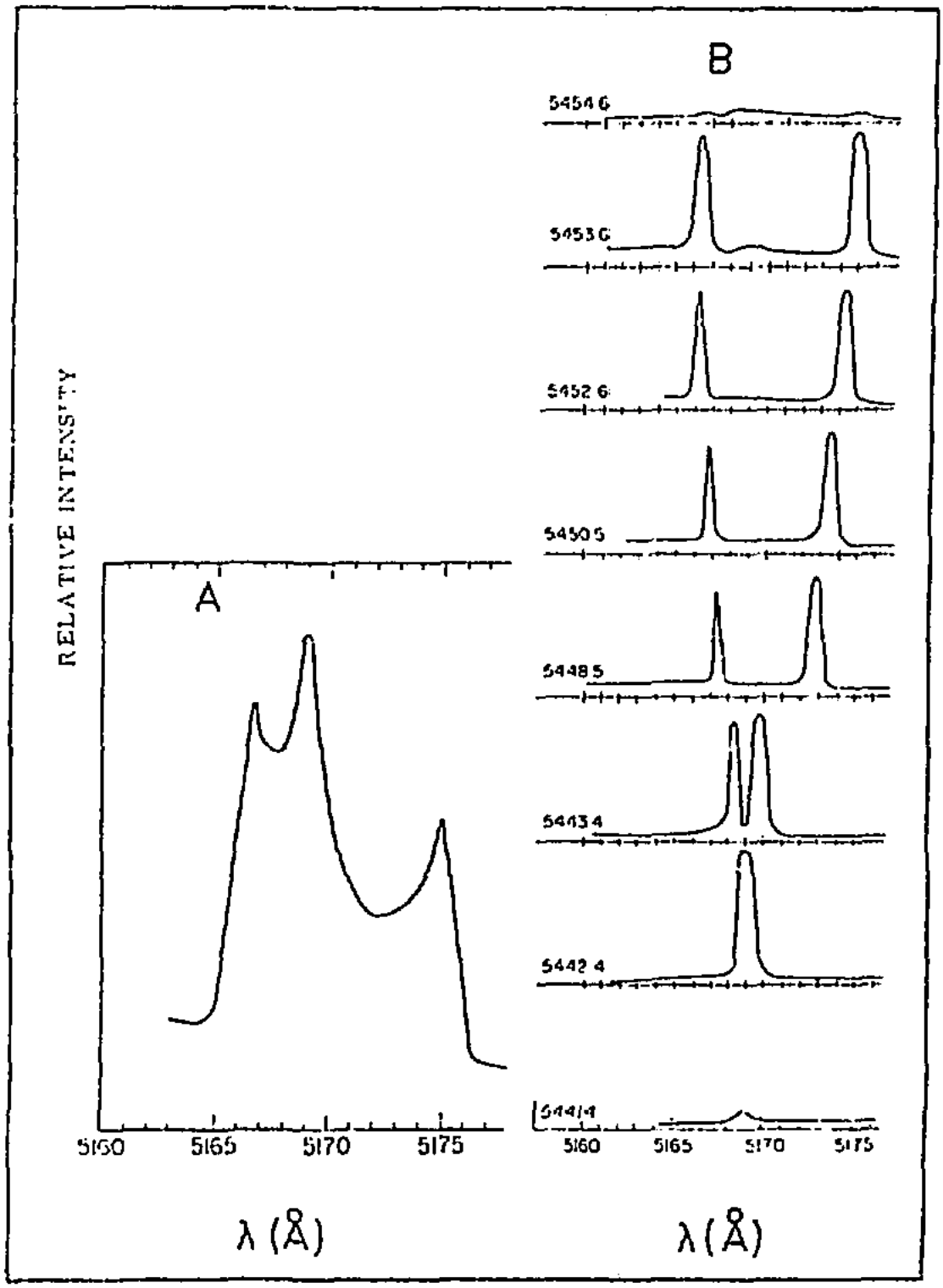

Fig. 1 A - Part of the σ absorption spectra of $ThBr_4 : U^{4+}$.
1 B - Surprising variation of strong fluorescence lines by scanning through absorption line of figure 1A. The excitation radiation is given in abscissa.

ABSORPTION SPECTROPHOTOMETRIC CHARACTERIZATION OF DIMORPHIC BERKELIUM-249 AND CALIFORNIUM-249 TRICHLORIDES AND DETERMINATION OF THEIR RELATIONSHIP THROUGH BETA DECAY*

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The preparation of UCl_3-type hexagonal $BkCl_3$[1] and $CfCl_3$[2] have been reported. Subsequently single crystals of $CfCl_3$ were used to establish the existence of a new $PuBr_3$-type orthorhombic phase and to refine the structures of both crystallographic forms.[3] We have utilized our microscope-spectrophotometer[4] to obtain absorption spectra from microgram-sized samples of $BkCl_3$ and $CfCl_3$ exhibiting each structure type. A $BkCl_3$ sample of each structure type was monitored spectrophotometrically to follow the ingrowth of californium into $BkCl_3$ via beta (β^-) decay [$t_{\frac{1}{2}}$ = 314 d]. We report here: (1) the existence of $PuBr_3$-type orthorhombic (denoted ortho) $BkCl_3$; (2) the spectral identification of ortho $BkCl_3$ and $CfCl_3$ and that of UCl_3-type hexagonal (denoted hex) $BkCl_3$ and $CfCl_3$; (3) the chemical consequences of the β^- decay of ortho $BkCl_3$ and hex $BkCl_3$; and (4) the temperature relationship between these ortho and hex trichloride phases.

The microscale preparation of halide samples suitable for absorption spectrophotometric analysis are given elsewhere.[4] The chloride samples were sealed in silica capillaries under 3/4 atm HCl gas and stored at room temperature. Phase changes were brought about by heating (and subsequently cooling) a chloride sample in situ by means of a resistance-heated platinum wire coil located externally to, and coaxially with, the sample-containing capillary. Standard X-ray powder diffraction techniques were used to acquire sufficient data from the macrocrystalline samples (a consequence of melting the samples to maximize optical transparency) to confirm the structure type.

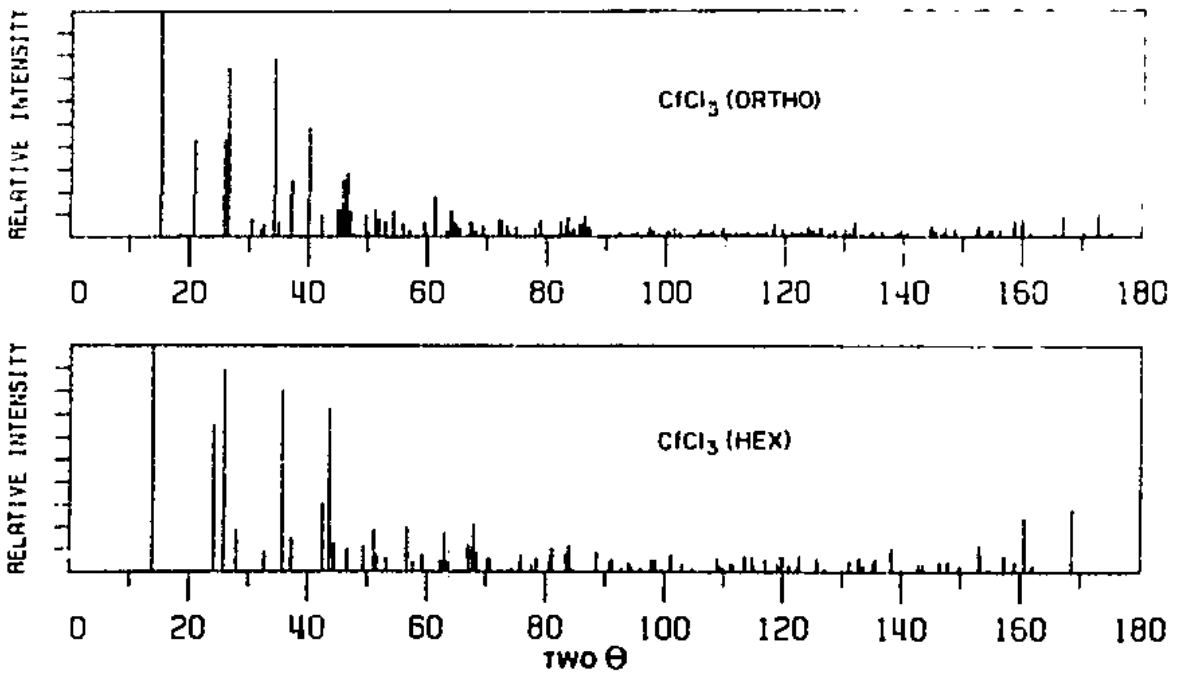

FIGURE 1

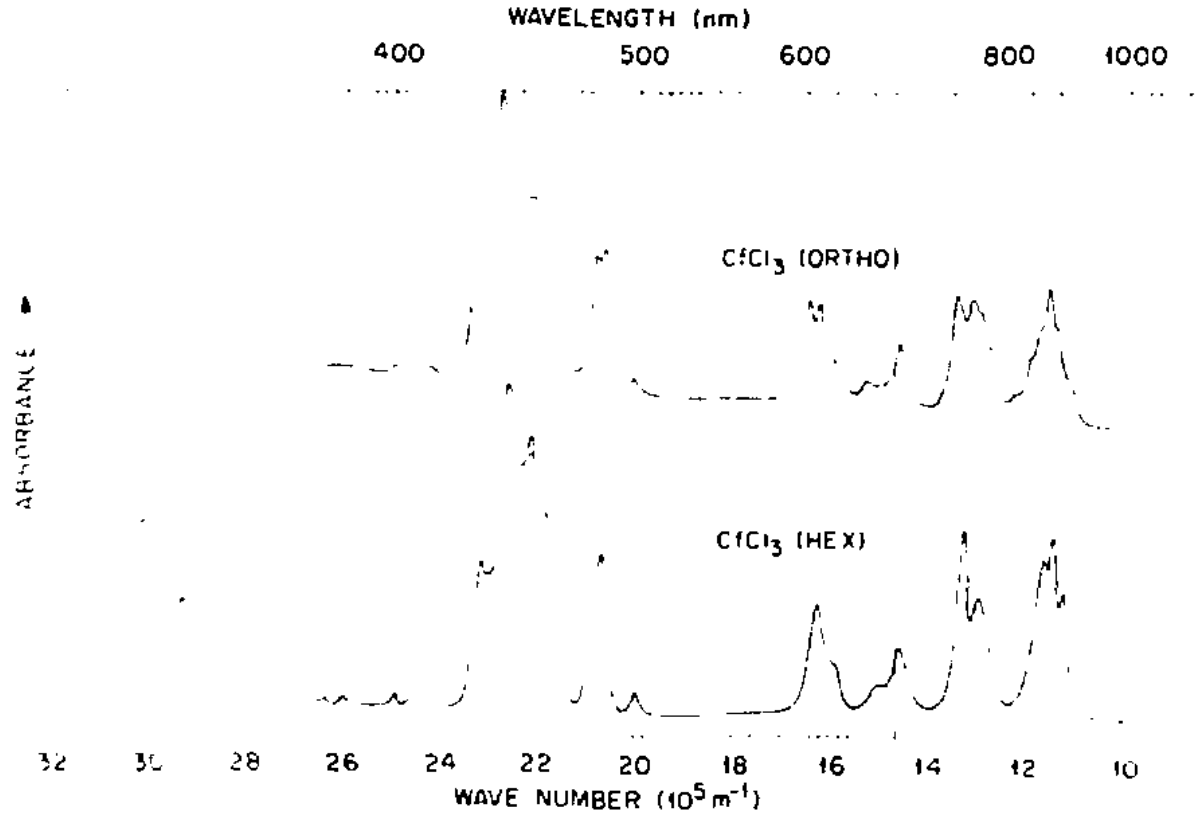

FIGURE 2

Theoretical powder diffraction patterns of hex $CfCl_3$ and ortho $CfCl_3$ Fig. 1) were calculated for CuK$\bar{\alpha}$ radiation by the computer program POWD[5] using reported structural parameters[3] but including no correction for sample absorption. Confirmation of the hex $CfCl_3$ structure was based on the presence of the four strong diffraction lines at 2θ = 13.9, 24.1, 35.7, and 43.5° and the concomitant absence of the characteristic diffraction lines of ortho $CfCl_3$ at 2θ = 15.1, 20.7, 26.4, 34.2, and 40.0°. Confirmation of the ortho $CfCl_3$ structure was achieved by a reversal of this procedure.

Absorption spectra of hex $CfCl_3$ and ortho $CfCl_3$ are presented in Fig. 2. They are easily distinguished by the different shapes (symmetric vs asymmetric; split vs unsplit) of the f-f absorption bands at about 16.2, 13, and 11.4 x 10^5 m^{-1}. A comparable set of absorption spectra for $BkCl_3$ will be presented. This is the first report of $PuBr_3$-type orthorhombic $BkCl_3$.

Absorption spectra from a sample of hex $BkCl_3$ and from a sample of ortho $BkCl_3$ were obtained over a period of several years to monitor the ingrowth of the californium daughter. The spectrum of the californium growing into the hex $BkCl_3$ matched that of hex $CfCl_3$ shown in Fig. 1. In the case of ortho $BkCl_3$, the spectrum of ingrown californium matched that of ortho $CfCl_3$ in Fig. 1. In both cases the aged $BkCl_3$ samples were also examined by X-ray powder diffraction to confirm that the structure of the ingrown $CfCl_3$ was the same as that of the parent $BkCl_3$. Thus, two investigative methods have shown that both the oxidation state and the local structure (environment) of the Bk ions are retained by the Cf ions resulting from β^- decay in the bulk-phase solid state. This result agrees with our earlier findings on dimorphic $BkBr_3$.[6]

In the earlier work on dimorphic $CfCl_3$, the temperature relationship of the two crystallographic modifications could not be determined.[3] A report of similar dimorphism in $GdCl_3$ concluded that ortho $GdCl_3$ is the low-temperature form with a transition (to hex $GdCl_3$) temperature of about 100°C.[7] In contrast, the results of our thermal annealing and quenching studies indicated that ortho $BkCl_3$ and ortho $CfCl_3$ are the high-temperature forms with phase transition temperatures close to their melting points, 603 and 545°C, respectively.

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NEUTRON DIFFRACTION STUDY OF ^{239}PuN

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The ^{239}Pu compounds have not been studied till now by neutron diffraction techniques due to their very high neutron absorption cross-section (about 1000 barns). The presence at I.L.L. Grenoble of a very high flux reactor and of very performant powder neutron diffractometer equipped with multi-detector, gave a good opportunity to undertake the study of such material.

^{239}PuN has been classified as a paramagnetic material becoming antiferromagnetic at T = 13K due to the shape of the magnetic susceptibility measurements. The aim of this experiment was to determine the neutron scattering length of ^{239}Pu for which only one measurement is available in the literature and to study the magnetic ordering at low temperature. No magnetic ordering has been found at 4K, the limit of the magnetic ordering which could be detected being μ_{ord} = 0.2 μ_B per Pu atom. The neutron scattering length determination of ^{239}Pu gave a value slightly higher than the old value given in the literature.

STUDY OF A STRUCTURAL PHASE TRANSITION ON A UMn_2 SINGLE CRYSTAL BY γ-RAY DIFFRACTION

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UMn_2 is a Laves phase compound which crystallizes in the Cu_2Mg type cubic system. Low temperature susceptibility measurements have suggested an antiferromagnetic transition around 240 K for this compound which is paramagnetic at room temperature. Successively no magnetic ordering was found at the transition but a structural distortion from cubic to a monoclinic cell was observed. This paper reports the results of a γ-ray diffraction investigation of this transition. Rocking curves were obtained as a function of temperature through the transition for the reflections [220] and [111]. Both rocking curves become broader and broader as the temperature is reduced, implying a very marked pretransitional effect.

MAGNETIC ANORMALY IN NEUTRON IRRADIATED US

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Fission fragment damage introduces a great number of defects, such as vacancies, interstitials and/or cluster of each simple point defect, in a fissile material. A simple calculation gives that about 10^6 lattice atoms are influenced by one fission event. Thus, the crystal structure shoud be altered. This fact has been confirmed in any fissile material, for example uranium monocarbide [1] and uranium mononitride [2] which show an elongation of the lattice parameter. We reported in a previous paper [3] that a magnetic ordering (AF1-magnetic structure) of UN varied with fission fragment damage. Therefore, the magnetic structure should be also distorted by an introduction of such defects. In the present study, we examined the effects on magnetic property of uranium monosulphide (US) which has the same crystal structure (NaCl-type) as UN, but having a ferromagnetic transition at a cryogenic temperature.

Fig. 1 shows changes of the lattice parameter and the electrical resistivity of US just after reactor irradiations. The irradiations were performed with JRR-3 at below 100°C. No remarkable changes are observed in both properties below an irradiation dose of 10^{16} fission/cm^3. After that dose, however, the lattice expands and the resistivity increases. In the same figure, we present the Curie temperatures (T_c) of US irradiated to a variety of fission dose. T_c were obtained from measurements of both magnetic susceptibility and electrical resistivity. It seems that a shift of T_c is followed to the lattice expansion. This behavior was quite similar to that

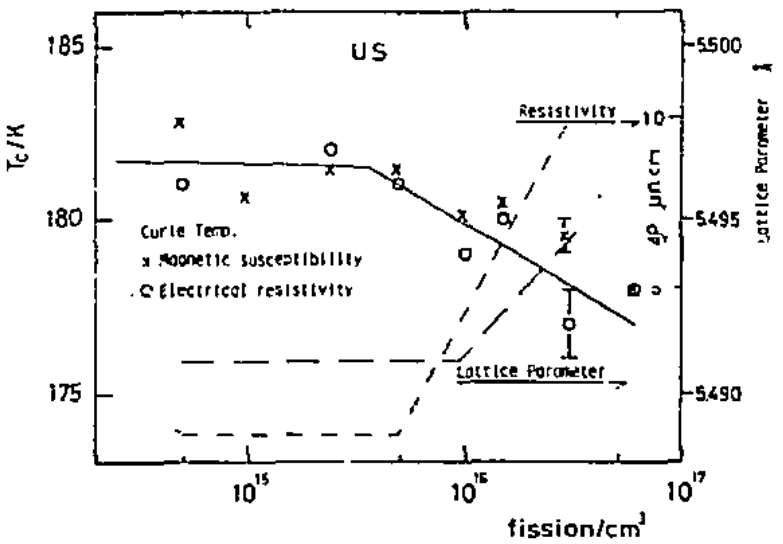

Fig. 1 Changes of lattice parameter (Å), resistivity (ρ) and Curie Temperature (T_c)

of UN, though this substance was antiferromagnet and T_N (the Néel temperature) shifted more widely [3].

Typical examples of the measured susceptibility (magnetization) of US with and without irradiation are illustrated in Fig. 2. The original (non-irradiated) US showed a normal ferromagnetic behavior and the all magnetic parameters (σ, μ_B, T_c and θ_p) were in good agreement with literature data [4]. On the other hand, the irradiated US revealed a big "cusp" before the magnetic transition. And the magnetic parameters were all changed comparing with the original. Curious was a fact that the lowered magnetization of the irradiated specimens at low temperature turned back to the original value (but not completely) by a further irradiation.

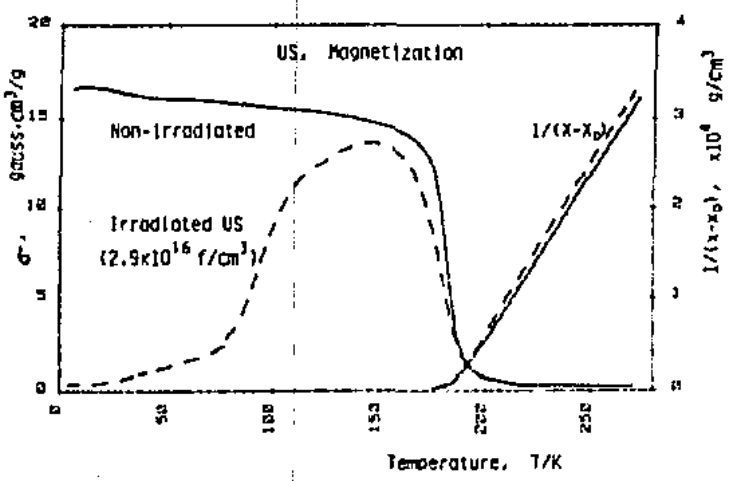

Fig. 2 Magnetization of US at 4 KG

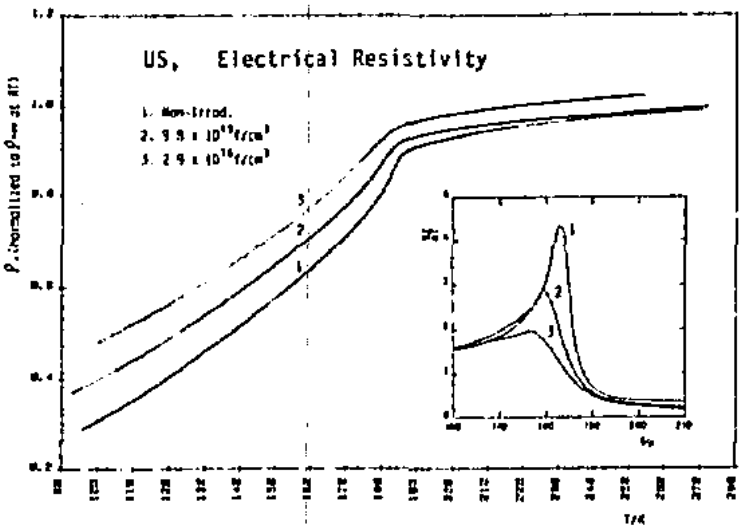

Fig.3 Resistivity (normalized) of US and the derivatives, $d\rho/dT$, at near T_c

Dependences of the electrical resistivity on temperature confirmed that shift of T_c obtained from the magnetic measurement, as shown in Fig. 3, in which we gave a drawing of derivatives of resistivity to temperature, $d\rho/dT$, near the Curie point. It should be also noticed here that the derivative was broader shape with increasing the fission dose or numbers of defects induced by fission fragment damage.

In the present stage, to interpret the anormaly in the magnetic behavior of the neutron irradiated US is quite difficult. Danan et al. [4] observed the big "cusp" in $(U_{0.8}Th_{0.2})S$, and the shift of T_c to lower temperatures in

$(U_xTh_{1-x})S$ corresponded to the lattice expansion by diluting ferromagnetic US with paramagnetic ThS. Many different models have been proposed to interpret that phenonenon. An "interconfiguration fluctuation model" proposed by the above authors could be probably applicable to our present results, considering with a defect structure of the neutron irradiated US. Of course, in order to get a precise model for that, we need more experimental evidences, such as magnetic form factor and specific heat.

This work has been performed under the Joint Research Program of JAERI. Drs. S. Nasu and H. Watanabe are greatfully acknowledged for the reactor irradiations of US samples. We express our thanks to Drs. C.H. de Novion and J.Morillo (CEN, Fontenay-aux-Roses), Drs. H. Blank, Hj. Matzke and L. Manes (EURATOM, Karlsruhe) and Dr. N. Achiwa (TU München) for their valuable discussions.

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FISSION-INDUCED MAGNETIC BEHAVIOR IN URANIUM MONONITRIDE

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Uranium mononitride(UN) has the NaCl-type crystal structure and an antiferro- to para- magnetic transition at 51.6 ± 0.5 K (1,2). Previously it was presented the variation of the magnetic ordering of neutron-irradiated UN by measuring the electrical resistivity(ρ) in a cryogenic temperature. It was found that the transition temperature (T_N) shifted with increasing fission dose. For a radiation-damaged magnetic metal, the electrical resistivity($\rho_{total}(T)$) is expressed as follows;

$$\rho_{total}(T) = \rho_{mo}(T) + \rho_{md} + \rho_d + \rho_i + \rho_p(T) \qquad (1)$$

where each term is corresponding to the electrical resistivity contributed to magnetic order, magnetic disorder, fission-induced defects, impurities and phonon, respectively. All terms could be determined from the experiments.

It is an aim of this work to clarify the magnetic disordering in the fission-damaged UN. The characterization of the samples was already presented elsewhere(2). The measurement of magnetic susceptibility(χ) was done by an automatically computer-controlled Faraday torsion balance. All magnetic parameters were calculated and plotted out with a micro-computer. For non-irradiated UN, the magnetic parameters are agreed well with another investigation(3). From temperature dependences of the magnetic susceptibility on various fission doses, magnetic parameters were calculated and shown in the table in comparison with non-irradiated one. It was found that T_N shifted to lower temperature with increasing fission dose. However at 3.6×10^{18} f/cm^3, T_N returned to the original temperature. The dependences on fission dose were interpreted with the fission-induced defects in the same manner to the electrical resistivity(2).

The magnetic susceptibility($\chi_{total}(T)$) for the fission-damaged antiferromagnetism is expressed as follows;

$$\chi_{total}(T) = \chi_{antiferro}(T) + \chi_{para}(T) + \chi_0 \qquad (2)$$

where each term indicates the contribution to the un-damaged antiferro-, damage-induced para- and Pauli para- magnetic part, respectively. Compared with the cryogenic electrical resistivity(Eq.(2)), $\chi_{antiferro}(T)$ and $\chi_{para}(T)$ are corresponding to $\rho_{mo}(T)$ and ($\rho_{md} + \rho_d$), respectively. From thermal recovery measurements of the electrical resistivity, it was found that there were three kinds of defect in the fission-damaged UN. In addition, all magnetic parameters returned to near the original values after annealing at 850 °C. It could be deduced that $\chi_{para}(T)$ originated in these fission-induced defects. Similarly the decreases of T_N and N_B would come also from them and the induced compressive lattice strain. This is consistent with T_N shift in UN under high pressure(4).

On the other hand, the magnetic behavior was treated theoretically with using the term of spin exchange interaction(J). After C.F. van Doorn(5), we used the molecular field approximation;

$$kT_N = A(-4J_1 + 6J_2) \qquad (3)$$

and from the RKKY interaction model for the face-centered cubic lattice, we obtained;

$$-6.46 \times (A/k)\, J_1' = T_N \qquad (4)$$

$$15.76 \times (A/k)\, J_2' = T_N \qquad (5)$$

where $J_1' = J_{RKKY}(a/\sqrt{2})$ and $J_2' = J_{RKKY}(a)$. Using these relations, the exchange interaction(J_1' and J_2') were calculated and shown in the table. They decreased with increasing fission doses. This means that the elongation of the lattice distance and the increase of the fission-induced defects weaken the exchange interaction between the magnetic spins.

In order to evaluate a perturbation of the magnetic spin ordering in the irradiated UN, a reduced magnetic susceptibility concerned to $\chi_{antiferro}(T)$ in Eq.(2) ($\chi(T)/\chi(T_N)$) were plotted to the reduced temperature(T/T_N) for the various fission doses. The reduced magnetic susceptibility of the fission-damaged UN increased more rapidly than the non-irradiated one. This behavior is quite similar to the case of the electrical resistivity. This could be explained with the term of the fluctuation of the exchange interaction. After C.C. Tsuei et al.(6), the exchange interaction is assumed to reflect the structural fluctuation. The degree of the disorder is defined as the root mean square of the deviation of the average exchange interaction between two nearest neighbor spins as follows;

$$\delta^2 = \langle \Delta J^2 \rangle / \langle J \rangle^2 \qquad (6)$$

In the present case, δ means the structural fluctuation which originates in the spatial distribution of the fission-induced defects(interstitials, vacancies and the clusters). It was found experimentally that δ became large with increasing fission doses. It is consistent with a relationship that the more rapidly the reduced magnetic susceptibility increases, the larger δ is.

In conclusion, the magnetic behavior of the irradiated UN can be well explained with the fission-induced defects and the interactions between the defects and the magnetic spins. However, by the amorphous magnetism, the magnetic behavior, above-mentioned, could be also well interpreted experimentally and theoretically(7). The present results are fairly consistent with that of many amorphous magnetic materials, perhaps because of the similarity of the crystal structure containing high concentration defects and amorphous materials.

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Magnetic Parameters of the Fission-damaged UN

FISSION DOSE (fissions/cm^3)	$\chi_0 \times 10^6$ (emu/gauss·g)	N_B (μ_B)	Weiss Constant	T_N (K)	J_1'	J_2'
Non Irradiated	0	2.75	-250	52	-8.0	3.3
5.1×10^{16}	0.10	2.49	-180	45	-7.0	2.9
3.7×10^{17}	1.35	2.07	-116	44	-6.8	2.8
1.8×10^{18}	1.57	1.93	- 99	42	-6.5	2.7
3.6×10^{18}	0.06	2.64	-213	53	-8.5	3.4

MEASUREMENT OF THE MAGNETIC RESPONSE FUNCTION IN UAs

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One of the most intriguing features of the 5f electrons in actinide systems is their dynamical susceptibility $\chi(\hbar\omega,\bar{Q})$ where energy is denoted by $\hbar\omega$ and momentum transfer by $\bar{Q}$. The static susceptibility, as measured by conventional magnetization experiments is the zero frequency response at q=0, so that the generalized susceptibility may be thought of as the magnetic response at a specific frequency and momentum transfer. Neutron scattering techniques permit measurement of the imaginary part of the susceptibility response $\chi''(\hbar\omega,Q)$ from which the static susceptibility $\chi(Q)$ can be obtained directly using the Kramers-Kronig relation. In most systems the frequency and momentum range of the neutron interaction is well matched to that of the magnetic electrons. The results will be discussed in terms of the scattering law $S(\hbar\omega,\bar{Q})$. Since neutron intensities and interactions are weak, large samples are required and this has so far confined measurements in actinide systems to U compounds.

We report here measurements performed on polycrystalline samples of UAs using the time-of-flight neutron spectrometer IN4 at the high-flux reactor, Institut Laue-Langevin, Grenoble, France. The incident neutron energy was 50 meV and measurements were taken over a wide range of momentum transfer Q. Since the neutrons also see inelastic processes involving the nuclei (phonons) we have measured the same spectra from samples of UAs and ThAs. No 5f electrons exist in the latter, allowing a simple measurement of the phonon scattering, which is the same in both compounds. Typical spectra at two values of Q are shown in the Figure. The strong central line is the elastic incoherent signal. To the right and left are neutron energy loss and gain spectra respectively. The apparent lack of symmetry is a consequence of the population of states, which depends on the temperature of the sample. At high Q the phonons only are seen, and can be readily modelled with two Lorentzians at low and high energy to represent the acoustic and optic modes, respectively. At low Q the magnetic form factor is non zero and we see magnetic scattering as well as some nuclear. The figures on the left-hand side clearly show this, and we can fit the magnetic scattering with a Lorentzian function centered at $\omega = 0$. Of particular importance is that, except for a reduction in intensity, the inelastic scattering in UAs has much the same shape at 80 and 150K.

Uranium arsenide (NaCl structure, a = 5.78 Å) orders with the type-I antiferromagnetic structure.[1] The response function in the paramagnetic state, a Lorentzian of half width $\Gamma/2 = 13 \pm 1$ meV ($\sim$ 150K) is similar to that found for other uranium and unstable moment systems.[2,3] However a very similar, $\Gamma/2 = 10 \pm 1$ meV, response function in the ordered state is most unusual. Experiments with a triple-axis spectrometer and single crystals of UAs have failed to find any evidence of sharp (spin wave) excitations,[4] and the present study shows that the response is strongly overdamped in energy. The inelastic magnetic scattering can be fit with a Lorentzian at all temperatures, the

half width varying between 8 ± 1 meV at 5K to 15 ± 2 meV at 250K. No sign of any crystal-field excitations below 40 meV has been found at any temperature.

We are also able to obtain a limited amount of Q information. In general the magnetic scattering falls off with the usual magnetic form factor; however, in the first Brillouin zone $|\vec{Q}| = |\vec{q}|$, where $\vec{q}$ is the reduced wave vector measured from a zone center, in this case the origin of Q-space. Our measurements show an increase in intensity for the magnetic scattering as Q varies from 0.8 to 1.5 $Å^{-1}$. The zone boundary at (110) has Q = 1.54 $Å^{-1}$. This shows a tendency for antiferromagnetic correlations at all temperatures, even though collective excitations cannot be seen.

These results will be discussed in the context of those obtained for other uranium systems and our current understanding of the dynamics of 5f systems.

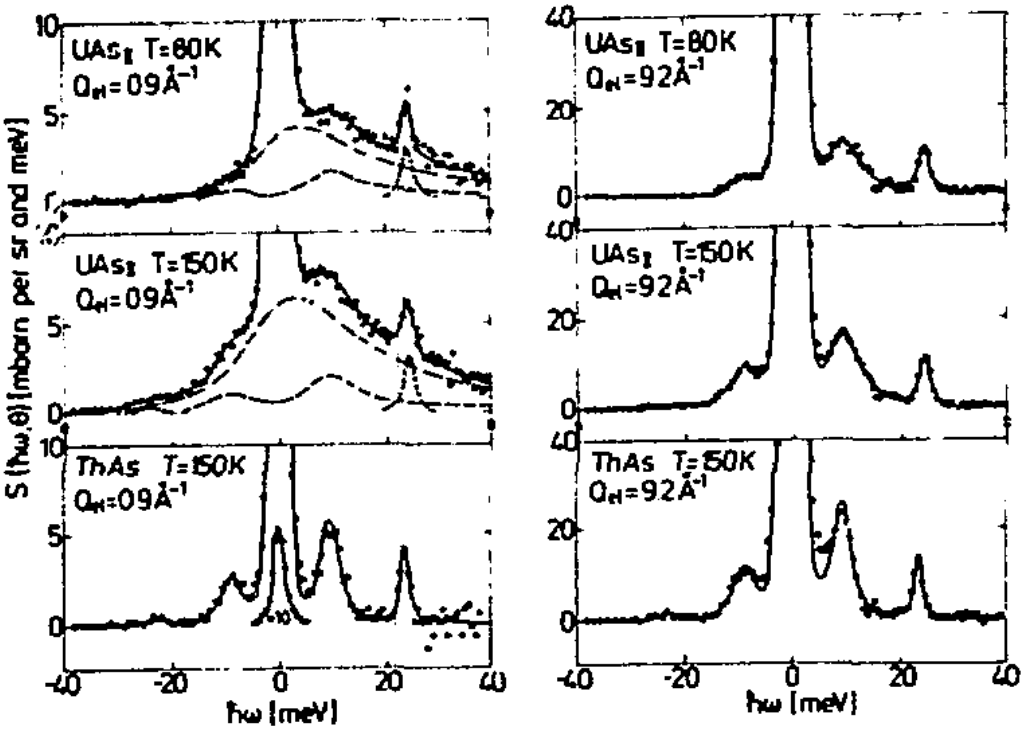

Fig. caption Scattering law as a function of energy for constant angle for UAs and ThAs. Plots on the right ($Q_{elastic}$=9.2 $Å^{-1}$) are phonons only and show well resolved acoustic and optic branches. Solid lines are fits to data. Plots on the left (note ordinate scale change) show clearly the magnetic (-.-.-) and phonon (- - -) contributions.

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A NEUTRON DIFFRACTION STUDY OF THE MAGNETIC ORDERING IN $NpAs_2$

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A neutron diffraction study of the magnetic ordering of $NpAs_2$ on a small single crystal sample has been performed. $NpAs_2$ orders at $T_N = 54$ K. In the temperature range 18 K < T < T_N the magnetic ordering consists of a pure sine wave modulation propagating along a <100> direction of the tetragonal unit cell of the $CuSb_2$-type structure. Over this temperature range the wave vector remains constant with a value $\vec{k}$ = <0.14, 0, 0> in reduced unit. The moment direction is parallel to the tetragonal c-axis and the two neptunium Bravais lattices are coupled ferromagnetically. At T = 18 K a first order transition occurs towards a ferromagnetic state. The magnetic moments remain aligned along the c-axis and have at low temperature a magnitude of 1.45 ± 0.1 μ_B.

INVESTIGATION OF THE MAGNETIC PHASE DIAGRAM OF UAs BY MAGNETIZATION AND NEUTRON DIFFRACTION EXPERIMENTS

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The magnetic phase diagram of UAs has been investigated on single crystal by mean of magnetization and neutron diffraction experiments. Magnetization measurements in field up to 200 kOe applied along the three symmetry directions <100>, <110> and <111> allow to define the transition lines between different magnetic phases of different magnetization. Neutron diffraction experiments in field up to 100 kOe parallel to <100> and <110> axes give the exact nature of these different magnetic phases.

Whatever the temperature and the magnetic field, all the ordered states are characterized by longitudinal waves with a wave vector $\vec{k}$ parallel to <100> axis and associated Fourier Components $\vec{m}_k$ parallel to $\vec{k}$.

Two regions have been evidenced in the (H,T) phase diagram.

1) A high temperature region above about $T_N/2$, in which the magnetic ordering is collinear. This is unambiguously established because a magnetic field applied along a <110> direction induces a single domain state. Up to 200 kOe the magnetic structure remains an antiferromagnetic type I ($\vec{k}$ = <100>) stacking of ferromagnetic (001) plans accordingly to the sequence +-+-, except in high field near T_N and $T_N/2$ where ferrimagnetic structures are observed ($k = [00\frac{2}{3}]$ ++- sequence of (001) ferromagnetic planes).

2) A low temperature region below $T_N/2$ where the magnetic ordering corresponds to a 2k-structure i.e. which consists of two coupled wave vectors parallel to two different <100> axes. Then the easy direction of magnetization is <110> as established by magnetization measurements. In the neutron diffraction spectrum it exists at least two perpendicular wave vectors and the intensities of the magnetic Bragg peaks associated to each of them are in well defined ratio. The magnetic structure is antiferromagnetic with $\vec{k}$ =<1/2 0 0>, in field lower than about 70 kOe and it is ferrimagnetic in higher field. In that case the ordering is described by a propagation vector $\vec{k}_\perp$ perpendicular to the field direction which keeps the value one half and a propagation vector $k_{//}$ which takes the successive value k = 4/7, 5/8, 2/3 at low temperature ($T \lesssim 20$ K) and only the value k = 2/3 at higher temperature.

These results, in addition to the determination of the phase diagram and the description of the different magnetic structures of UAs confirm the previous study of uranium monopnictides under an applied stress. In this study multi-k structures can be accounted for by a competition between anisotropic exchange interactions which lock the k-vector along <100> directions and one ion anisotropy which favours <110> or <111> moment directions.

Moreover UAs exhibits a unique phase transition between a collinear structure at high temperatures and a 2k-structure at low temperatures. This behaviour cannot be understood without including, in addition to crystal field anisotropy some higher order terms which by their thermal variation drive the transition.

s(d)-f MODEL AND MAGNETISM OF NARROW-BAND CRYSTALS

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The problem of the indirect exchange interaction of the localized spin S via conduction electrons in a crystal described by the s(d)-f Hamiltonian, involving the interelectron interaction in the Hubbard approximation, is considered. In the case of strong intratomic interactions (with the parameters of s-f interaction I and s-s interaction U), analysis of the high temperature susceptibility expansion and of the effective Hamiltonian makes it possible to obtain expressions for the paramagnetic extrapolation temperature T_p and effective paramagnetic moment m_{eff} for an arbitrary conduction current concentration $0 \leqslant x < 1$ as well as expressions for the ordering temperature T_N, the effective spin moment S_{eff} and the exchange Heisenberg parameter J(m-n) in the case of x=1.All these expressions are consolideted in the table for both signs of I. The following notations are used: K is the Boltzmann constant, g the Landé factor, B_{m-n} the transfer integral between sites m and n , W the band width, r the structure factor equal to 1/24, 1/32, 1/64 for an sc, bcc and fcc lattice respectively. The negative sign of J(m-n) and T_p reveals the antiferromagnetic nature of the effective coupling.The spin S dependence of the T_N and T_p temperatures is unusual.

The spectrum of the states with high multiplicity at infinite I (double-exchange approximation) in the limiting cases of the electron (N_e=1) and one hole in the half-filled band (N_h=1) is investigated. For the maximum crystal spin S_{max} and for S_{max}-1 the enrgy is the same: Bt_g(B is the transfer integral between the nearest neighbours, q the quasimomentum, t_q the usual electron band energy in the B units) at N_e = 1, $-Bt_q$ at N_h=1 for the positive I and $2SBt_q/(2S+1)$ at N_e=1, $-2SBt_q/(2S+1)$ at N_h=1 for the negative I.

The crystal wave function has the form

$$F(S^Z_{max} - 1) = \sum_n c_n F_n + \sum_{nm} c_{nm} F_{nm} ,$$

where F_n is the state with a spin deviation on the site n with an electron (hole) on it, F_{nm} is the state with a spin deviation on the site n and with an elctron (hole) on the

Expressions for the effective spin moment, the effective exchange integral, the ordering temperature, the paramagnetic temperature and the effective paramagnetic moment.

	S_{eff}	$J(m-n)$	T_N	T_p	m_{eff}
I>0	S+1/2	$-\frac{2B^2_{m-n}}{(2S+1)^2(U+2SI)}$	$\frac{(2S+3)rW^2}{3K(2S+1)(U+2SI)}$	$-\frac{2S+3}{3K(S(S+1)+x(S+3/4))}\cdot(\frac{x^2(2S+3)}{4(U+2SI)}+\frac{x(1-x)S(S+1)}{(2S+1)^2I})rW^2$	$g(S(S+1)+x(S+3/4))^{1/2}$
I<0	S-1/2	$-\frac{2B^2_{m-n}}{(2S+1)^2(U-2(S+1)I)}$	$\frac{(2S-1)rW^2}{3K(2S+1)(U-(2S+1)I)}$	$-\frac{2S-1}{3K(S(S+1)-x(S+1/4))}\cdot(-\frac{x^2(2S-1)}{4(U-2(S+1)I)}-\frac{x(1-x)S(S+1)}{(2S+1)^2I})rW^2$	$g(S(S+1)-x(S+1/4))^{1/2}$

site m. For the sc lattice at N_e=1 and positive I, N_h=1 and negative I, for example, one has

$$c_n = a(k,q)e^{-ikn};$$

$$c_{nm} = a(k,q)e^{-ikn}(A_o(t_k - t_q)(e^{iq(n-m)} - A_{n-m}/A_o)\, b_1/b_2 + b_2 e^{iq(n-m)}),$$

where $a(k,q) = v^{-1}b_2(b_1A_o(t_k - t_q) + b_2^2)^{-1}$;

$$2A_n = i^{1-n_x-n_y-n_z} \int_0^\infty e^{it_qX/2} J_{n_x}(X)\, J_{n_y}(X)\, J_{n_z}(X)\, dX ;$$

$t_k = \cos k_x + \cos k_y + \cos k_z$, $J_m(X)$ is the Bessel function of the order of m, v the dimensionless volume of the Brillouin zone;

$b_1 = 1/(2S+1)$, $b_2 = (2S/2S+1)^{1/2}$ for N_e=1 and

$b_1 = 1/2S$, $b_2 = (2S-1)^{1/2}(2S)^{-1/2}$ for N_h=1.

The solutions for N_e=1 at negative I and for N_h=1 at positive I have a more complicated form. The states with k=q correspond to S_{max}, and the states with k≠q to S_{max}-1. The states of S_{max}-1 with the given q have an infinite degeneracy. The ferromagnetic states have no energy preference as compared with the spin wave states.

$NpAs_2$: MAGNETIC FORM FACTOR OF Np AND TENTATIVE CRYSTAL FIELD MODEL

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Single crystal growth of the neptunium compound $NpAs_2$ has been achieved at CEN-FAR.

A quantity of small crystals has been used to make new susceptibility measurements on truly single phase samples. Then, the biggest crystals (with volumes not larger than $0.2mm^3$) have been used in polarized neutron diffraction experiments to measure the magnetic form factor of the Np ions.

$NpAs_2$ is tetragonal, anti-Fe_2As type [1]. The refined crystallographic parameters at helium temperature are found as : a = 3.930 (5) Å, c = 8.137 (5) Å, z (Np) = 0.281 (3), z (As) = 0,639 (3). This corresponds to a ratio $\frac{c}{a}$ = 2.07 versus the room temperature value given by [1] : $\frac{c}{a}$ = 2.048.

$NpAs_2$ is ferromagnetic at 4.2 K with a very strong magnetic anisotropy. In the (001) plane and under a 4.6 T applied magnetic field, the susceptibility is constant and weak : $\chi_{\perp} \# 5.10^{-6}$ emn/g. Along the easy direction (c axis), the magnetic moment is close to 1.46 μ_B.

In absence of magnetic field H, the Curie temperature T_c is about 18 K [2, 3]. Under H = 0.3 T, T_c was reported at about 22 K [4]. The present experiments prove that T_c is shifted up when H increases. Under H = 4.6 T and up to 31.5 K, the saturation magnetization M versus temperature T variation follows a linear law $M = M_o (1 - 0.0012\ T)$.

In the ferromagnetic region, 58 reflexions until $\frac{\sin\theta}{\lambda} = 0.67\ Å^{-1}$ fit well a Np^{4+} form factor. The best value of b(Np) to interpret the data, account taken of our previous investigation on NpO_2 (5) is :

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$$b(Np) = 1.015\ (15) \times 10^{-12}\ cm$$

A point charge model (PCM) approach based on the valencies Np^{4+}, As^{2-} doesn't explain the magnetic data satisfactorily. The ground state wave function is $\alpha|\pm\frac{9}{2}\rangle + \beta|\pm\frac{1}{2}\rangle + \gamma|\frac{7}{2}\rangle$ (in the Russel-Saunders $^4I_{9/2}$ multiplet). As this state is found very rich in $|\pm\frac{9}{2}\rangle$, the ordered moment is far too high ($\simeq 3.2\mu_B$). The results are only slightly improved when the charges on one of the As layers are lowered to take into account experimental stereochemical observations.

A crystal field analysis has then made for the isostructural (with very close lattice parameter values) U As_2. Here, a good set of eigenfunctions is easily found for the low lying energy levels, providing fair agreement with all experimental data (magnetic moments, magnetic entropy,...). Going back to the crystal field potential, this process leads to some changes in the parameters without any change in their signs with respect to PCM. The main features are all terms negative except the tetragonal sixth order one, axial sixth order term negligible. The axial fourth order term is dominating and tetragonal terms are important which was not observed in the PCM.

Applying this potential to $NpAs_2$ gives now very satisfactory results. In the ground state, $\alpha \# 0.7$, $\beta \# 0.6$, $\gamma \# 0.3$, α and γ have opposite signs. The resulting ordered moment directed along the easy axis is now close to $1.5\mu_B$. And the perpendicular component is nearly 0 as it is given by the expression :

$$g(2.5\beta^2 + 3\alpha\gamma)$$

where the two terms inside brackets are nearly equal and have opposite signs.

Extension of this model to other An X_2 compounds is considered.

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MAGNETIC AND ELECTRICAL PROPERTIES OF THE NEPTUNIUM BINARY COMPOUNDS $NpSb_2$, $NpTe_{2-x}$

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Magnetic susceptibility, electrical resistivity and Mössbauer effect measurements in the temperature range 4.2 - 300 K have been carried out on three different NpX_2 type binary compounds : $NpSb_2$, $NpTe_2$, $NpTe_{1.8}$. In all of them, the Np ions were thought to be trivalent (1,2) contrarily to $NpAs_2$ where they are now shown to be tetravalent (3,4).

$NpSb_2$ is orthorhombic, $LaSb_2$-type. Ir orders ferromagnetically below T_c = 45 K with an ordered moment deduced from magnetization measurements as $1.3\mu_B$ and from Mössbauer data as $1.9\mu_B$. The paramagnetic moment ($\mu_p = 2.87\mu_B$) and isomer shift agree with a 3+ valency for the Np ions. The resistivity, as measured on pressed powder pellets is semi-metallic in character with a maximum centered at T_c and a room-temperature value of 0.026Ω/cm.

$NpTe_2$ and $NpTe_{1.8}$ are tetragonal, anti Fe_2As type (like $NpAs_2$) with slightly different lattice parameters and the ratios $\frac{c}{a}$ equal to 2.035 and 2.07, respectively. None of them undergoes magnetic ordering down to 4.2 K. The paramagnetic moments above 200 K are 3.04 and $2.88\mu_B$ respectively, still in fair agreement with the Russell-Saunders (RS) value of $2.68\mu_B$ for a $^5I_4$ term ($5f^4$ configuration). Mössbauer isomer shift (measured only on $NpTe_2$) is in accordance with the 3+ valency. Room temperature resistivity values are higher than in $NpSb_2$ by three orders of magnitude. When the temperature is decreased, the resistivity does not change much in $NpTe_2$ but displays a tendency towards semi-conducting behaviour in $NpTe_{1.8}$.

For all three compounds, the inverse susceptibility versus temperature curves are curvilinear below about 100 K. The concavity towards the T axis is especially important in $NpTe_{1.8}$. This behaviour and the low value of the ordered moment observed in $NpSb_2$ as compared to the theoretical RS free ion value : $2,40\mu_B$, are analysed successively in a crystal field model and by delocalization effects of the 5f electrons.

A detailed comparison of the observed data is made with the corresponding data measured on the Np^{4+} ions in $NpAs_2$ (5).

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FIRST ORDER MAGNETIC PHASE TRANSITION IN THE TETRAGONAL K_2NpO_4

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Among the magnetic compounds of the 5f transition metal ions only very few show a first order magnetic phase transition. Several Np intermetallic compounds were reported to have a first order magnetic transition. $NpPd_3$, $NpCu_2Si_2$ and NpS are the only Np intermetallic compounds known to show distinct first order transition at low temperatures[1]. Though much research is devoted to the subject of magnetic phase transition, the reasons determining in which compound, a first order magnetic phase transition will be seen, are not clear.

The first order phase transition in the intermetallic compounds of Np could be explained in terms of the Blume's microscopic mechanism[2] assuming a non-Kramers Np ion ground states (NpIII and NpV).

We report here for the first time a Np nonmetallic oxide bonded compound, $K_2 Np^{VI}O_4$ which is a Kramers ion ($5f^1$, $^2F_{5/2}$ configuration) and exhibits a first order magnetic phase transition.

The ^{237}Np Mossbauer studies of the 59.6 Kev. transition show a quadrupole splitted absorption spectrum ($eq_{eff}\ Q$ = 58 MHz) with isomer shift of - 57 (1) mm/s above the ordering temperature T_0. When decreasing the temperature a sudden onset of magnetic ordering is observed at T_0 = 19.5 (5)K where at $T_0 \pm 0.3$ K coexistence of the ordered and paramagnetic states is recognized. Below 19K a saturated magnetic hyperfine spectra with $g_n\mu_n H_{eff}$ = 1.09 MOe hyperfine constant, is observed. No isomer shift change below T_0 is detected. The ordered magnetic moment is thus predicted to be $\mu_{ord} = 0.6\ \mu_B$. The susceptibility curves of the K_2NpO_4 above T_0 where analyzed in terms of Curie-Weiss law yielding an effective moment $\mu_{eff} = 1.37\ \mu_B$ and θ = - 150 K. Below T_0 a ferromagnetic behaviour was observed. No sharp transition or anomaly is observed at T_0, which is common for ferromagnetic transition.

The present results are discussed in terms of possible cooperative Jahn-Teller deformation in association of magnetic ordering similar to UO_2[3].

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MAGNETIC SUSCEPTIBILITY OF BERKELIUM COMPOUNDS AND METAL[§]

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Magnetic susceptibility measurements have been made on multi-microgram quantities of the compounds BkF_3, BkF_4, BkO_2 and BkN in the temperature range 4.2K to 300K and in magnetic fields up to 1600G. All but the BkN exhibited a Curie-Weiss behavior for the susceptibility over the entire temperature range, i.e., $\chi = N \mu_{eff}^2/3k\,(T+\theta)$. A plot of $1/\chi$ versus T at 1600G for the BkF_3 sample is shown in Figure 1. This illustrates the linear behavior given by the Curie-Weiss law. A plot of $[\sigma(T)/\sigma(T\to 0)]^2$ versus T for one of the BkN samples, where σ is the specific magnetization, is shown in Figure 2. Both samples exhibit a transition to an ordered state at a Tc of 87.7K as determined by a straight-line fit to the linear region. It is not possible to determine if the transition is ferromagnetic or ferrimagnetic from these measurements since the ordered moment is only .29 μ_B. Close agreement between the ordered moment and μ_{eff} would verify ferromagnetism, but disagreement between the values does not rule it out unless it persists to higher magnetic fields. Above this transition temperature the BkN samples also exhibited a Curie-Weiss behavior. The following table summarizes the results of these measurements.

Sample	Mass (μg)	Theoretical[a] μ_{eff} (μ_B)	Exp.[b] μ_{eff} (μ_B)	θ(K)	T_c(K) or T_N	% Cf[c]
BkN#1	14.2	9.72	7.79	-66.4	87.7	5.6
BkN#2	59.7	9.72	7.87	-42.4	87.7	3.9
BkF_3	143.5	9.72	9.38	77.9	-	3
BkF_4	44.2	7.94	7.80	-8.0	-	2
BkO_2	56.6	7.94	7.92	250	-	3
Bk metal	338.7	9.72	9.67	183	22	2

[a]Based on a 3+ or 4+ ionic core with a high temperature moment given as explained in the text.

[b]Corrected for Cf daughter content due to decay assuming $\mu_{eff} = 10.6\ \mu_B$ and additive susceptibilities.

[c]Cf daughter content at time of measurement.

The four compounds were prepared from freshly purified ^{249}Bk chloride solutions. The BkF_3 material (trigonal, LaF_3 type) was obtained by carefully drying an aqueous fluoride precipitate at 200°C. The BkF_4 (monoclinic, UF_4-type) was prepared by extensive treatment of the above BkF_3 with F_2 at 300-400°C. The BkO_2 (cubic, fluorite-type) was formed by calcination of an aqueous oxalate precipitate to 1000°C in air. The BkN (cubic, NaCl type) was prepared by direct combination of the elements at elevated temperatures; the Bk metal was prepared by reduction of BkF_4 with Li metal.

The measured effective moments for the fluoride and oxide compounds agree with the theoretical free-ion effective moments calculated from a simple Hund's Rule picture and assuming L-S coupling. The high degree of ionicity indicated by the data is to be expected due to the large electronegativity of

the anions. However, the measured moment of the BkN with its less electronegative nitride anion would indicate a valence of +4 for the Bk ion in this picture. Obviously, the nitride is a more complicated system than the others and probably is in fact a semimetal. This is indicated by its physical appearance (metallic) and the fact that it orders magnetically, indicating some contribution to coupling of the Bk moments from conduction electrons as Bk metal.

The motivation for studying the nitride and the other pnictides of the heavy actinides[1] is to investigate the nature of the magnetic coupling of the f local moments. The actinide-monopnictides (N, P, As, Sb, and Bi) form a series of binary compounds with fcc (NaCl-type) structure[2] in which the An-An spacing increases with the heavier pnictogen. They thus provide a series to probe the range and sign of the magnetic coupling in these semimetals. The coupling probably arises from two sources: one is coupling through the conduction electrons via RKKY oscillations in the conduction-electron spin density about magnetic ions; and the other is by superexchange due to overlap of the anion-cation wave functions.[3] In the RKKY picture there is a conduction-electron polarization effect[4] which would tend to lower the effective local moment if coupled antiferromagnetically to it, but this effect is thought to be too small to account for a 1.9 μ_B decrease over the expected 3+ moment. Most likely the superexchange (a manifestion of covalent bonding) is necessary to account for such a decrease in the moment. This simply means that a pure ionic picture is not suitable for describing the magnetic behavior in the actinide monopnictides.

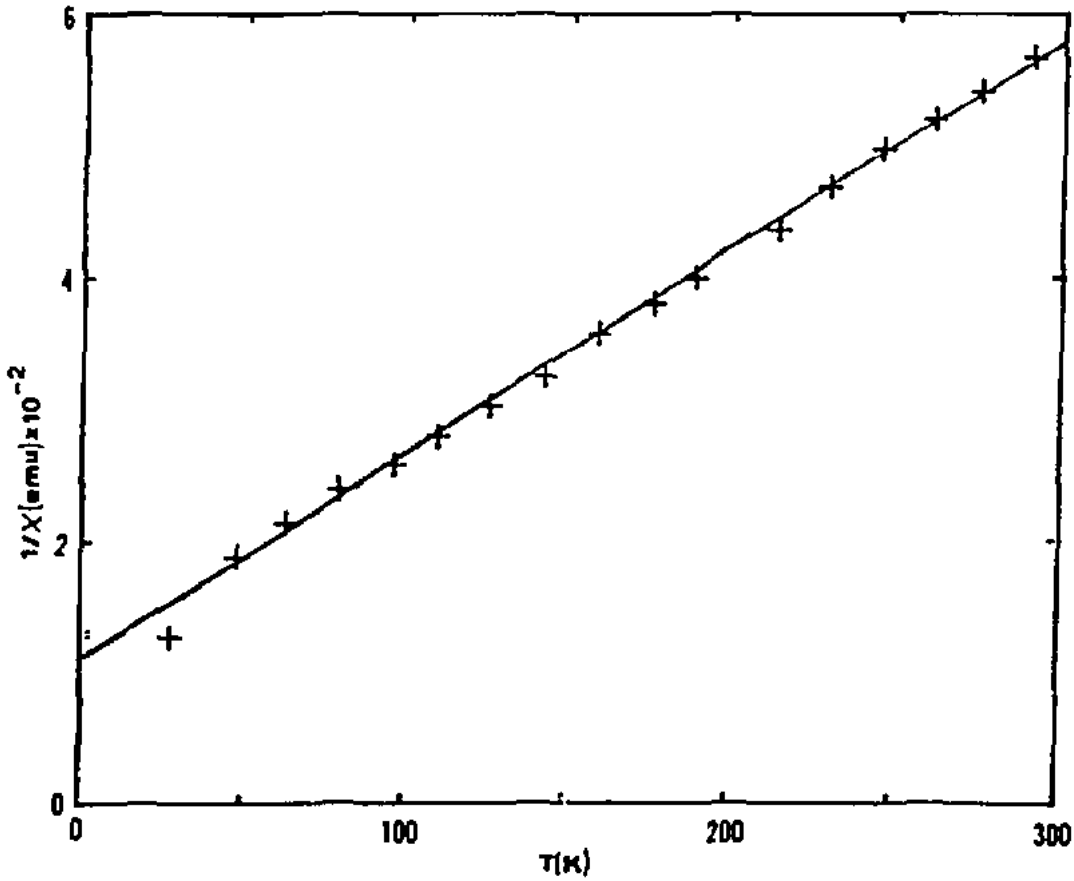

Figure 1

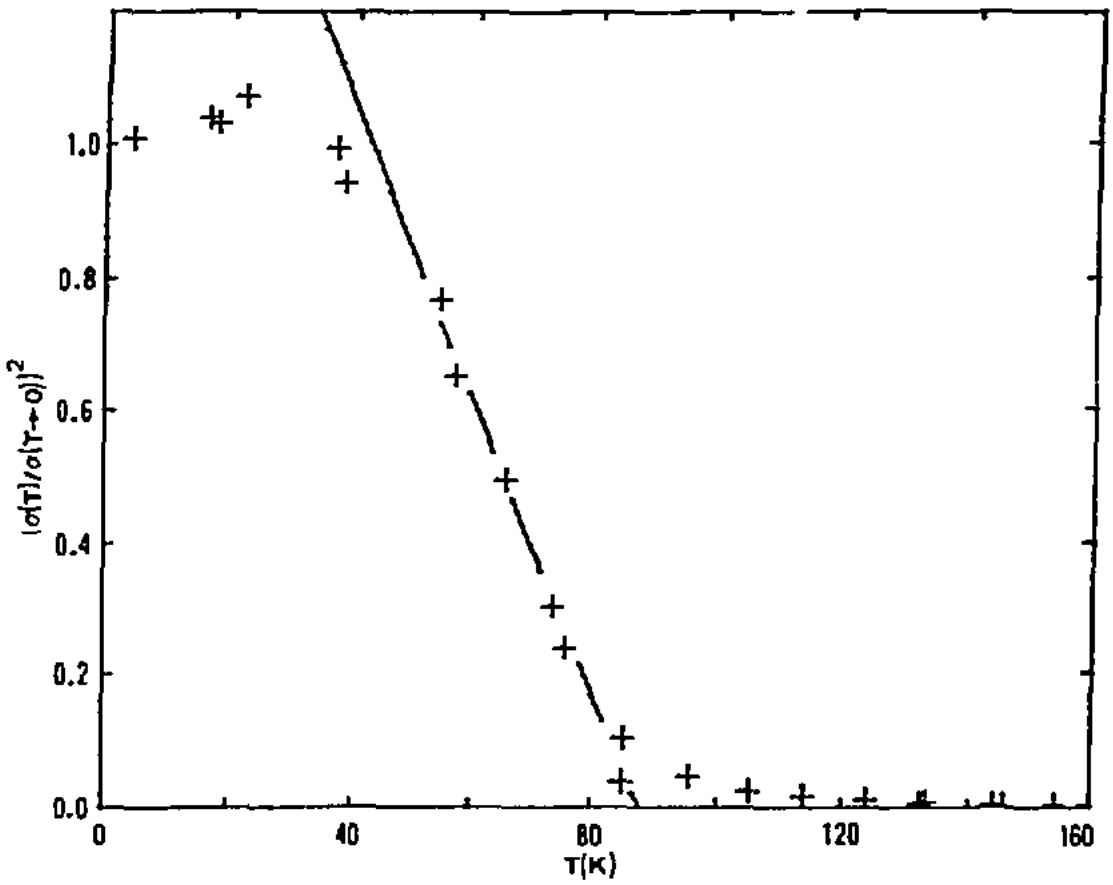

Figure 2

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MAGNETIC BEHAVIOUR OF THE $U_{1-x}Th_xP$ SYSTEM

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UP and ThP have the NaCl type structure. UP is an antiferromagnet of type I ordering below T_N = 125 K. Magnetic and other investigations of UP indicated a very sharp transition at 23 K (for references see[1]), where the ordered moment changes from 1.7 to 1.9 μ_B on going from higher temperatures.

ThP was reported to be a highly non-stoichiometric compound, but recently our neutron-diffraction examination[2] has shown that the composition of this compound is close to stoichiometry[2]. ThP shows a weak, temperature-independent paramagnetism ($\chi = 0.24 \times 10^{-6}$)[3].

The magnetic properties of the solid solutions UP - ThP were investigated previously by Chechernikov et al.[4] and Adachi et al.[5]. The former (measurements between 80 - 700 K) and the latter (4.2 - 300 K) authors indicated paramagnetic properties above $x = 0.5$ and 0.45, respectively.

It is the aim of this work to verify the results obtained by both groups of authors cited above and to construct the magnetic phase diagram of the UP - ThP system. Since U and Th atoms are probably not of the same valence in their monophosphides, a possible change in the electronic structure may be expected when one substitutes uranium for thorium in this solid solution.

The UP - ThP samples were prepared by sintering the mixtures of UP and ThP powders in desired composition between $0.1 \leq x \leq 0.9$ at 1900°C in vacuum. X-ray examination showed that in order to get the proper values of the lattice constants (Vegard's law) the sintering had to be repeated two or three times at 1900°C, each instance lasted at least one hour. Magnetic measurements at temperatures 4.2 - 300 K at weak (6 kGs) and in strong magnetic fields (up to 140 kGs) were carried out by the Faraday and moving-sample methods, respectively. The neutron-diffraction experiment was made in Swierk, on the reactor Eva.

The magnetic studies show that for low thorium concentration ($x = 0.1$) two effects compared to pure UP were observed. First, the appearance a small susceptibility peak at the temperature just above the moment jump transition, and second, a large broadening of the susceptibility peak at the temperatures close to T_N, but with a distinct mark at 120 K. The samples with higher thorium concentrations ($0.15 \leq x \leq 0.30$) show the tendency of developing a new low temperature susceptibility maximum at about 20 K, of disappearing the moment-jump transition, of forming a distinct susceptibility peak at 40 K and of shifting T_N to lower temperatures. For the 0.40 sample close lying (at 25 and 40 K) susceptibility maxima which shift to lower temperatures with a

slight increase of the composition to $x = 0.42$, are observed. However, the most striking feature is the fact that starting from $x = 0.5$ and ending at $x = 0.8$ one strong susceptibility peak still exists, defining T_{max}. For $x = 0.6$ the susceptibility at T_{max} achieves a fairly high value of 92×10^{-6} emu/g per solid solution. It should be noted that for all the cases the magnetic susceptibility was always independent of the magnetic field.

The $x = 0.3$ sample magnetized to 140 kGs shows a transition to the metamagnetic state with large histerezis and small remanent magnetization. The samples with a higher thorium content show a linear dependence of the magnetization in the whole magnetic field range studied.

Neutron diffraction studies of three samples: $x = 0.15$, 0.23 and 0.43 indicate the ordered state at low temperatures. The first two samples exhibit the coexistence of two magnetic phases at 4.2 K, namely AF I and AF IA (simple and doubled along one direction magnetic unit cell in comparison to a chemical one). At 50 K the $x = 0.15$ sample shows only one phase AF I, with the ordered moment being 2.02 μ_B, which falls to 1.8 μ_B at 80 K. The samples with $x = 0.23$ at 88 K and $x = 0.42$ at 4.2 K exhibit only the "ferromagnetic" contribution to the nuclear peaks with a rather high value of the ordered moment being 2.5 μ_B in both cases. This point must be cleared up by further studies because the magnetic measurements give no evidence of ferromagnetism in these samples. It should also be noted that in order to fit the room temperature neutron-diffraction patterns for the $x = 0.15$, 0.23 and 0.42 samples it was necessary to assume some phosphorus deficit, being 0.97, 0.94 and 0.93, respectively.

The obtained results are quite different from the results reported previously[4,5]. Now it is clear that the authors of the previous works did not obtain really solid solutions. Adachi et al.[5] did not give the lattice constants of UP - ThP for their solid solutions at all, while Chechernikow et al.[4] presented the lattice constant versus composition curve showing in contrast to our work a large deviation from Vegard's law up to 50 % mol. ThP.

Finally, it should be mentioned here that the magnetic behaviour of the UP - ThP system maybe is similar to that of UAs - ThAs,[6,7] where at temperatures close to T_N there is a transition into a modulated magnetic structure, and it differs from that of USb - ThSb system[8] for which the ferromagnetic properties have been detected at the composition of 20 % mol. ThSb.

The summary of all of these results is shown in the Figure in the form of the tentative magnetic phase diagram of the UP - ThP system.

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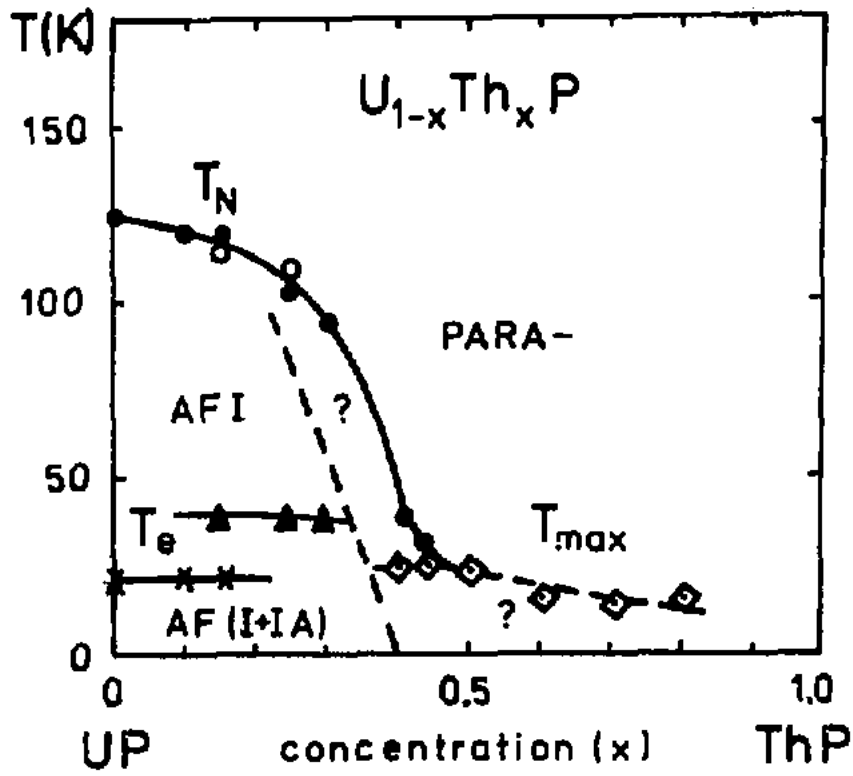

Figure. Tentative magnetic phase diagram of the UP - ThP system. Full circles represent magnetic and open ones neutron--diffraction results.

MAGNETIC PROPERTIES AND HYDROSTATIC PRESSURE EFFECTS OF $U_x Th_{1-x} As$ COMPOUNDS

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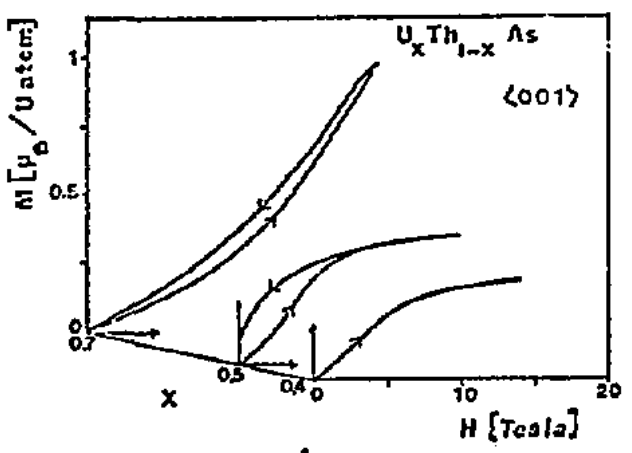
The unusual and anisotropic magnetic properties of uranium and cerium monopnictides of Na Cl-structure are attributed to very anisotropic exchange interaction mechanism via the conduction electrons (1,2). Consequently, substitution of uranium atom in UAs by non-magnetic thorium which has a different valency may lead to crucial changes in the exchange forces, in supplement of the normal expected exchange decrease, as supported by the experiments performed on $U_xTh_{1-x}As$ compounds up to $x \geq 0.7$ (3-5). For low concentration of thorium, three antiferromagnetic phases are observed, in increasing temperature : type IA, I and Modulated phase respectively. As x decreases, the phase I disappears first for $x = 0.9$, then the phase IA for $x = 0.7$.

In this paper, the magnetic properties of $U_xTh_{1-x}As$ are reported for magnetic field applied along a <001> direction. Fig.1 and 2 show respectively the magnetization curves in high field at 4.2 K for three different values of x and the thermal variation fo magnetization for $x = 0.7$ at 9.5 Tesla and for $x = 0.4$ at 8 Tesla. The long range antifer omagnetic order H observed for



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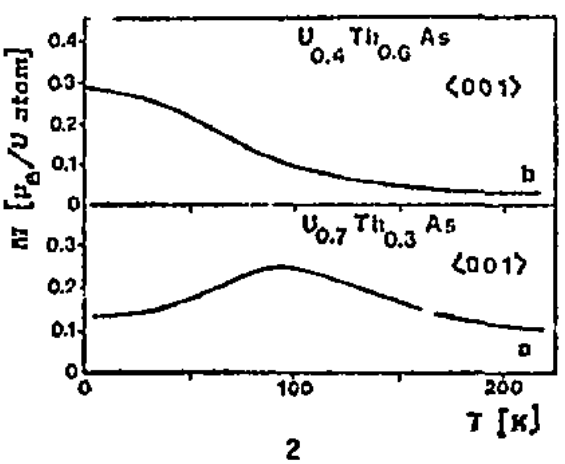

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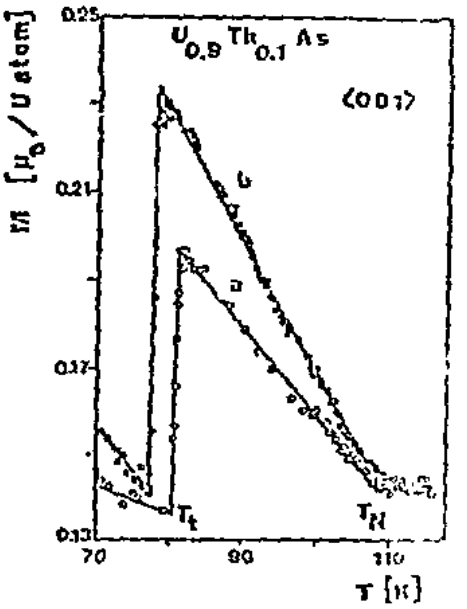
$x \geq 0.7$ (5) disappears with x decreasing and the exchange forces seems to tend towards a ferromagnetic nature as let to suppose Fig. 1 and 2. However, neutron diffraction experiments are needed to confirm this analysis. Similar behavior has been observed by Cooper et al. for $U_xTh_{1-x}Sb$ (6,7).

Fig. 3 shows the thermal variation of the magnetization of $U_{0.9}Th_{0.1}As$, with increasing temperature at 5.09 Tesla, for two different pressures (a : 1 bar ; b : 5810 bar). An abrupt increase of the susceptibility is observed at the transition temperature T_t(IA → M) equal to 81.5 K. The modulated antiferromagnetic phase M vanishes at T_N = 108 K. T_t decreases linearly with pressure at the rate of 0.6_0 K.kbar^{-1} as for the IA → I transition in UAs (8). The pressure variation of T_N is smaller and consequently, the effect of pressure consists to an increase of the M modulated phase region at the expense of the IA phase. Another effect of pressure is the increase of the susceptibility value of the phase M, this variation is not linear as for example at T = 90 K (Fig. 4). This result is



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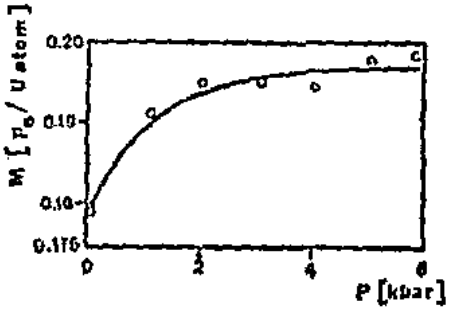

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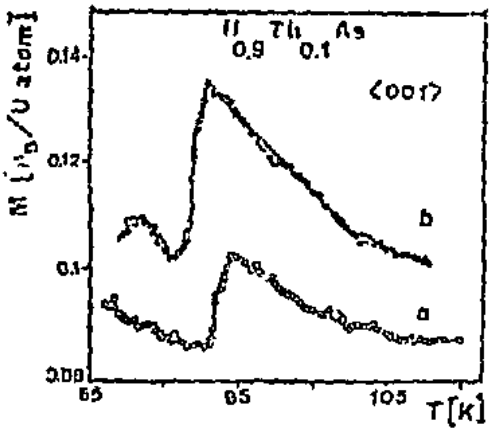

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confirmed in low field as shown by the thermal variation of magnetization at 3.1 Tesla (Fig. 5) for two pressures (a : 1 bar ; b : 5560 bar). The saturation of the magnetic susceptibility with pressure let to suppose this effect might be due to domain arrangement, however other kind of experiments are needed to discuss in more details this last result.

The authors are grateful to Prof. G. Aubert, Director of "Service National des Champs Intenses" at Grenoble, providing facilities and encouragements. The authors are indebted to Engineers J.C. Picoche and P. Rub and Technician G. Dampne for their constant experimental help.

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NEW EXPERIMENTAL EVIDENCE ON THE 25 K TRANSITION IN NpO_{2+x}

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The behaviour of NpO_2 at low temperatures has been extensively studied but, till now, no satisfactory explanation has been given to the problem of the transition detected in specific heat and magnetic susceptibility measurements at 25 K. In the following, new evidence is presented and discussed.

a) The existence of the transition has been confirmed by careful susceptibility measurements, but the shape of the χ (T) curve below the transition is different from that of an antiferromagnet (1). Furthermore extensive neutron diffraction experiments on a NpO_2 single crystal are unable to detect magnetic ordering, the limit of detectability having being lowered to $\mu_{ord} < 0.1 \mu_B$ per Np atom (2).

b) Recent Mössbauer experiments (3) on NpO_{2+x} show spin relaxation phenomena strongly dependent on the oxygen excess x and temperature. They may be interpreted in terms of Orbach-Blume spin lattice relaxation process in a split cubic Γ_8 quartet of Np^{+4}.

c) In the above quoted neutron diffraction experiment (2), a search was made of a lattice distortion in the oxygen sublattice giving rise to a Jahn-Teller effect. Two different types of distortion were investigated, but no distortion was detected greater than $\Delta = 0.01$ Å for the oxygen displacement. This value is however just equal to the order of magnitude predicted by the theoretical model of (4) : this model can therefore neither be excluded nor confirmed. Recent Mössbauer studies on $Np_x U_{1-x} O_2$ solid solutions (5) seem to confirm this model.

d) The particular dependence of the spin relaxation phenomena on the oxygen excess x in NpO_{2+x} presented in (3) may be understood in terms of the variation of the crystal field when clusters of oxygen interstitials are formed in agreement with a thermodynamic treatment of grossly stoichiometric oxides (6).

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MOSSBAUER AND MAGNETIZATION STUDIES OF $U_{1-x}Np_xO_2$ FLUORITE SOLID SOLUTION

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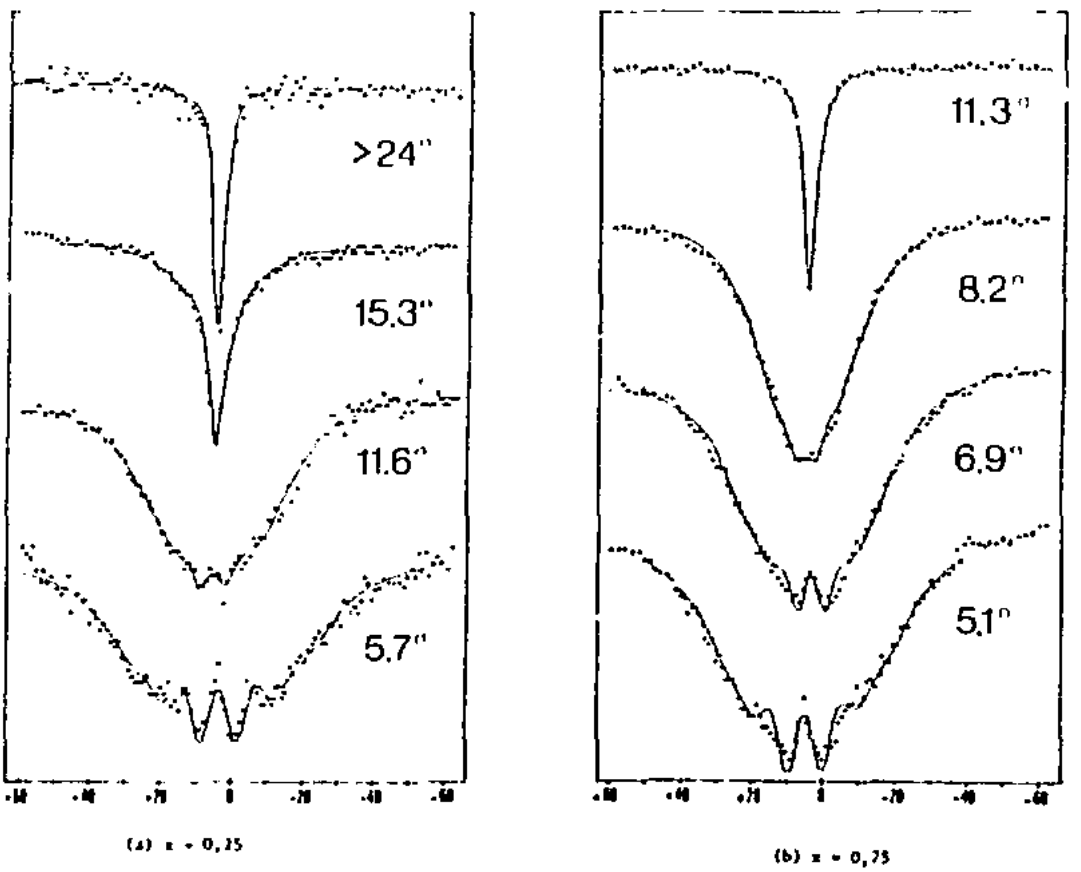
The magnetic structure and the nature of the transition of the actinide dioxides UO_2 and NpO_2 have been recently subjected to extensive and theoretical studies [1 to 7]. UO_2 is known to order antiferromagnetically (T_N = 30.8 K) by a first order magnetic phase transition while NpO_2 does not order down to 1.2 K. We have performed Mossbauer and magnetization studies on the fluorite $U_{1-x}Np_xO_2$ ($0.15 < x < 0.75$) solid solution (SS). We report the negative experimental observation of the Jahn-Teller effect predicted by Solt and Erdos[5,6] ; possible explanation of this result is given.

Some of the $U_{1-x}Np_xO_2$ Mossbauer spectra (59.54 keV transition of ^{237}Np) temperatures are displayed in figure 1. Above the ordering tempera- ngle absorption line of full width at half maximum (FWHM) mm/s is observed ; below T_O typical relaxation magnetic spectra ... recognized. The Mossbauer isomer shifts in all the present SS



(a) x = 0,25 (b) x = 0,75

Fig. 1

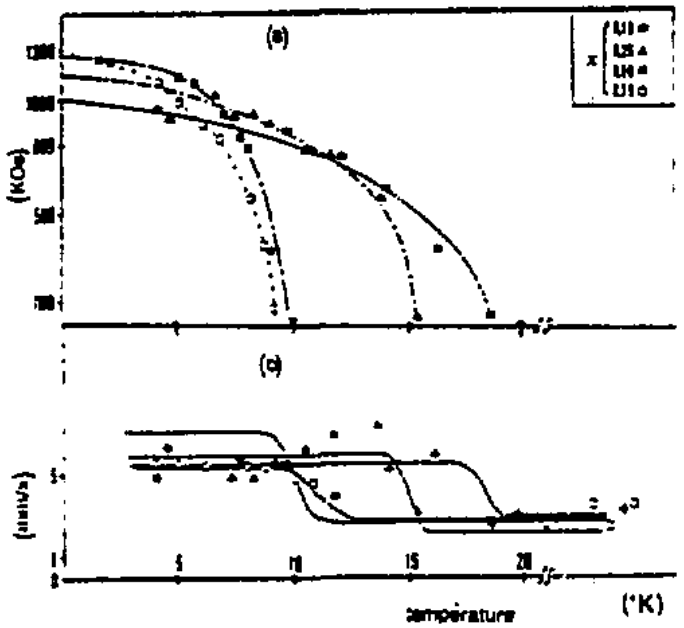


Fig. 2

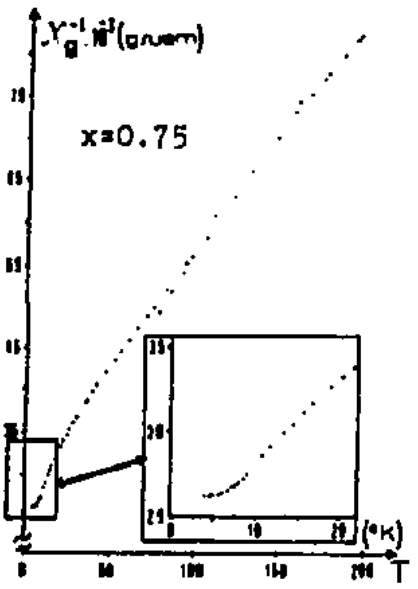


Fig. 3

above T_O are identical to NpO_2 pointing that the Np ion is in a 4+ ($^4I_{9/2}$) charge state of a cubic $\Gamma_8^{(2)}$ quartet ground state. The random distribution of the Np ions within the fluorite cubic U sublattice certainly introduce a spread in the induced hyperfine field ; for this reason we have used the general theory of Gabriel[8] with the additional assumption that the FWHM Γ of each absorption line is given by

$$\Gamma = \Gamma_O + \gamma_L (m_e, m_O) + \Gamma_R$$

Γ_O is the FWHM for pure NpO_2 at 77 K (3 mm/s), γ_L was previously described[9] and Γ_R represents the magnetic field distribution broadening below T_O. All the Mossbauer absorption spectra could be fitted with this procedure. Figure 2 shows the evolution versus T for hyperfine field H_{eff} (a) and $\Gamma_O + \Gamma_R$ (b).

Susceptibility measurements were performed with a conventional Faraday electrobalance in the temperature range 4.2 to 300 K. Above 50 K, all the $U_{1-x}Np_xO_2$ SS follow a simple Curie-Weiss law (figure 3) ; when T decreases we observe an ordered range (between 0 and T_N). For $U_{0.85}Np_{0.15}O_2$ a clear transition appears - T_N = 27(2) K- very similar to the UO_2 compound (figure 4).

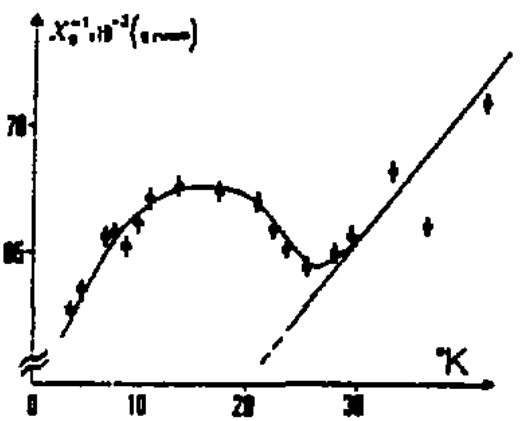


Fig. 4

Experimental and theoretical parameters deduced from our measurements are summarized in the table ; they lead us to the following conclusions :

. all the present $U_{1-x}Np_xO_2$ order magnetically at low temperatures, where U site orders at higher temperatures than the Np site ($T_N \geq T_O$) ;

. a constant decrease in T_N and T_O as x increases is shown ;

. the Brillouin behaviour of H_{eff} argue for a dominant exchange mechanism below T_O ;

	x	$O(UO_2)$	0.15	0.25	0.75	$1(NpO_2)$
Mossbauer effect	$H_{eff}(0)$ (kOe)		1000(40)	1120(40)	1210(50)	
	T_o (°K)		18.8(2)	15.3(2)	9.2(3)	
	μ_{ord}/Np (μ_B)	(1.8)[10]	0.5(1)	0.6(1)	0.65(9)	~0.01[4]
Susceptibility	T_N (°K)	30.8[10]	27(2)	23(5)	8(2)	25 ?
	μ_{eff} (μ_B)	3.6(?)	2.95(8)	3.43(6)	3.0(1)	2.95[3]
	θ_c (°K)	-244(16)	-180(12)	-180(12)	-132(20)	-22[3]

. above T_N, Np ion in the SS stays Np^{4+} ($^4I_{9/2}$) with a degenerated $\Gamma_8^{(2)}$ ground quartet independent of the U neighbours ;

. below T_N, the ground quartet may split as a result of the crystalline field originated by the oxygen deformation. Between T_N and T_o, this splitting is not observed by the Mossbauer technique perhaps because of the fast relaxation times. Below T_o, the magnetic field will additionally split the Γ_8 quartet and a change in correlation times would explain the observed relaxation Mossbauer spectra.

Present measurements are not sufficient to conclude. Neutron diffraction and X-ray diffraction experiments will have to be performed to investigate lattice distorsions coupled with magnetic transition.

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MOSSBAUER EFFECT STUDIES OF Np_xPu_{1-x} ($0.3 \leq x \leq 1$) DIHYDRIDES

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Mossbauer effect studies on Np_xPu_{1-x} ($0.3 \leq x \leq 1$) dihydrides having the CaF_2-type structure have been performed within the temperature range 4.2-77K.

The dihydrides were prepared by the direct reaction between hydrogen and the arc melted alloys of Np_xPu_{1-x}. The hydrogen compositions were adjusted to range within the right-hand side of the plateau regions of the corresponding pressure-composition isotherms. All the measured samples consisted thus of a mixture of the nonstoichiometric dihydride in equilibrium with the saturated solid solution of hydrogen in the metallic alloy.

All the observed Mossbauer absorption spectra of the 59.6 keV gamma rays of ^{237}Np consisted of the superposition of a broad single line at 25±1 mm/sec corresponding to the dihydride[1] and a complex split structure typical to Np metal[2]. The FWHM of the dihydride line is weakly temperature dependent ranging between 6 to 4 mm/sec in the temperature range 4.2-77K. No influence of the plutonium concentration (i.e. 1-x) either on the isomer shifts or on the line widths has been observed for the dihydrides lines of the various investigated alloys.

Recently, Aldred et al.[3] carried out magnetic susceptibility measurements on the dihydrides of plutonium and neptunium. They obtained antiferromagnetic ordering in PuH_2 at about 30K while no ordering has been observed in NpH_2 down to 4K. The magnetic behavior of NpH_2 has been interpreted by these authors in terms of crystal field splitting resulting in a Γ_3 doublet ground state.

The aim of the present study was to check wether a partial substitution of the Np atoms by Pu atoms in the dihydride will yield a magnetically ordered compound. In a magnetically ordered $Np_xPu_{1-x}H_2$ one would expected that the Γ_3 ground state doublet of Np would be split by the magnetic field produced by the Pu sublattice. In such case either magnetically split Mossbauer absorption spectra or magnetic broadening of the absorption line will be

displayed. Such phenomenon was observed in the $Th_xU_{1-x}O_2$ system[4] where the Γ_8 ground state quartet of the Np was split by the magnetic field produced by the U sublattice below its ordering temperature. The fact that no such behavior has been observed in the present study down to 4.2K point to the absence of magnetic ordering of the $Th_xPu_{1-x}H_2$ compounds up to 70 a/o substitution of the Th atoms by Pu.

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PRESSURE INDUCED DELOCALIZATION OF MAGNETIC ELECTRONS IN NEPTUNIUM LAVES PHASE INTERMETALLICS†

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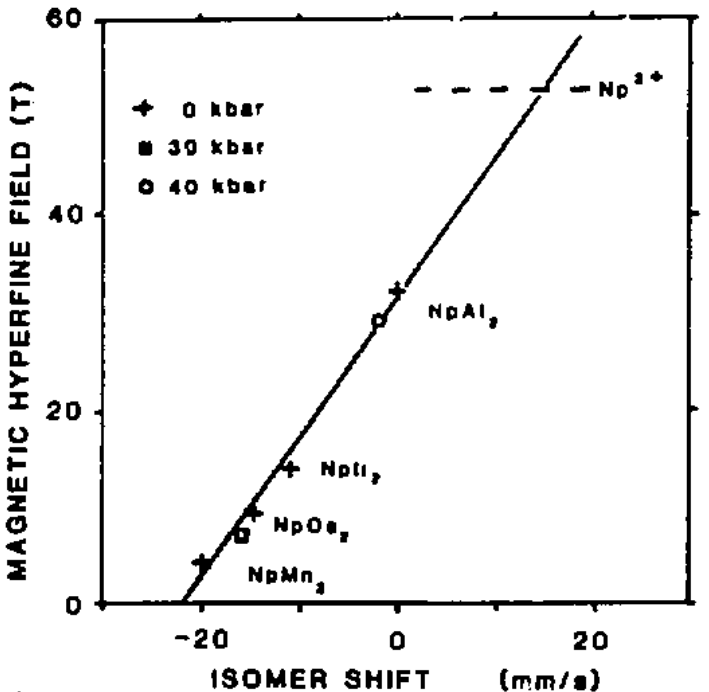
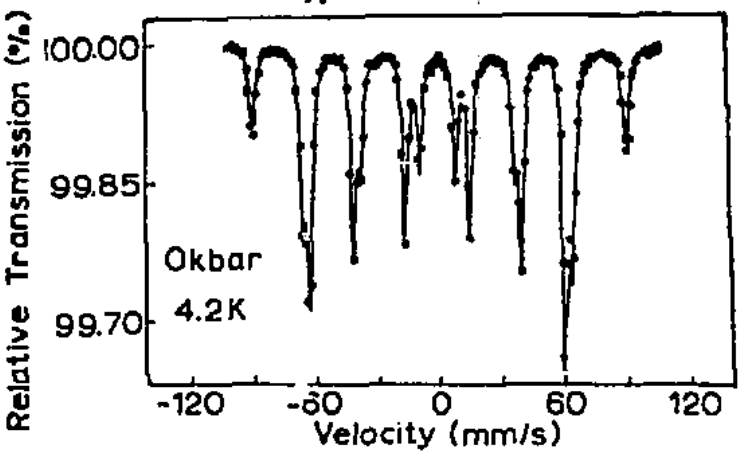
It has long been recognized that the magnetic properties of intermetallic compounds of the light actinides depend strongly on the actinide-actinide spacing.[1] The cubic Laves phase compounds of neptunium (NpX_2) have provided some of the clearest evidence for this correlation. Extensive investigations have been previously carried out using magnetization, resistivity and Mössbauer measurements to study the magnetic properties of $NpAl_2$, $NpIr_2$, $NpMn_2$, $NpRu_2$ and the psuedo-binaries $NpOs_{2-x}Ru_x$.[2-6] Within these compounds, the lattice parameter changes from 7.785 Å for $NpAl_2$ to 7.459 Å for $NpRu_2$, while the magnetic properties vary from primarily local moment behavior ($NpAl_2$) through itinerant magnetism ($NpOs_2$) to non-magnetic ($NpRu_2$). The 60 keV Mössbauer resonance in ^{237}Np provides an excellent tool for investigating the magnetic properties of these materials. It has been previously noted that spectral parameters such as the saturation magnetic hyperfine field, B_o, and the isomer shift, S, can be correlated with the magnetic properties. This is illustrated in Figure 1, where one sees that both B_o and S decrease proportionately with increasing itinerant character. Here we report on high pressure Mössbauer measurements on the most localized of these compounds, $NpAl_2$. Similar data has been previously presented for the more itinerant compound, $NpOs_2$.[6] In addition to the hyperfine parameters B_o and S, the temperature dependence of the hyperfine field has been used to determine the Curie temperature at various pressures. The values of B_o and S obtained at the maximum pressure measured for both compounds are also plotted in Figure 1. These follow the general correlation observed for the various Laves phase intermetallics, substantiating the idea that the reduction in interatomic spacing is a primary factor in determining the magnetic properties.



A pure magnetic hyperfine spectrum for the Np Mössbauer resonance consists of sixteen lines positioned symmetrically with respect to S. In a magnetically ordered material, the alignment of the magnetic moments in the exchange field produces a small electric field which introduces some asymmetric positioning of the lines. The resulting pattern is illustrated by that for $NpAl_2$ at 4.2 K and ambient pressure, shown in Figure 2. In particular one should note the symmetry in intensities and widths of the inner four lines, centered around zero velocity.

A high resolution scan of these inner four lines reveals that the symmetry is not maintained at high pressures. While the ambient pressure spectra show normal behavior, the lines at positive velocity are significantly broadened while those at negative velocities are largely unaffected (see Figure 3). This becomes increasingly pronounced as the pressure is increased. Such line-broadenings are indicative of hyperfine fields which fluctuate at a rate comparable with hyperfine frequencies. However, Ferromagnetic relaxation[9] such as previously proposed for these compounds[10] will always result in a symmetric broadening of lines placed symmetrically about S. The behavior observed here can be understood on the basis of the following two state model: The electronic structure of the Np ion fluctuates rapidly between a localized magnetic configuration (having $B_o = B_l$ and $S = S_l$) and totally itinerant configuration ($B_o = 0$ and $S = S_i$). If the fluctuation rate in comparison with hyperfine frequencies, then the observed spectral parameters will be an average value determined by the populations p_l and $p_i = 1 - p_l$ of the two configurations. This is reflected in the correlation of Figure 1. The solid lines of Figure 3 represent computer fits to the lineshapes within such a model in which we have taken $S_i = -21.5$ mm/sec from the value at which $B_o = 0$ in Figure 1, while leaving S_l, p_l and the fluctuation rate as free parameters. B_l was determined from S_l by the correlation of Figure 1. From the fits to the spectra, we find $S_l = +6$ mm/sec ($H_l = 430$ T) with both p_l and varying with pressure.

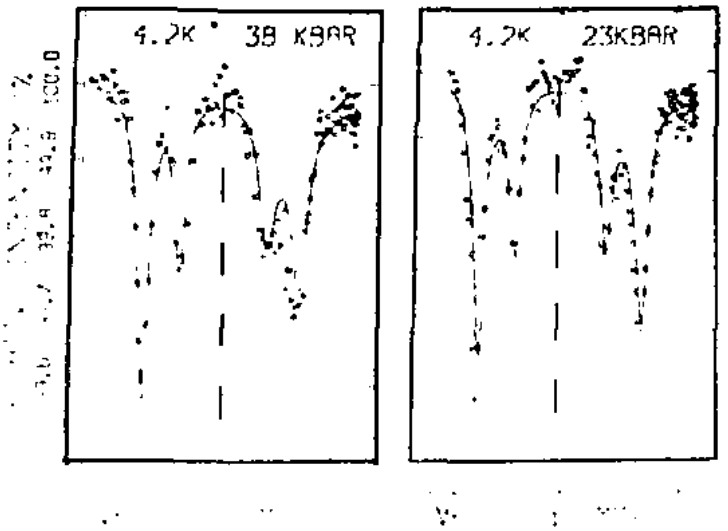


From the above results we draw the following conclusions:

(i) In both $NpAl_2$ and $NpOs_2$ the reduction of lattice constant by the application of external pressure causes a delocalization of the magnetic 5f electrons. Although $NpAl_2$ has a predominantly localized character, it can not be considered fully so in view of the strong variation of B_o with pressure. This should be contrasted with the pressure independence of B_o in $NpCo_2Si_2$. The systematics of the data at ambient pressure (Figure 1) show that the change in lattice constant is the predominant factor in determining the degree of localization.

(ii) The line-broadenings show the presence of fluctuation phenomena which have been interpreted with a crude two state (localized-itinerant) model. The degree of localization is found to decrease with increasing pressure. For example, in $NpAl_2$, the solid line of Figure 3 corresponds $p_l = 0.67$ at 38 kbar compared with a value of 0.77 at 0 kbar. The corresponding values

for $NpOs_2$ at $p_1(0) = 0.20$ and $p_1(30) = 0.16$, demonstrating the much higher degree of delocalization in this case. The hyperfine field B_1 for the "localized" case is reduced to approximately 80% of the free ion Np^{3+} value, presumably due to the presence of crystalline electric field effects. Such effects are expected to be much more pronounced in the light actinides than in their rare-earth counterparts because of the larger radial extent of 5f electrons compared to 4f electrons.



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HIGH-PRESSURE MÖSSBAUER STUDY OF UTe[+]

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Compounds of the actinide elements have recently attracted strong interest caused by a variety of their magnetic properties, which range from anomalous paramagnetism to localized and itinerant magnetic order, respectively. Such behaviour is due to the 5f electrons which may exhibit properties ranging from localized to itinerant, in contrast to the well-localized 4f electrons of the rare-earth elements. Information on magnetic interactions in the ordered state may be obtained from magnetic hyperfine fields studied by Mössbauer spectroscopy.

We report here on a high-pressure Mössbauer study of UTe at 4.2 keV in the pressure range up to 30 kbar using the 35-keV nuclear gamma resonance of ^{125}Te. UTe orders ferromagnetically at T_C=104 K[1]. The experiments were performed in order to study the volume dependence of the magnetic interaction in UTe via the transferred magnetic hyperfine field at the ^{125}Te nucleus. The UTe sample was prepared by a solid-vapor reaction of U (depleted in ^{235}U) with isotopically enriched ^{125}Te (to 98%) in an evacuated and sealed quartz tube at 600°C. In the measurements a single-line ^{119}Sn^{125m}Te source was employed, and the UTe absorber was pressurized using an opposed-anvil device with sintered B_4C anvils. The pressure at the sample was measured in-situ by means of a superconducting Pb manometer.

In the pressure range studied so far, we find that the isomer shift S increases with pressure, while the magnetic hyperfine field B_{hf} remains essentially constant within the experimental accuracy of ±3%. Since the nuclear charge radius is larger in the excited state of ^{125}Te as compared to the groundstate, the increase of S corresponds to an increase of the total electron density at the ^{125}Te nucleus.

The magnetic hyperfine field at the ^{125}Te site arises from the net electron spin density at the ^{125}Te nucleus produced by the U-5f moments. There are two mechanisms contributing to this net spin density at the ^{125}Te nucleus, namely (i) conduction-electron polarization and (ii) overlap/covalency effects between the 5f electrons and the outer electrons of the diamagnetic Te ion[2]. Both mechanisms are proportional to the U-5f moment, but are expected to depend rather differently on the unit-cell volume. We have to assume that the U-5f moment decreases with decreasing unit-cell volume, similar as in the "S case[3]. Then, the observed insensitivity of the ^{125}Te hyperfine field on pressure implies that the effects of a decrease in the U-5f moment are compensated in UTe by an increase in the overlap/covalency effects described by mechanisms (ii). A more quantitative analy-

sis of the experimental data must wait for a measurement of the pressure dependence of T_c for UTe, which is in progress in our laboratory.

+ Supported by the SfB-161 of the Deutsche Forschungsgemeinschaft and the Kernforschungszentrum Karlsruhe.

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^{237}Np MÖSSBAUER SPECTROSCOPY IN BINARY COMPOUNDS

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Some compounds, $NpAs_2$, $NpSb_2$ and $NpTe_2$ have been studied by various techniques such as magnetic susceptibility, electrical resistivity and neutron diffraction. $NpAs_2$ crystallizes in the tetragonal, anti-Fe_2As type structure. This material is ferromagnetic below 18 K, antiferromagnetic between 18 K and 54 K, and paramagnetic above 54 K [1,4]. $NpSb_2$ is ferromagnetic below 45 K and paramagnetic above [2]. It has an orthorhombic, $LaSb_2$-type crystal structure. $NpTe_2$ again is tetragonal but remains paramagnetic down to 4.2 K [2].

Here we report on Mössbauer measurements using the 60 keV resonance in ^{237}Np to gain insight into the magnetic properties of these compounds and into their formal valence state of the Np ion.

The results of our measurements at 4.2 K are summarized in table. Mössbauer spectra $NpAs_2$ between 4.2 K and 60 K are shown in Fig. 1. Low temperature (4.2 K) spectra for $NpSb_2$ and $NpTe_2$ are depicted in Fig. 2 and 3, respectively.

Properties of NpX_2 compounds at 4.2 K.

H_{hf} is the hyperfine field at the nucleus Np, μ is the electronic moment for Np ion derived from H_{hf}, e^2qQ is the quadrupole interaction, I.S. is the isomer shift relative to $NpAl_2$

Parameters	$NpAs_2$	$NpSb_2$	$NpTe_2$
Crystallographic structure	Tetragonal	Orthorhombic	Tetragonal
Magnetic structure	Ferromagnetic	Ferromagnetic	Paramagnet
H_{hf} kOe	2900	3700	0
μ μ_B	1.5	1.9	-
e^2qQ mm/sec	+ 24	~ 0	+ 12
I.S. mm/sec	+ 3	+ 18	+ 28

$NpAs_2$ at 4.2 K shows a single magnetic hf pattern consistent with ferromagnetic order. Using the linear correlation between H_{hf} and μ from [3] we obtain μ = 1.5 μ_B at the Np ion. Earlier magnetization measurements gave a much lower number (μ = 0.56 μ_B). A strong magnetic anisotropy has probably prevented the full orientation of spins. Our result is confirmed by recent neutron diffraction data [4]. The neutron result also indicates an incommensurate sinusoidal spin structure with a period over approx. 7 Np atoms in the antiferromagnetic regime. This is borne out by the hf patterns observed above 18 K which show the presence of several distinct hf field. A good fit of the pattern at 25 K (see Fig. 1) could be obtained with a set of five hf fields. They can be related to sinusoidal spin modulation over seven Np sites (Fig. 4). Above 54 K a single, slightly broadened line is seen consistent with the quadrupole interaction given in table.

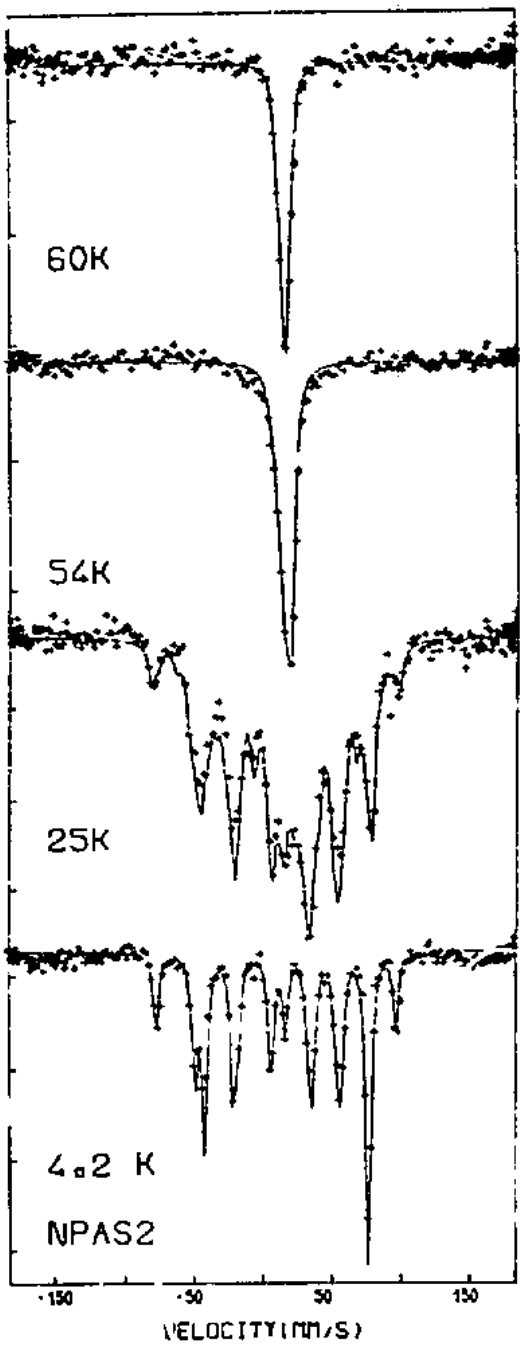

Figure 1. Mössbauer spectra of $NpAs_2$
at 4.2 K : ferromagnetic state
at 25 K : antiferromagnetic state
above 54 K : paramagnetic state

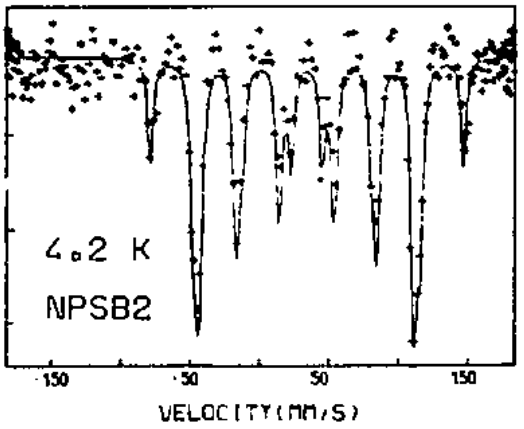

Figure 2

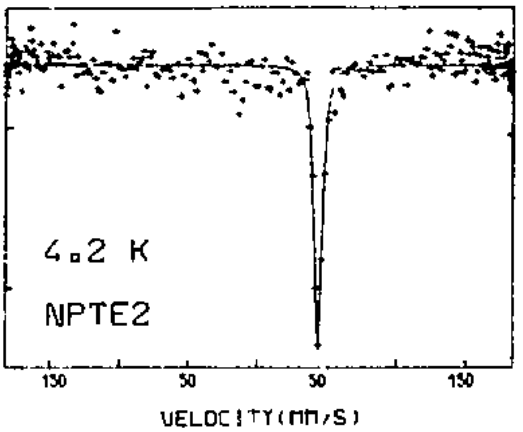

Figure 3

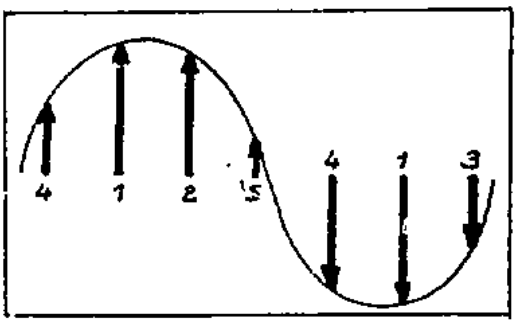

Figure 4. Model for the localized moments on Neptunium atoms in $NpAs_2$ at 25 K

1 : H_{hf} = 2950 kOe.
2 : H_{hf} = 2780 kOe.
3 : H_{hf} = 2400 kOe.
4 : H_{hf} = 1700 kOe.
5 : H_{hf} = 500 kOe.

$NpSb_2$ shows a single magnetic hf pattern as expected for ferromagnetic order. Its different hf field and moment are probably caused by the change in crystalline field interaction due to the different crystal structure. The single line seen throughout in $NpTe_2$ confirms its paramagnetic state.

From the value of its paramagnetic moment (2.87 μ_B) and from its isostructure with $LaSb_2$ it has been concluded that Np is trivalent in $NpSb_2$. Our isomer shift value is in agreement with such an assignment. In contrast $NpAs_2$ is isostructural with UAs_2 which suggests a Np^{4+} ion. A Np^{5+} assignment is also possible, the Np^{3+} state is ruled out from the magnetic form factor. Our isomer shift data is consistent only with Np^{4+} but not with Np^{5+}. The paramagnetic moment is uncertain since the sample used in earlier measurements [1] contained a mixture of phases. From its paramagnetic moment one would assign Np^{3+} in $NpTe_2$. This is supported by the isomer shift value.

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^{231}Pa Mössbauer resonance at 4.2 K in Pa metal using a Th metal source

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Isotopically enriched ^{230}Th (> 99.9 %) metal has been prepared by Van Arkel reduction from the oxide. The cubic metal source is used after neutron irradiation (8 h irradiation in a flux of 10^{12} n/cm^2 s) for measurement of the 84 keV Mössbauer resonance of ^{231}Pa. The measurement of Pa metal, with both source and absorber at 4.2 K, reveals seven resolved resonance lines (Fig.1) and indicates a striking improvement of experimental resolution in comparison to the formerly used source host of $^{230}ThO_2$[1]. The spectrum of Pa metal is analyzed in terms of a superposition of two quadrupole subspectra (solid line in Fig.1). The spectral intensities of the two subspectra are equal ; the isomer shifts are equal : 0.01 ± 0.05 mm/s vs Th metal. The principal components of the electric field gradients of axial symmetry are $eq_z(1) = +(2.27 \pm 0.04)10^{18}$ and $eq_z(2) = +(2.01 \pm 0.04)10^{18}$ V/cm^2 respectively. The resonance width is fitted to 0.35 ± 0.03 mm/s (constrained equal for all spectral components). The ratio of the quadrupole moments of the 84 keV level and ground level of ^{231}Pa is fitted to -0.31 ± 0.03.

Although the experimental linewidth still exceeds the minimum theoretical value by a factor of three, it is significantly more narrow than for the commonly used source host of ThO_2[1] and is considered acceptable for the future application of the ^{231}Pa Mössbauer resonance to the precise determination of hyperfine parameters. The narrowing of the emission linewidth in the metal in comparison to the oxide is attributed to decreased paramagnetic relaxation effects (via conduction electrons in metal vs diamagnetic insulating ThO_2) and possibly to reduced sensitivity of the metallic host to neutron irradiation associated radiation damage.

The deduced ratio of quadrupole moments is in agreement with nuclear theory[1].

The observation of two distinct quadrupole sites in Pa metal at 4.2 K is inconsistent with the bct crystal structure reported from X-ray diffraction at 300 K[2]. This discrepancy suggests the occurrence of a crystal structure transition to a lower lattice symmetry between 300 and 4.2 K. This suggestion is reasonable in view of the several successive crystal phase transitions known for most of the other actinide metals[3] ; also, the resistivity anomaly at 100 K may indicate a phase transition[4]. Unfortunately, Mössbauer experiments at 100 K would be difficult owing to the decreased Debye Waller factor as calculated with a typical θ_D of 225 K known for instance for Am metal.

In summary, the improved experimental resolution of the ^{231}Pa Mössbauer resonance achieved with cubic Th metal source provides a promising outlook for precise hyperfine interaction measurements. The ratio of quadrupole moments of 84 keV and ground levels of ^{231}Pa is -0.31 ± 0.03, in good agreement with nuclear theory. The observation of two quadrupole sites of equal intensities in Pa metal at 4.2 K is tentatively attributed to a crystal phase transition from the bct room temperature structure, occurring possibly at 100 K as suggested from a resistivity anomaly.

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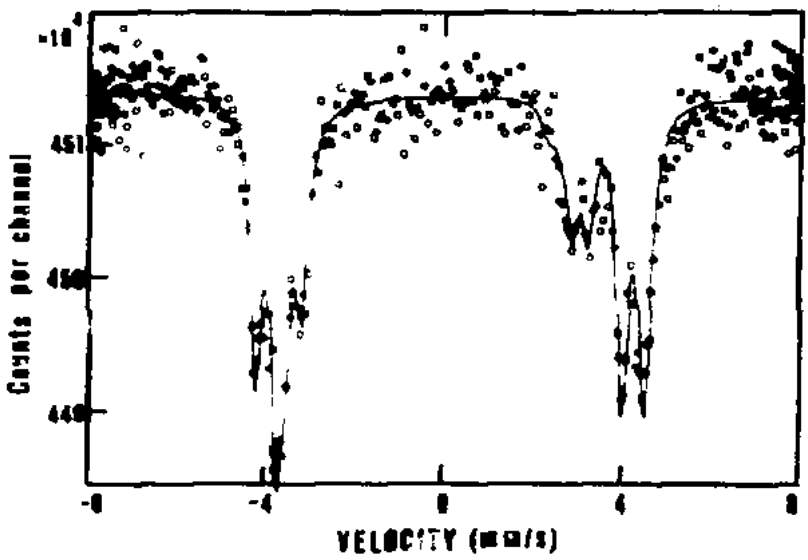

Fig.1 : ^{231}Pa Mössbauer spectrum of Pa metal vs Th metal source, both at 4.2 K.

^{1}H NMR AND MAGNETIC SUSCEPTIBILITY IN $ThNiAlH_x$ AND $UNiAlH_x$

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New intermetallic hydrides of ThNiAl and UNiAl have been prepared by hydrogen absorption at high pressure/40 atm/. The H/ThNiAl and H/UNiAl ratios were 2.5 and 1.9, respectively. The room temperature X-ray examinations showed that the hexagonal structure of ThNiAl or UNiAl matrix remains also after hydrogenation. Although, the volume of unit cell increases by ca 10%.

The ^{1}H pulsed and cw NMR experiments were made as a function of temperature. The temperature dependence of spin-lattice relaxation time(T_1) as a function of reciprocal temperature 1000/T for $^1ThNiAlH_x$ is shown in Fig.1.

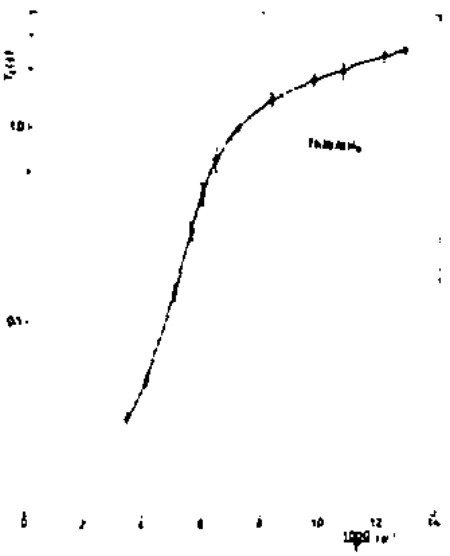

Fig.1

Starting at room temperature, T_1 increases when temperature is lowered. Simultaneously, cw spectrum at room temperature shows narrow line (below 1 Oe). Thus, we conclude that the main contribution to the relaxation in the range of 1000/T= 3.4 - 6.2 is the self-diffusion of protons in the crystal lattice. In turn, at still lower temperatures we observe broad resonance line (8.8 Oe) with second moment equal to 9 ± 1 Oe^2 at 77 K.

The T_1 in this region fits well Korringa[1] relation $T_1T=C$ where C is equal to 200sK.

The spin-lattice relaxation time in $UNiAlH_x$ is few order shorter than that observed in thorium related hydride. Also, the temperature dependence is different from that shown in Fig.1. Moreover, the NMR signal disappears below ca 120 K. Second moment values showed as a function of temperature in Fig.2, increase with lowering temperature and there are no data for temperatures below ~ 8 K.

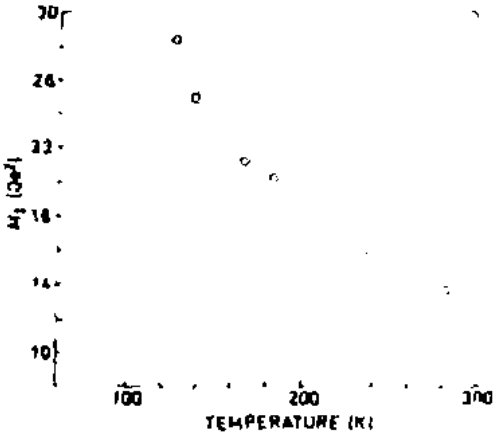

Fig.2

The magnetic susceptibility measured in temperature range 4.2 - 292 K shows the maximum at temperature of 122K. Those results strongly suggest that studied hydride orders antiferromagnetically below 120K. In that case, one may expect [2] that the T_1T would follow the

$$T_1T = C_m(T - \Theta) \qquad (1)$$

relation. In Fig.3, the T_1T data are presented as a function of temperature.

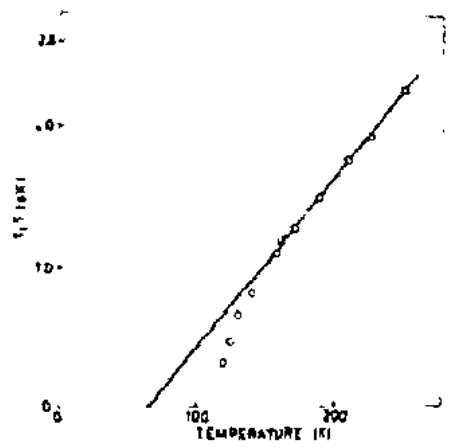

Fig.3

They fit well Eq.1 and deviate only in the temperatures near

120 K.

We have measured also the magnetic susceptibility in pure compound UNiAl. It is temperature dependent and shows maximum at 23 K. If it would connect with magnetic ordering then it is interesting to note that hydrogen increases that temperature by more than factor 5.

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THE SPINGLASS BEHAVIOR OF $Y_{1-x}Gd_xAl_2$

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During the last years a lot of efforts has been done to understand the phenomenon "spinglass" and to clear up the question wether the transition to the spinglass state is a true phase transition or more similar to a gradual transition like in a real gl .

Up to now, in the temperature range around this "transition" no anomaly has been observed in the specific heat. One of the most characteristic properties of a spinglass is the sharp cusp in the temperature dependence of the magnetic susceptibility.[1] The discussion has been renewed by the discovery of a frequency dependent freezing temperature T_f in some metallic and isolating spinglasses measured by the ac susceptibility method.[2,3,4,5] This time dependence of T_f is caused by all kinds of short range magnetic clusters. Further investigations show that ferromagnetic nearest neighbour interaction correlates with strong $T_f(\nu)$ shifts and antiferromagnetic interaction with $T_f(\nu)$ shifts.[6] In spinglass models where a phase transition is postulated, the cusp of the susceptibility should not depend on frequency for usual ac measurements.[7]

From this point of view one can only hope to decide the existence of a phase transition by measuring a system with ideal solubility, without direct exchange and nearest neighbour interactions.

Neutron scattering measurements show evidence that in systems with no observable variation of T_f a rapid Korringa process dominates the relaxation spectrum of the spin system.[8] As at low temperatures paramagnon

excitations have been observed in UAl_2 [9,10], we presume that this process can perhaps support the relaxation rate.

Therefore we have diluted $GdAl_2$ into UAl_2 and we have performed ac- and dc-measurements of the magnetic susceptibility between 0.05 K and 300 K in fields up to 10 kG on $U_{1-x}Gd_xAl_2$ ($0 \leq x \leq 0.1$). UAl_2 is a well-known spin fluctuation system and $GdAl_2$ orders ferromagnetically at 170 K. The high temperature susceptibility $\Delta\chi = \chi_{U_{1-x}Gd_xAl_2} - \chi_{UAl_2}$ follows a Curie law for $x < 0.1$. For higher Gd concentrations we extrapolate a negative Curie temperature in the plot $\Delta\chi^{-1}$ vs T which indicates the onset of antiferromagnetic interactions between nearest neighbours or clusters.

At low temperatures the "zero field" susceptibility shows a sharp maxima at T_f which increases and is shifted to higher temperatures proportional to the concentration x (Fig. 1).

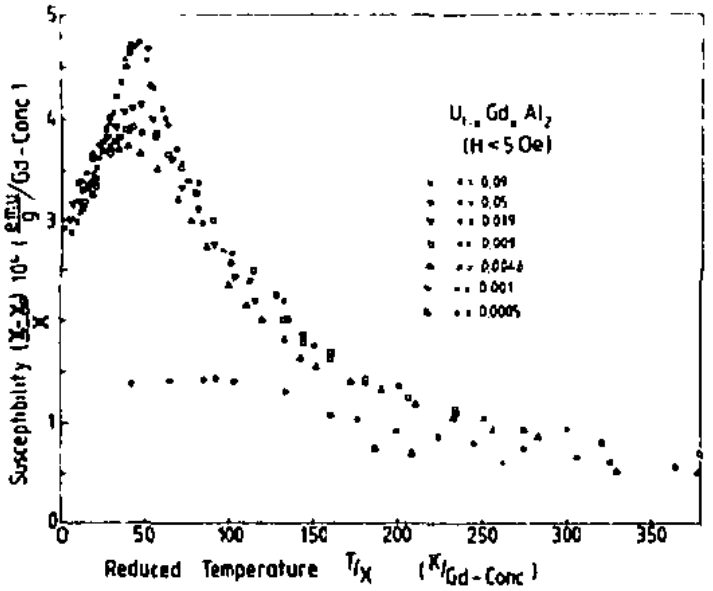

Fig.1: Reduced magnetic susceptibility $\Delta\chi/x$ vs reduced temperature T/x of $U_{1-x}Gd_xAl_2$ (x = Gd concentration)

No frequency dependence of T_f ($\nu \sim 10 - 5 \cdot 10^3$ c/sec) has been seen for $x < 0.1$. For higher concentrations we have observed a weak shifting of T_f in agreement with the model of antiferromagnetic clusters. We find a "freezing temperature" $T_f = 40 \cdot x$ (K) and observe the validity of the scaling laws like in the archetypical systems AuFe and CuMn. From the value $\Delta\chi\big|_{T \to 0}$ we extrapolate a RKKY interaction strength of $2.1 \cdot 10^{-26}$ (eVcm^3) which is stronger than in the comparable rare earth systems but weaker than in those with transition metals.

Our measurements reveal that the solubility of Gd in the UAl_2 matrix is very good up to $x < 0.1$. Therefore extensive investigations would be worth to perform.

This work was supported by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 125.

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de Haas-van Alphen Measurements of U_3P_4 and U_3As_4*

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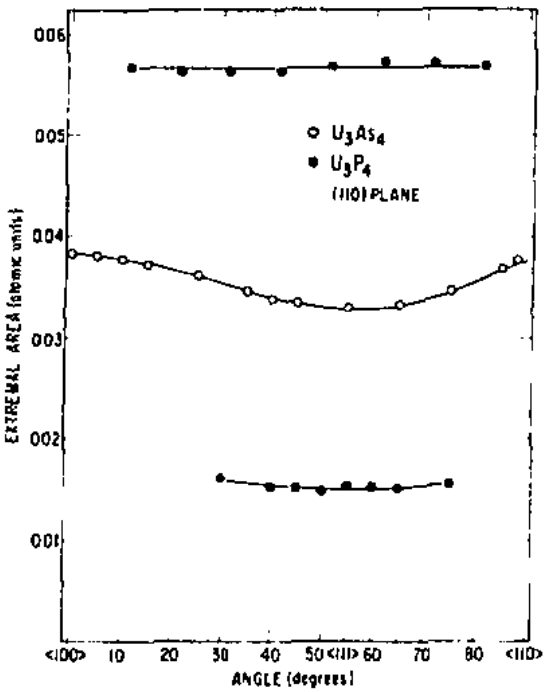
The degree of itinerancy among the 5f electrons in actinide compounds is one of the most important factors determining the magnetic, electronic and transport properties in these materials. Fermi surface studies give direct, detailed information about the itinerant electrons and are thus very useful for understanding the behavior of the 5f electrons and their influence on other properties of the system. Several Fermi surface studies of itinerant 5f actinides have appeared,[1,2] giving information on the band structure and hybridization effects. In this paper we present the first de Haas-van Alphen study of the Fermi surface in magnetically ordered actinides, the compounds U_3As_4 and U_3P_4.

In U_3As_4 we observe a single closed sheet of effective mass 5.1 ± 0.1. In U_3P_4 we see two closed sheets whose volumes differ by a factor of about 8, the larger sheet having a mass of 8.1 ± 0.7. These results are consistent with a semimetallic type band structure producing a large hole sheet at Γ and several symmetrically placed electron sheets of smaller volume which exactly compensate the hole sheet. The large effective masses suggest conduction states may be hybridized with the f states, though more experimental work needs to be done to decide this question.

U_3P_4 and U_3As_4 crystallize in a Th_3P_4 type bcc structure.[3] They are ferromagnetic[4] below 138K and 198K, respectively, and show unusually large magnetic,[5] magnetostriction[6] and resistivity[7] anisotropy. The magnetic structure consists of an unusual non-collinear three sublattice arrangement[9] giving rise to a large anisotropy field with <111> the easy magnetic direction. The saturation moment[10] in the <111> direction in U_3As_4 is 1.8 μ_B/U atom, corresponding to an internal field $4\pi M_{sat}$ = 4.2 kG. In U_3P_4, the <111> saturation moment[11] is 1.2 μ_B/U atom, giving and internal field $4\pi M_{sat}$ = 3.1 kG. A field of 300 kG is insufficient to saturate either material[11] along <100>.

de Haas-van Alphen data were taken in both compounds in fields to 150 kG at temperatures between 0.3 and 0.8K using the field modulation technique with the field in the (110) plane. Spherical samples of approximately 1 mm diameter were prepared from crystals with residual resistivity ratios ($R_{300}/R_{4.2}$) between 300 and 550 grown by chemical vapor transport.[12]

The measured extremal cross sectional areas are shown in the figure. A single branch is observed for U_3As_4, corresponding to a single closed sheet with an area anisotropy of about 16%. In U_3P_4 two nearly isotropic branches are observed with areas differing by a factor of about 4. If both branches correspond to closed sheets, their volume difference is a factor of 8. The signals in U_3P_4 were generally weaker than in U_3As_4, so that the two branches we observe may well extend across the entire (110) plane, but are too weak to detect near <100> and <110>. In U_3As_4 we have measured the effective internal saturation field by making a linear fit of the oscillation number to $1/(H_{applied} + H_{eff})$ with H_{eff} as an adjustable parameter. The best fit gave $H_{eff} = 0.75$ kG, much smaller than the expected value for spherical samples, $8\pi/3\ (M_{sat}) = 2.8$ kG. We do not understand the reasons for this discrepancy but we suspect it may be related to the unusual non-collinear magnetic structure. In the figure we have ignored the small correction to the areas caused by $H_{eff} \neq 0$. Because $H_{eff} \ll H_{applied}$ this correction is never more than 4%. Assuming closed sheets and no ferromagnetic splitting of the bands (i.e., ignoring H_{eff}), the volume of the single observed sheet in U_3As_4 corresponds to 0.043 electrons/formula unit, and that of the large sheet in U_3P_4 to 0.078 electrons/formula unit.



We interpret the area data in terms of a semi-metallic band structure producing a large sheet of holes at Γ and several smaller electron sheets located symmetrically in the zone which exactly compensate the hole sheet. In U_3P_4 the volume difference between the two sheets suggests 8 nearly spherical electron pockets located along the Γ–P line. We do not observe any smaller branches in U_3As_4, though this could be due to sample quality and the experimental problems of measuring small area orbits at high field. Our compensated semimetal model is closely related to the indirect gap semiconducting band structure expected for Th_3P_4 and Th_3As_4 on the basis of electrical and optical measurements.[13] It also qualitatively explains (1) the low positive value of the Hall constant[14] as being due to compensation effects, (2) the positive thermopower[14] as being due to dominant holes on the large sheet, and (3) the "semiconducting type" of critical behavior in the resistivity[15] at the Curie point.

The large masses we observe in U_3P_4 and U_3As_4 suggest that the conduction states may contain some f character, a possibility that is consistent with the low saturation moment and with the positron annihilation estimate[16] for the number of valence electrons in Th_3As_4 and U_3As_4. However, we note

that comparable masses have been observed in metals with nearly full or nearly empty d bands, that the non-collinear magnetic structure complicates the interpretation of the saturation moment, and that valence measurements by positron annihilation inherently contain appreciable experimental error. Thus the question of 5f electron delocalization in U_3As_4 and U_3P_4 requires more detailed experimental study.

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AMORPHOUS ACTINIDE ALLOYS*

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Amorphous alloys have recently been the subject of considerable research, and many aspects of their structure and properties are now reasonably well established. However, relatively little is known about amorphous actinide alloys even though the initial observation of the amorphisation of a uranium alloy was reported nearly 20 years ago.[1] This paper, based on both published and unpublished experimental results, examines glass forming tendencies in a wide range of actinide alloys. In addition, certain actinide alloys are unique in the sense that they can be readily amorphised by either liquid quenching or irradiation. The contrast in structure and properties of an amorphous U-Fe alloy produced by both techniques is also discussed.

The following table summarizes the amorphisation behavior of actinide alloys formed by either liquid quenching or irradiation. Metallic glasses generally form near eutectic compositions (preferably deep eutectics) and thus most of the alloys examined have compositions near their respective eutectics. In all cases, x-ray diffraction was used as the primary tool in determining whether the alloy was at least partially amorphous. The table shows that a large number of actinide alloy systems (nineteen to-date) will form a predominantly amorphous structure given a sufficiently rapid quench from the liquid state. That these actinide systems should readily form metallic glasses is a result of several favorable glass forming factors; these include a low "reduced" melting temperature and melting temperature depression[9] as well as atomic radius ratios similar to those of alloys with good glass forming tendencies. Additionally, Elliott and Giessen conclude that the sizable 5f-electron contribution to bonding in the early actinide metals (U, Np and Pu) favors low symmetry or random/amorphous arrangements of the atoms.[10] This may also contribute to the unusually high viscosites in the early actinides (especially Pu) at their melting temperatures.[11] Eutectic alloys based on these actinides would probably have high viscosities and this would contribute significantly to their strong glass forming tendencies.

While nearly all of the alloys examined exhibit a strong tendency to form glasses, the table shows that the uranium alloys require a lower cooling rate than do either the plutonium or neptunium alloys. The comparatively greater glass forming tendency of the uranium alloys is due, at least in large part, to the 2-3 times greater amount of the binary component in the U-X eutectics tested then in the Pu-X and Np-X eutectics. Another factor is the much lower thermal conductivity of Pu and Np,[12] which reduces the effective quenching rate in these metals and hence reduces the glass forming tendency.

A Listing of Amorphous Actinide Alloys which are at Least Partially Amorphous after either Liquid Quenching (LQ) or Irradiation (IRR).

Alloy System	Composition (Range) at.%	Preparation Method	Comments	References
Th-Fe	(20 to 70)	LQ		3
U-Fe	(≲14 to >40)	LQ		1,5,6,8
	14	IRR		6,8
-Mn	(≲20 to >35)	LQ		5
-Co	(≃24 to >40)	LQ		5
-Ni	(≃24 to >40)	LQ		5
-Cr	(20 to 40)	LQ		4,5
-V	(20 to 40)	LQ	Amorphous	4,5
	30	LQ	Not Amorphous	Present Study
-Si	25	IRR		2
-Os	30	LQ		Present Study
-Ir	30	LQ		Present Study
-Pd	(30 to 40)	LQ		Present Study
Np-Mn†	14	LQ		Present Study
-Fe	14	LQ		Present Study
-Co	14	LQ		Present Study
-Ga	(30 to 40)	LQ		Present Study
Pu-Mn†	(~10 to >14)	LQ		Present Study
-Fe	(~15 to >20)	LQ		Present Study
-Co	20	LQ		Present Study
-Ni	(~12 to >30)	LQ		Present Study
-Cu	(~14 to >20)	LQ		Present Study
-Ru	20	LQ		Present Study
-Ga	37	IRR		7

†Both the Np and Pu-based alloys require faster cooling rates (~10^7 x 10^8 K/sec) than the U-based alloys (~10^5 to 10^6 K/sec) in order to form metallic glasses by liquid quenching.

The compounds U_6Fe, U_3Si, and Pu_5Ga_3 are unique in that they have been amorphised by neutron irradiation.[1,2,6-8] Of these, the U-Fe alloy has been best characterized and, compared to the liquid-quenched glass, the irradiation-produced alloy has: (a) a reduced degree of short-range order, (b) a larger, narrower exothermic peak upon crystallization, (c) a lower density, (d) a smaller resistivity, (e) a lower hardness, and (f) a higher superconducting transition temperature.[6,8] These results are quite consistent with a decreased degree of structural relaxation in the irradiation-produced amorphous alloy.

* Work performed under the auspices of the U. S. Department of Energy.

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SOLID STATE CHEMISTRY

CRYSTAL CHEMICAL STUDIES OF ACTINIDE MOLYBDATES*

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Actinide molybdates have been implicated in the formation of undesirable "insoluble" Pu-containing residues in dissolver solutions.[1] Although several actinide molybdate phases have been reported, the literature is greatly confused; inaccurate and even incorrect crystal structure determinations abound. We are attempting to sort out this area by crystal structure determinations of key compounds. The structure of orthorhombic (low temperature) "UMo_2O_8", prepared by a skull melting technique, has been refined to R = 5.8%. Our study reveals a layer structure in which sheets containing pentagonal bipyramidal uranium and octahedral molybdenum polyhedra are connected by short (U-O = 2.06 Å), nearly linear (U-O-U = 178°) U-O-U-O linkages. Thus, the structure is correctly formulated as a mixed oxide. Interestingly, this type of layer structure and U-O-U separation occurs in other seemingly unrelated actinide oxide phases, including U_3O_8, UVO_5, and UO_2Br. In such structures there seems to be a failure of Zachariasen's bond length-bond strength relation to accurately describe the observed very short U-O bond distances.

We have also determined the structure of the hexagonal (high temperature) form of "$ThMo_2O_8$", prepared by skull melting, and refined to R = 3.2%. This form is a true molybdate, correctly written $Th(MoO_4)_2$, whose structure differs radically from that of the mixed oxide orthorhombic uranium structure. The hexagonal structure contains MoO_4 tetrahedra (Mo-O = 1.62 - 1.86 Å) which bridge three dimensionally both nine-coordinate (Th-O = 2.32 - 2.54 Å) and six-coordinate (Th-O = 2.28 - 2.50 Å) thorium atoms. Each oxygen in the structure appears to bridge one Mo and one Th.

Other MMo_2O_8 (M = actinide) phases (including hydrates) have been reported, including a plutonium compound reported from actual fuel-rod workups. We have prepared an orthorhombic $ThMo_2O_8$ complex (not isomorphous to the orthorhombic UMo_2O_8 phase described above but isomorphous to a reported $PuMo_2O_8$ phase) by heating hexagonal $Th(MoO_4)_2$ at 900°C for 24 hrs. General structural relations between all of these actinide molybdates and their crystal chemical relevance to troublesome Pu-coordination will be discussed.

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* This work performed under the auspices of the U.S. Department of Energy.

TERNARY ACTINIDES-MOLYBDENUM CHALCOGENIDES. SYNTHESIS AND MAGNETIC SUSCEPTIBILITY OF $ThMo_6S_8$, UMo_6S_8 AND UMo_6Se_8

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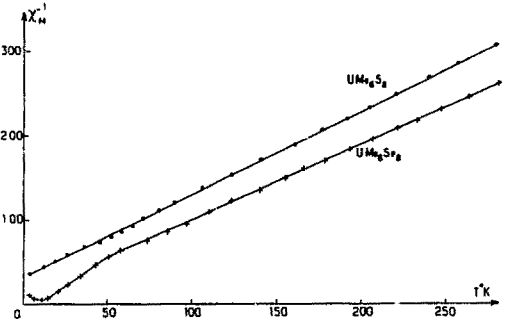
The ternary molybdenum chalcogenides $M_xMo_6X_8$ (M = metal ; X = S, Se, Te) have attracted considerable interest in the last few years due to their very unusual superconducting properties, [1] including the observation of upper critical fields (≃600 kG for M = Pb) and the coexistence of superconductivity and long range magnetic order (M = rare earth RE = Ho, Dy, Gd, Er...) [2, 3, 4]. These properties change from one compound to an other, with the ionic size, the valency and the magnetic behavior of the inserted M element.

Replacing a rare earth by uranium may have two main effects :
- a change of the charge transfer from M to the Mo_6 cluster and then a change of the density of state at the Fermi level ;
- an enhancement of the magnetic interactions in the M sublattice.

The ternary thorium or uranium-molybdenum chalcogenides $ThMo_6S_8$, UMo_6S_8 and UMo_6Se_8 have been prepared from intimate mixtures of AX_2 (A = Th, U), Mo, X, pressed into pellets and heated in fused silica tubes at T = 1180° C during 24 hours. In spite of the fact that all handlings were made in a dry and desoxygenized glove box, small amounts of the oxychalcogenides ThOS, ThOSe, UOSe could not be avoided in the final products. The existence of $ThMo_6S_8$ and UMo_6S_8 had already been mentioned [5], but UMo_6Se_8 is a new compound and $ThMo_6Se_8$ could not be prepared. The lattice parameters, calculated from least square refinements, have the following values (hexagonal unit cell) :

$ThMo_6S_8$	a = 9.05 Å	c = 11.43 Å	V = 810 Å^3
UMo_6S_8	a = 9.02 Å	c = 11.36 Å	V = 800 Å^3
UMo_6Se_8	a = 9.36 Å	c = 11.82 Å	V = 897 Å^3

The magnetic susceptibility of the uranium compounds has been investigated by the Faraday method in the temperature range 4.2 - 300° K and in the applied field = 4 kœ. The susceptibility of UMo_6S_8 (figure) fits a Curie-Weiss law $\chi = C/(T-\theta_p)$ with a negative paramagnetic Curie temperature (θ_p = -33° K) ; the effective magnetic moment $\mu_{eff} = (8c)^{1/2} = 2.87\ \mu B$ is close to the usually reported values for U^{4+} ion with a large crystal field splitting of the ground term. The susceptibility of UMo_6Se_8 follows a Curie-Weiss law above 55° K with θ_p = -13° K and $\mu_{eff} = 3.0\ \mu B$. Below 55° K, the slope of the χ^{-1} vs T curve increases, with a positive intercept of the temperature axis, and the susceptibility goes through a maximum at T = 10° K. This behavior is significant of an antiferromagnetic ordering of uranium, with the probability of a metamagnetic transition in higher applied field.



It is to be noticed that the binary USe_2 is also an antiferromagnet with $T_N = 12°$ K [6], but the same low temperature behavior was observed for samples containing an excess of uranium (with observable USe_2 as impurity), as well as for samples containing an excess of molybdenum (with Mo_3Se_4 or $MoSe_2$ as impurity). The highest reported magnetic ordering temperature among the $REMo_6X_8$ family is $T_N = 2.25°$ K for $CeMo_6S_8$ [7] and uranium compounds have generally higher ordering temperature than rare earth compounds due to the largest spatial extent of the 5f electron wave functions.

As some of the rare earth molybdenum selenides have rather high superconducting critical temperatures[8] ($LaMo_6Se_8$: $T_c = 11°$ K), substitution of RE by U in the same lattice position would lead to promising pseudo-ternaries $RE_{1-x}U_xMo_6Se_8$ in view of the competition between superconductivity and long-range magnetic order.

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STERIC EFFECTS IN AMIDE AND OTHER COMPLEXES OF URANIUM TETRACHLORIDE AND N-THIOCYANATE

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Following on the study [1] of the disproportionation of "$(\eta^5C_5H_5)_2UCl_2$", we have investigated similar phenomena in the complexes of $[(\eta^5C_5H_5)U(NCS)_3L_2]$, where L is an oxygen or nitrogen donor ligand [2]. Compounds in which L = Ph_3PO or $(Me_2N)_3PO$, for which ΣCAF = 0.76, can be isolated, but those for which ΣCAF = 0.72 (L = thf or py) disproportionate readily:

$$3[(\eta^5C_5H_5)U(NCS)_3L_2] + 2L \rightleftharpoons [(\eta^5C_5H_5)_3U(NCS)] + 2[U(NCS)_4L_4]$$

where L is an amide ligand (CAF = 0.74, that is, in the critical border region) the complexes $[(\eta^5C_5H_5)U(NCS)_3L_2]$ can be isolated in some cases but in others disproportionation may occur, a result which depends upon the second order steric crowding. Thus where L = CH_3CONMe_2, stable complexes are only obtained when two or more hydrogen atoms of the acid CH_3 group are replaced by methyl groups. The results are shown in Fig. 1.

Above the stable region a dissociation equilibrium may exist between complexes of differing coordination number and the free ligand, as found for UCl_4 complexes [3]:

$$[UCl_4.2.5L]_n (\Sigma CAF = 0.80) \rightleftharpoons n[UCl_4L_2] (\Sigma CAF = 0.75) + 0.5nL$$

$$[U(NCS)_4.L_4] (\Sigma CAF = 0.84 \rightleftharpoons [U(NCS)_4L_3] (\Sigma CAF = 0.74) + L$$

In these cases the equilibrium may be affected to some extent by the solvent, but the major factor is steric crowding. Thus compounds of composition $[UCl_4L_2]$, in which the environment of the uranium atom is relatively under crowded, are stabilised by ligands of larger secondary size, such as $(CH_3)_2CHCON(CH_3)_2$ (dmiba) and $(CH_3)_3CCON(CH_3)_2$ (dmpva) which destabilises the first order overcrowded compounds of the type $[U(NCS)_4L_4]$.

Unusual composition and structures may occur when the values of CAF anticipated (but overcrowded) compounds are not in the stable region (see Fig. 1); examples of this behaviour are the unusual (for uranium(IV)) pentagonal bipyramidal coordination geometry of $[U(NCS)_4(dmiba)_3]$ [4] (= $UCl_4.2.5depa$; depa = $C_2H_5CON(C_2H_5)_2$) [5].

This work was supported by the grant of a studentship to L. Xing-fu by the Peoples Republic of China.

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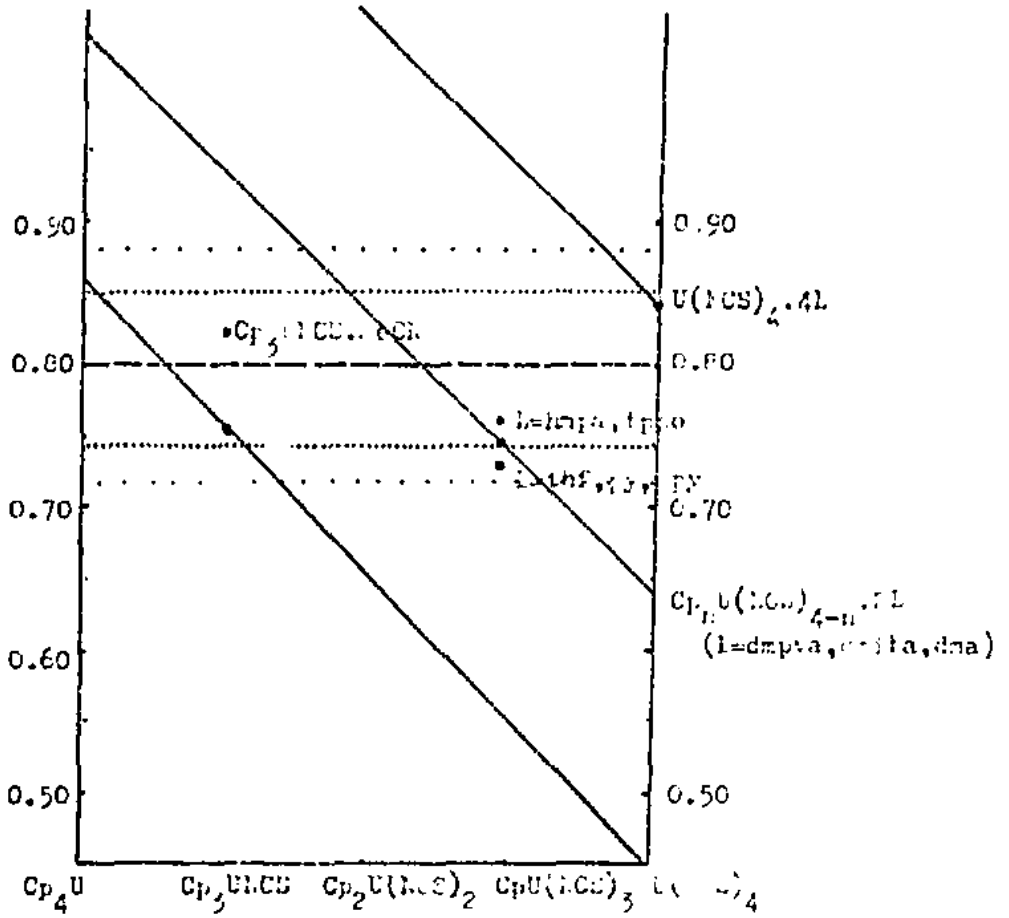

Fig(IV) ΣCAF estimation of cyclopentadienyl-thiocyanato-uranium(IV)-electron donor ligand systems

COMPLEXES OF THROIUM TETRACHLORIDE AND TETRATHIOCYANATE WITH AMIDES

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Thorium tetrachloride and thorium tetrathiocyanate form complexes with a series of amides of the type $RCONR'_2$; the steric effects [1] resulting from the use of bulky substituents R and R' on the dissociation of the tris and tetrakis complexes:

$$ThCl_4.L_3 \rightleftharpoons ThCl_4.L_n + (3-n)L$$

$$Th(NCS)_4.L_4 \rightleftharpoons Th(NCS)_4.L_{n'} + (4-n')L$$

have been studied [2].

The crystal structure of some of the complexes of the above type are being investigated.

* Supported by the Government of the People's Republic of China.

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A TREATMENT OF COORDINATION SATURATION AND STERIC EFFECTS IN ACTINIDE COMPOUNDS

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High (>6) coordination numbers are commonly exhibited by the actinide elements in their compounds and, in contrast to the d transition elements, the coordination number is limited essentially by steric crowding [1] rather than by electronic considerations. The first order steric crowding can be treated quantitatively in terms of the Cone Angle Factor* (CAF), an approach which will be described in detail. This approach has been applied [2] to about 25 uranium compounds of known structure and the results indicate that the stable region for these compounds comprises those for which $\Sigma CAF = 0.80$, $\sigma = 0.025$, whereas compounds in which ΣCAF is greater than $0.80+3\sigma$ or less than $0.80-3\sigma$ rarely exist. An increase or decrease in the coordination number for compounds for which ΣCAF is within the critical border regions may provide a driving force for chemical rearrangement to occur because of the steric effects.

This work was supported by the grant of a studentship to L. X-f. by the Peoples Republic of China.

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* The term "cone angle factor" as used here means the calculated angle of the cone comprising the metal atom at the apex and the primary coordinating atom.

PREPARATION AND PROPERTIES OF SOME CARBONATES OF PENTAVALENT AND HEXAVALENT ACTINIDES*

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Ammonium plutonyl carbonate, APUC, $(NH_4)_4PuO_2(CO_3)_3 \cdot H_2O$, ammonium uranyl carbonate, AUC, $(NH_4)_4UO_2(CO_3)_3 \cdot 2H_2O$, and mixed ammonium uranyl-plutonyl carbonates with the general composition $(NH_4)_4(U_xPu_{1-x})O_2(CO_3)_3 \cdot H_2O$ have been prepared by precipitation with ammonium carbonate from the respective nitrate solutions.

Plutonyl carbonate, PuO_2CO_3 was prepared by saturating a suspension of $PuO_3 \cdot 0.8H_2O$,[1] with carbon dioxide for a period of several hours.

The ammonium double carbonates have been studied by x-ray crystallographic methods. They were found to be monoclinic with the following lattice constants:

Formula		a(Å)	b(Å)	c(Å)	β°	D(gcm^{-3})
$(NH_4)_4UO_2(CO_3)_3 \cdot H_2O$ [2]	yellow	12.824	9.356	10.654	96.42	2.73
$(NH_4)_4(U_{0.7}Pu_{0.3})O_2(CO_3)_3 \cdot H_2O$	green	12.744	9.295	10.628	96.03	2.76
$(NH_4)_4(U_{0.5}Pu_{0.5})O_2(CO_3)_3 \cdot H_2O$	grayish-green	12.852	9.329	10.620	96.51	2.74
$(NH_4)_4(U_{0.3}Pu_{0.7})O_2(CO_3)_3 \cdot H_2O$	deep green	12.736	9.403	10.732	96.39	2.71
$(NH_4)_4PuO_2(CO_3)_3 \cdot H_2O$	fern green	12.882	9.279	10.477	97.05	2.79

The lattice data of green $(NH_4)_4NpO_2(CO_3)_3 \cdot H_2O$ have not yet been determined.

The thermal decomposition of the ammonium actinyl carbonates has been studied by means of mass spectrometric analysis of the gaseous decomposition products, by DTA, and by x-ray diffraction.

Thermal decomposition of $(NH_4)_4UO_2(CO_3)_3 \cdot H_2O$ and of $(NH_4)_4(U_{0.7}Pu_{0.3})O_2(CO_3)_3 \cdot H_2O$ proceeds in a single step, yielding U_3O_8, or $(U_{0.7}Pu_{0.3})_3O_8$ in an oxidizing atmosphere, UO_2 or $(U_{0.7}Pu_{0.3})O_2$, respectively, in a reducing atmosphere.

The compounds $(NH_4)_4(U_xPu_{1-x})O_2(CO_3)_3 \cdot H_2O$ with x = 0.5, 0.3, and 0 decompose in two steps:

In the first step, rust brown $(U_{0.5}Pu_{0.5})O_2CO_3$, yellow-brown $(U_{0.3}Pu_{0.7})O_2CO_3$ or light brown PuO_2CO_3 are formed at approx. 150°C,

at approx. 200°C, these carbonates decompose to form mixtures of PuO_2 and U_3O_8, as is to be expected from the U-Pu-O phase diagram, [3,4].

Attempts to prepare anhydrous PuO_2 by careful decomposition of PuO_2CO_3 were not successful. Rather, the decomposition proceeds directly to PuO_2 with evolution of oxygen.

The preparation of $(NH_4)_4AmO_2(CO_3)_3 \cdot H_2O$ was attempted by reacting a solution of Am(VI) in $^2HNO_3$ with $(NH_4)_2CO_3$. However, immediate reduction to light-brown, insoluble $(NH_4)AmO_2CO_3$ (or possibly, $(NH_4)_7AmO_2(CO_3)_2$) takes place. The corresponding neptunium(V) carbonate, $(NH_4)NpO_2CO_3$ has also been prepared.

Experimental techniques and detailed results will be presented.

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CRISTALLOCHEMICAL PROPERTIES OF NEW TRANSURANIUM (Np, Pu, Am) TERNARY OXIDES WITH TRANSITION ELEMENTS (V, Mo, W) AND SOME SELFIRRADIATION EFFECTS

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New transuranium ternary oxides have been synthetized by solid state reaction -at the milligram scale- and identified by X ray diffraction
. trivalent state : Pu_2MoO_6, Pu_2WO_6, $Pu_2(WO_4)_3$, Am_2MoO_6, Am_2WO_6, $Am_2(MoO_4)_3$ and $Am_2(WO_4)_3$;
. tetravalent state : $Np(VO_3)_4$, $Np(MoO_4)_2$, $Np(WO_4)_2$ and $Pu(MoO_4)_2$.

We were able to determine stoichiometry and thermal stability of thirty six transuranium double compounds by studies of liquid-solid equilibrium diagrams Np, Pu or Am molybdates (or tungstates)-alkali molybdates (or tungstates) by differential thermoanalysis.

Structural properties of these new oxides were essentially established on powder samples ; as shown in Table 1 many of them were related to well known structural families.

Table 1. Lattice parameters of some transuranium ternary oxides

Compound	a (Å)	b (Å)	c (Å)	β (°)	Structural type
Pu_2MoO_6	4.051(1)		15.851(9)		Ln_2MoO_6 [1]
$Am_2(WO_4)_3$	7.733(3)	11.593(4)	11.507(4)	109.63(3)	scheelite
$Np(WO_4)_2$	9.506(5)	14.243(6)	10.237(5)		α-$Th(MoO_4)_2$ [2]
$Na_2Np(WO_4)_3$	5.240(3)		11.414(4)		scheelite
$LiAm(WO_4)_2$	5.258(3)		11.423(3)		"
$K_2Pu(MoO_4)_3$	17.538(9)	11.992(6)	5.243(4)	104.80(6)	"
$Na_4Np(WO_4)_4$	11.337		11.736		"
$K_8Np(MoO_4)_6$	10.488(3)	17.608(6)	7.822(3)	116.73(3)	palmierite
$K_5Am(MoO_4)_4$	10.335(4)	5.965(4)	7.708(3)	116.57(3)	"
$Li_2Np(WO_4)_3$	9.777(3)	5.651(2)	5.053(2)	93.77(4)	wolframite
$Am_{0.120}WO_3$	3.827(1)				perovskite
$Np(VO_3)_4$	8.481(3)		28.723(8)		$Np(VO_3)_4$

Single crystals of $Np(VO_3)_4$ were obtained by fusion (1173°K) followed by slow cooling (6°K h^{-1}) to 773°K ; they were sealed in a capillary to avoid external contamination. Diffracted intensities were collected with a four-circle diffractometer ; the space group is I4$_1$/a and the Np atoms occupy 8(e) positions. Np atoms have eight O-atom neighbours, at an average distance of 2.32 Å, located at the corners of irregular polyhedra (figure 1). The O-atom environment of the two different V atoms is tetrahedral ; endless chains of

tetrahedra are formed running parallel to the xy direction (figure 2). The piling up of the polyhedra, linked only by the shared corners, confers great stability to this structure. The value of the ionic radius given by Shannon[3] for Np^{4+} (0.98 Å, eight-coordination) shows that the Np-O distances (2.287 to 2.348 Å) here measured for the first time, are that expected.

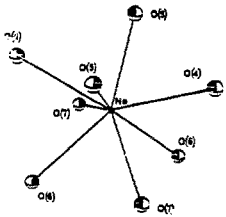

Fig. 1

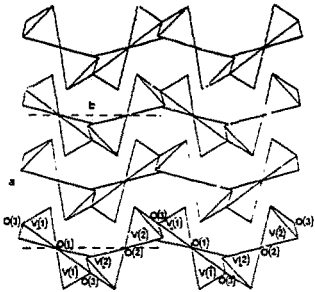

Fig. 2

The X-ray diffractograms of some ^{239}Pu and ^{241}Am ternary compounds show, after some months, a clear lattice alteration. We have observed a contradictory time evolution of the lattice parameters (Table 2) which show the need of new studies about radiolytical phenomena.

Table 2

Compound	t (months)	a (Å)	b (Å)	c (Å)	β (°)
$^{239}Pu_2(WO_4)_3$	0	7.777(2)	11.652(3)	11.566(3)	109.85(2)
	9	7.757(6)	11.634(10)	11.543(10)	109.8(1)
	16	7.752(3)	11.621(5)	11.550(5)	109.34(6)
$^{239}Pu_{0,105}WO_3$	0	3.824(1)			
	9	3.827(1)			
	16	3.828(1)			

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EFFECTS OF HEREDITY AND ENVIRONMENT ON THE CHEMICAL CONSEQUENCES OF THE DECAY OF ^{253}Es IONS IN SOLID STATE COMPOUNDS*

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Thermalization of recoil species resulting from α or β^- decay in the solid state could be considered as a process of charge-compensated ion implantation. Except for the charged species that escape the bulk phase, natural radioactive decay can maintain a charge balance as shown for the following cases. For α decay:

$$_zA^{n+} \rightarrow {}_{z-2}A^{(n-2)+} + {}_2He^{2+}$$

followed by neutralization of the He^{2+} to yield ultimately $_{z-2}A^{n+}$ and He. Likewise for β^- decay:

$$_zA^{n+} \rightarrow {}_{z+1}A^{(n+1)+} + {}_{-1}e^{1-}$$

followed by reaction of the free electron to yield ultimately $_{z+1}A^{n+}$. Thus, this natural process is quite different from ion implantation carried out in the laboratory where charge compensation is not possible or, at best, possible only in the crudest sense. Consider also that radioactive decay is a single atom event, i.e., in each decay event in the solid state, the recoil ion can find itself in a matrix of 10^n host species.

In bulk-phase Bk halides[1,2,3] it has been shown that the Cf daughter species thermalize in the same oxidation state and crystal structure as that of the parent. This is understandable considering the weak energy (0.28 eV) of the Cf recoil. In bulk-phase Es halides, it has been shown that the progeny ions are also of the same oxidation state as the parent and postulated that the local-order structure of the progeny compounds is the same as the parent.[4] The maintenance of oxidation state in either α or β^- decay of the bulk-phase actinides seems to be a consequence of the charge balance, as given in the above equations, and is dependent on the initial oxidation state of the parent, an effect of heredity. Since radioactive decay in the solid state results in the replacement of some matrix ions one at a time, the local-order (local structure) of the transmuted ion may be determined by the environment, or local structure, into which it is implanted. If this is correct, there are several consequences; for example, it would be possible to infer the structure of Es compounds by determining the structure of progeny compounds. This could resolve the inherent difficulty of determining the structure of Es compounds by standard X-ray diffraction techniques.[5] It has been shown that f-f absorption spectra of lanthanides and actinides in the bulk-phase solid state are dependent on local order (the building block of long-range order) and are unique for a given crystal structure.[6] Thus, absorption spectral information can be used to establish local order and infer solid state (crystal) structure.

The hypotheses, that with actinide species (1) progeny oxidation state is an effect of heredity and (2) local order is a function of environment, were tested using absorption spectroscopy. Solid state mixtures of approximately 10 or less mole% ^{253}Es (II or III) halides in lanthanide (III) halides of various structures have been prepared. Samples of dilute Es(III) halides in alkaline earth halides were also synthesized. The spectra of these samples were obtained when the samples were freshly prepared and again at various subsequent times to establish the oxidation state and coordination of the progeny (particularly Cf) as they grow into the solid state host. As an auxiliary study, samples of $\leq$ 10 mole% Cf(III) in the same lanthanide (III) halides were also prepared to see if the coordination (structure) of Cf(III), as interpreted from spectral data, is influenced by the lanthanide (III) halide. This latter experiment is of interest as a possible adjunct proof of our hypothesis. The results of these studies should elucidate the influence of heredity and environment on the final chemical and physical state of progeny species resulting from ^{253}Es decay in the solid state.

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SILICATES OF THREEVALENT ACTINIDES

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By solid-state reactions of actinide dioxides with SiO_2 in air (An = Am,Cm) or under reducing atmosphere (An = Pu,Am) binary actinide silicates of the types $An_{9.33}\square_{0.67}(SiO_4)_6O_2$ (An Pu-Cm), $An_8(SiO_4)_2$ (An = Pu-Cm), and $Am_2Si_2O_7$ have been obtained for the first time [1]. Besides $ThSiO_4$ and $PaSiO_4$ these are the only actinide silicates to be prepared by solid-state reactions.

The $An_{9.33}\square_{0.67}(SiO_4)_6O_2$ and $An_8(SiO_4)_2$ silicates are isotopic with the corresponding rare earth compounds and crystallize in the hexagonal apatite-structure.
Formation conditions and lattice parameters are

Formula type	An	Formation conditions	Lattice Parameters (Å) (± ≤ 0.005)	
			a	c
$An_{9.33}(SiO_4)_6O_2$	Pu	H_2/1400°C/2d	9.589	7.019
	Am	Ar/1350°C/3d	9.569	7.002
	Cm	air/1350°C/3d	9.557[+)]	6.982[+)]
$An_8(SiO_4)_6$	Pu	H_2/1400°C/3d	9.595	7.037
	Am	air/1400°C/3d	9.565	7.014
	Cm	air/1350°C/3d	9.564[+)]	8.213[+)]

[+)] 4h after preparation

$Am_2Si_2O_7$ crystallizes in a pseudo-orthorhombic lattice with a = 8.639 Å, b = 12.940 Å, and c = 5.396 Å.

The cation vacancies in the apatite structures can be filled by substitutions of the type $1/3\ An^{3+} + 2/3\ \square \rightarrow 1\ Me^{+}$ (Me^{+} = Li,Na) and $4/3\ An^{3+} + 2/3\ \square \rightarrow 2\ Me^{2+}$ (Me^{2+} = Mg,Ca,Sr,Ba). The polynary actinide silicates, e.g., $LiPu_9(SiO_4)_6O_2$, $Mg_2Am_8(SiO_4)_6O_2$, and $Ba_2Cm_8(SiO_4)_6O_2$ are obtainable at much lower temperatures than the corresponding binary silicates. Formation conditions and lattice parameters of selected compunds are

Compound	Formation conditions	Lattice Parameters (Å) (± ≤ 0.005)	
		a	c
$LiPu_9(SiO_4)_6O_2$	H_2/1100°C/3d	9.566	6.999
$NaAm_9(SiO_4)_6O_2$	H_2/1100°C/3d	9.576	7.007
$Mg_2Pu_8(SiO_4)_6O_2$	H_2/1250°C/3d	9.559	6.973
$CaCm_8(SiO_4)_6O_2$	H_2/1200°C)3d	9.517[+)]	6.986[+)]
$SrCm_8(SiO_4)_6O_2$	H_2/1200°C/3d	9.565[+)]	7.069[+)]
$BaCm_8(SiO_4)_6O_2$	H_2/1200°C/3d	9.653[+)]	7.123[+)]

[+)] 4h after preparation

There seems to be a solid solution of SrO in $Sr_2An_8(SiO_4)_6O_2$ as shown by the different lattice parameter of the composition $Sr_3An_6(SiO_4)_6$.
Whereas the Am(III)- and Cm(III)-silicates are stable in air at room temperature, a slow decomposition of the Pu(III)-compounds occur with the formation of PuO_2.
The Am- and especially the Cm-compounds show a slow increase in lattice parameters due to self-irradiation effects. For a $Ca_2Cm_8(SiO_4)_6O_2$ the change in lattice parameters follo the equations

$$\Delta a/a = 4.1 \cdot 10^{-3}\ \{1-\exp(-0.06 \cdot t(h))\}$$

and

$$\Delta c/c = 2.8 \cdot 10^{-3}\ \{1-\exp(-0.03 \cdot t(h))\}$$

This gives

$a = 9.509$ Å and $c = 6.984$ Å for t=o

as compared to the measured values

$a = 9.517$ Å and $c = 6.986$ Å for t=4h.

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ACTINIDE HYDROXYSULFATES*

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Actinide compounds of the general formula $An(OH)_2SO_4$ are under study both from a synthetic and spectroscopic point of view. Synthetically the compounds comprise a series in which the onset of hydrolytic behavior leads to catenated $An(OH)_3^{+}$ species containing bridging hydroxides and the structure reveals the initial stages of polymer formation. Spectroscopically the compounds present the opportunity to study the effects of essentially the same symmetry crystal field on the energy level structures of a series of An^{4+} ions, thus in principle greatly aiding the theoretical interpretation of the spectra.

Uranium hydroxysulfate precipitates from a solution of U(IV) in dilute sulfuric acid in a hydrothermal reaction at 140°C. Infrared spectra contain absorptions expected for hydroxy and sulfate moieties. Visible spectra are typical for U(IV). X-ray powder diffraction patterns are consistent with the previously determined single crystal structure. Substitution of deuterium for hydrogen allows unequivocal assignment of the OH bands in the infrared. Conditions for the formation of $U(OH)_2SO_4$ are very critical. Even small variations in the requisite conditions produce compounds of different compositions.

Neptunium hydroxysulfate forms under conditions identical to those which produce the uranium compound. Infrared and visible spectra are consistent for a compound isostructural with the uranium species. X-ray powder diffraction patterns confirm the isomorphicity. Refined unit cell parameters display the trend expected due to the actinide contraction.

Plutonium subjected to the conditions under which the aforementioned hydroxysulfates form does not produce an identical compound. The product which does form is under investigation and attempts to prepare $Pu(OH)_2SO_4$ are continuing.

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ON THE COHESIVE PROPERTIES OF THE LIGHT ACTINIDE METALS

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The effect of spin-orbit coupling upon the band structures of the light actinide metals has been examined by comparing results obtained from the Pauli and Dirac equations. In the limit of small spin-orbit coupling the ratio of f-electrons in the $j = 5/2$ and $j = 7/2$ bands approaches 6/8 and the Pauli and Dirac solutions become identical. We have calculated this ratio in ab initio self-consistent relativistic band calculations for the metals Ac-Pu and have found that it changes from the ideal ratio of .75 in Ac to 2.1 in Pu. The effect upon the lattice parameter of this preferential occupation of the $j = 5/2$ band has been computed with the relativistic equivalent of the pressure formula[2]. The effects are small for Ac-U but there is an increase in the lattice parameter for Np and Pu which brings the theory[1] into very close agreement with experiment.

The cohesive energies were obtained as the difference between the total energies of the valence electrons[3] in free atom and band calculations in which the cores were frozen. The decreasing trend in the cohesive energy across the series was obtained correctly. Spin-orbit coupling effects upon the total energy in the band structure calculation increase across the series to 27 kcal/Mole for Pu. The interpretation of the results is compared with interpolation theories[4].

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CAUSES FOR THE VARIABLE SUPERCONDUCTING TRANSITION TEMPERATURE IN URANIUM METAL

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The superconducting transition temperature (T_c) for α-phase uranium, as reported by different experimentalists, covers the temperature range from $\leq 0.1K$[1] to $1.3K$[2] at ambient pressure. An answer to this variability is suggested by the space group, D_{2h}^{13} Pmnm, assigned to the recently determined structure for α'-phase uranium[3-5] along with the association of a charge-density wave (CDW) to a periodic lattice distortion in α-phase uranium[3].

The appearance of the space group D_{2h}^{13}, also found in the shape-memory effect (SME) alloy AgCd', is consistent with a suggestion made previously that a close-packed, layer-type (CPL) martensitic structure was indicated for the low-temperature phase of uranium[5]. This author has recently proposed[6] that there could be multiple effects as a consequence of a low-temperature martensitic α-U → α'-U transformation, which is indicated by the D_{2h}^{13} structure for α'-phase uranium. Besides charge-density waves (CDWs), these effects were listed as: valence fluctuations, discommensurations, solitons and even shape-memory effect (SME).

Electron-phonon interactions are considered to be responsible for both superconductivity and martensitic transformations. The effects of impurities on a martensitic transformation in A-15 compounds has already been considered by Bhatt and McMillan[7], as well as the relationship of such a transformation to superconductivity. There is a similarity in the α-phase uranium structure and the A-15 (β-tungsten) structure as pointed out by Pauling[8]. He noted that the two strongest bonds in uranium, as in the A-15 structure, bind the atoms together in straight "strings" extending through the crystal. It will be shown how impurities appear to affect completion of the α-U → α'-U transition and why there appears to be only filamentary superconductivity when the transition goes to completion at ~ 43K.

Fröhlich[9] is attributed by Phillips[10] with being the first to note that high values of T_c imply lattice instabilities. It will be suggested how valence fluctuations and CDWs, resulting from a martensitic transformation in α-phase uranium, contribute to lattice instabilities and therefore to the observed T_c. The answer appears to involve domain formation, discommensurations, and whether the possible CDWs are commensurate or incommensurate at the superconducting transition temperature, T_c.

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ACTINIDE CHEVREL PHASES
$An_{1+x}Mo_6Se_8$ WITH An = Np, Pu, Am

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Chevrel phases are ternary molybdenum chalcogenides of general formula $M\,Mo_6Se_8$ where M stands for a metal which can be monovalent (Na^+, Li^+), divalent (Pb^{2+}, Mg^{2+}) trivalent (RE^{3+}) or even tetravalent (Th^{4+}). The rare-earth compounds are of special interest because the sulfides and the selenides are superconductors with high critical temperatures and more over with high critical fields. Among these ternary molybdenum selenides $CeMo_6Se_8$ was not found to be superconducting down to 0.1 K and this is thought to be due to interactions between the cerium 4f electrons and the conductions electrons. In this context it was interesting to study the behaviour of the actinides in the chevrel phases. We have prepared and studied ternary molybdenum selenides $An_{1+x}Mo_6Se_8$ with $x = 0$ and 0.2 and An = ^{237}Np, ^{239}Pu, ^{241}Am.

They cristallize in the rhomboedral system of $PbMo_6Se_8$ type like the corresponding rare earth compounds and the lattice parameters of all the actinide compounds are close to those of $NdMo_6Se_8$. Their idealized structure consists of Mo_6Se_8 clusters surrounding the actinide ions. The cation An themselves are considered to be surrounded by 8 selenium ions in a quasi cubic symmetry. In such a structure the lattice parameters are not very sensitive to the size of the metal which explains that the lattice parameters of neptunium, plutonium and americium ternary molybdenum selenides are quite close one to the other.

The occurence of superconductivity in the actinide chevrel phases was searched by magnetic susceptibility and electrical resistivity measurements.

$Np_{1+x}Mo_6Se_8$ ($x = 0$ and 0.2) was found to be superconducting at 5.6 K. At this temperature it becomes diamagnetic and the electrical resistivity, measured on cold pressed pellets, drops by a factor of ten.

$Pu_{1+x}Mo_6Se_8$ and $Am_{1+x}Mo_6Se_8$ were not found to be superconducting down to 2.5 and 3.5 K respectively. Their electrical resistance lies in the ohm range and is pratically temperature independent. The magnetic susceptibility χ of the americium compound is weakly temperature dependent between 150 and 300 K with a rather low numerical value (χ varies from 1000 to 1200 uem CGS/Am atom). At lower temperature χ shows a Curie Weiss type contribution attributed to paramagnetic impurities. Between 150 and 300 K, after substracting the diamagnetic and Pauli paramagnetic contributions which are close to the $LaMo_6Se_8$ magnetic susceptibility, the remaining contribution of the Am ions is $\chi = (942 - 0.843\ T)10^{-6}$ uem CGS/Am atom which suggests a trivalent state of Am.

$Pu_{1+x}Mo_6Se_8$ follows a Curie Weiss law from 2.5 to $\sim$ 30 K with a paramagnetic effective moment $p = 0.85\,\mu_B$/Pu atom which also suggests a 3+ oxydation state of the Pu ions. Above 30 K a strong curvature of the curve $\chi = f(1/T)$ was observed. After substracting the diamagnetic and the conduction electrons contributions, like in the case of americium, the curve $\chi = f(1/T)$ above 150 K was analysed in terms of crystal field effects leading to an effective moment depending upon the temperature and varying from $0.85\,\mu_B$ in the low temperature region to $1.12\,\mu_B$ at room temperature thus approaching the free Pu^{3+} effective moment.

A similar treatment applied to $NpMo_6Se_8$ gives a variation of the Np effective moment (p) ranging from p = 1.87 μ_B at 100 K to 2.44 μ_B at 300 K approaching the free Np^{3+} moment value. At lower temperature a Curie Weiss law is followed from 6 to 30 K, with p = 1.25 μ_B/Np atom. Between 30 and 60 K a change of slope is observed likely due to crystal field effects. On the other hand the existence of Np^{3+} ions was confirmed by Mössbauer effect measurements [1].

It is rather surprising to find superconductivity in the neptunium Chevrel phase and not in the plutonium and americium ones. Two kinds of arguments can be taken into account to explain this situation.

The low temperature behaviour of the magnetic susceptibility of $Np_{1+x}Mo_6Se_8$ suggests a singlet ground state which can favoured the occurence of superconductivity compared with $PuMo_6Se_8$ where Pu^{3+} has the 5 f^5 configuration in which the ground state is a Kramers doublet. This argument does not hold for americium (Am^{3+} has a 5 f^6 configuration with J = 0). In this case, superconductivity could have been destroyed by self radiation damage, and this effect can also be taken into account for the plutonium compound.

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SPECIFIC HEAT STUDIES OF α AND δ Pu*

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Plutonium, due to its 5f electron bonding, has many unusual properties. We report low temperature specific heat measurements on α phase Pu, α' phase Pu with 1.8 at.% Al entrapped in the α lattice by pressure transformation of the delta phase (isopressing), and four composition of δ phase $Pu(Al_x)$, with x = 1.8, 3.4, 5.2, and 11.2 at.%. These measurements are intended as a beginning in our effort to characterize Pu and its allotropes and alloys as throughly as possible via specific heat data in order to gain new, fundamental insights into the nature and consequences of the 5f bonding in Pu.

The samples are prepared as thin (~.001") foils by an arc smashing technique reported on elsewhere.[1] Discs 1/4" in diameter are then punched and measured in an x-ray diffractometer to determine phase purity and lattice parameters. The ~15 mg samples are then measured in a small sample calorimeter, which has been used previously to measure Pa and Am samples of similar small size.[2,3] As can be seen in Figure 1 for α-Pu, it is sometimes necessary to measure the specific heat of a material to as low a temperature as possible in order to correctly obtain γ and N(0), where

$$C/T = \gamma + \beta T^2 + \delta T^4 + \ldots . \qquad (1)$$

and

$$N(0)\,(1 + \lambda) = .4244\,\gamma \qquad (2)$$

$$\theta_D = \left(\frac{1944}{\beta}\right)^{1/3} \times 10 \qquad (3)$$

The units of γ and β are in mJ/g-atom-K^2 and mJ/g-atom-K^4 respectively, λ is the electron phonon coupling constant, θ_D is the Debye temperature proportional to the lattice stiffness, and N(0) is the electronic density of states at the Fermi energy. As seen in Figure 1, data below $T^2 = 70\ K^2$ or T = 8.4 K is essential for α-Pu in order to obtain the correct intercept (γ) on the C/T versus T^2 plot. Small sample calorimetry has the advantage, therefore, that the self-heating of the sample may be minimized by merely making the sample smaller, allowing lower temperatures to be reached.

The α' phase of Pu(Al) is anomalous in that the Al, although smaller than the host α lattice, expands the α-Pu: 1.8 at.% Al increases the volume of the α lattice by 1.8%. The measurement of the specific heat of α'-$Pu(Al)_{1.8}$ indicates that this lattice expansion is accompanied by a large decrease (30%) in the lattice stiffness as measured by the Debye temperature, θ_D. Thus, the upper curve in Figure 1 for α'-Pu has a high slope, γ, and

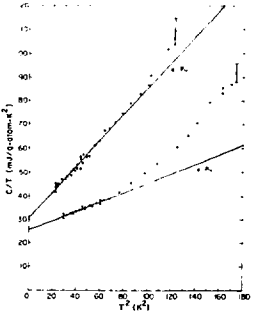

Figure 1

a larger lattice specific heat βT^3, eq. 3. It should be noted that Gordon, et al.[4] measured the specific heat of α-Pu^{239} between 7.2 and 13.5 K and obtained γ = 23.0±5.0 mJ/g-atom-K^2 and θ_D = 183±20 K versus the results of Figure 1 for α-Pu^{239} of γ = 25.0±1.0 mJ/g-atom-K^2 and θ_D = 215±5 K. The disagreement in the θ_D values may be due to the ability of the small sample calorimeter to go below 6 K, or to the greater amount of the total specific heat measured due to the sample in the present work (57% versus 19% for Gordon, et al. at the lowest temperature of measurement), or to differences in sample purity. A measurement of the specific heat of α-Pu^{242} was made using the small sample calorimeter and γ = 22.0 ±1.0 mJ/g-atom-K^2 and θ_D = 192±10 K values were obtained, versus the result of Gordon et al. for α-Pu^{242} between 4.1 and 10 K of γ = 22.0±1.0 mJ/g-atom-K^2 and θ_D = 177±10 K. The possibility of a real isotope effect is being pursued.

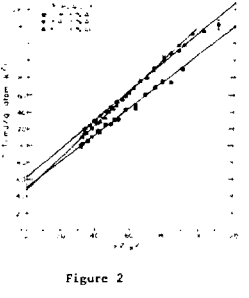

Figure 2

The low temperature specific heats of three compositions of δ-$Pu(Al_x)$ are shown in Figure 2, where x = 1.8, 3.4, and 5.2 at.%. Data for a fourth composition, x = 11.2 at.%, (not shown for clarity) lies shifted slightly downward from the lowest curve, with γ = 44±2 mJ/g-atom-K^2 and θ_D = 106±5 K. Several points are of interest concerning these δ-$Pu(Al_x)$ results. The γ values, which vary rapidly with Al concentration (a sign of a jagged density of states versus energy distribution), are twice as high as that for α-Pu. Prior to this work, no measurements of the low temperature specific heat (and thus of γ) of δ phase Pu had been made[5] below 20 K. Previously, α-Pu had been thought to have the largest γ and N(0) (it is probably ≤0.2) of any allotrope of any element. There new, much higher values for δ-$Pu(Al_x)$ imply that hypothetical pure δ-Pu would have γ = 53±10 mJ/g-atom-K. Thus, this fcc δ-Pu, with less evidence for 5f electron bonding character then the monoclinic α-Pu phase, nevertheless has more than twice the electronic density of states at the Fermi energy than any other known allotropic form of an element.

Another point to note from the data of Figure 2 is that the slope β, and thus θ_D, is relatively unaffected by Al composition and is between 100 and 110 K for all four compositions.

Further specific heat work on these and other allotropes and alloys of Pu is continuing.

* Work performed under the auspices of the Department of Energy.

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ANOMALOUS VOLUME EXPANSION OF PLUTONIUM ALLOYS†

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This study examines anomalous expansion effects in α-Pu alloys by x-ray diffraction with solutes of nearly the same size but of different valencies. The solute pairs selected are: Al^{+3} (R = 1.432 Å) and Ti^{+4} (R = 1.462 Å), both of which are smaller than α-Pu (R = 1.523 Å); and Sc^{+3} (R = 1.641 Å) and Zr^{+4} (R = 1.602 Å) both of which are larger than α-Pu. All four solutes are capable of stabilizing the delta phase to room temperature on quenching. Metastable alpha solid solutions are subsequently formed by pressure transformation (isopressing) of the retained delta phase.

Lattice parameters and atomic volumes of monoclinic α-Pu(Al), α-Pu(Ti), α-Pu(Sc) and α-Pu(Zr) alloys are given in Table I. The β-angle of the monoclinic cell remains nearly constant. The lattice parameters of α-Pu(Al) and α-Pu(Ti) increase linearly with composition in all three crystallographic directions, as may be seen in Table I. The expansion effect is greatest for the trivalent solute aluminum (Al) and less for the tetravalent solute titanium (Ti) even though these solutes have approximately the same metallic radii. Actually, the metallic radius of Ti is 0.03 Å larger than that of Al, but the expansion effect is substantially smaller for Ti than for Al. The lattice parameters of α-Pu(Sc) and α-Pu(Zr) alloys also increase about linearly with composition in all three directions. In this case, however, the expansion effect appears to be about the same for both solutes, although the metallic radius of trivalent scandium (Sc) is slightly larger than that of tetravalent zirconium (Zr) by 0.04 Å. The lattice parameters depart slightly from Vegard's Law,* but the expansion effect appears to be independent of the differences in the Sc and Zr valencies. Both solutes have atomic sizes larger than the α-Pu.

Table I. X-ray Diffraction Results for α-Pu and Isopressed Pu-rich Alpha Solid Solutions.

Composition (at. %)	Lattice Parameters (Å) a	b	c	Volume of unit cell (Å³)
0 (Pure Pu)	6.174	4.820	10.963	319.5
Al 1.8	6.206	4.856	10.996	324.4
2.5	6.221	4.862	11.024	326.3
3.4	6.236	4.876	11.044	328.7
3.8	6.258	4.890	11.077	331.7
Sc 3	6.224	4.862	11.001	326.0
4	6.225	4.870	11.018	327.1
5	6.237	4.881	11.020	328.4
Ti 3	6.206	4.843	10.993	323.6
4	6.200	4.846	10.984	323.1
5	6.206	4.848	10.989	323.8
Zr 4	6.236	4.881	11.008	328.0
5	6.249	4.886	11.027	329.5

Ellinger et al.[1] have reported the atomic volumes** ($\bar{V}_A$) as a function of composition of Pu-Sc alloys, as shown in Fig. 1a. Both terminal solid solutions, i.e., δ-Pu(Sc) and α-Sc(Pu), deviate positively from Vegard's Law, as may be seen. Ellinger assumed that the size of the Sc atoms remained unchanged in each phase because Sc is known to exist only in the trivalent state. Atomic volumes of the plutonium atoms were calculated based on this assumption and these are shown in Fig. 1b as a function of the Sc content. A Vegard's Law (straight) line extrapolated to pure Pu from the hexagonal α-Sc(Pu) solid solution atomic volumes indicates an atomic volume for Pu in trivalent Sc of approximately 26.3 Å^3 (see Fig. 1a). We claim that plutonium is approximately trivalent in δ-Pu at this atomic volume.

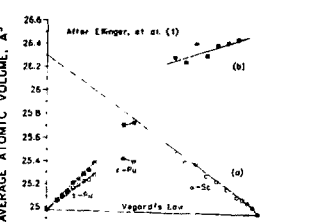

Figure 1.

These results can be discussed using a simple model which combines valence and pressure effects. The large number of phases which occur in Pu coupled with the large volume changes involved in these crystallographic phase changes indicates that the f-level occupancy is different in these different phases. There appears to be no clear evidence for the presence of localized moments in any of the Pu phases. Therefore, it seems likely that any 5f-electrons present in Pu are delocalized. Johansson[2] has shown that the α→γ-Ce transition involves the delocalization of one 4f-electron. The ratio of the accompanying volume change (ΔV_A) to the mean volume ($\bar{V}_A$) of the α- and γ-phases is $\Delta V_A/\bar{V}_A = .16$. We can further conclude from these size changes relative to the overall lanthanide contraction that a delocalized 4f-electron screens approximately .44 of a nuclear charge.[3] If we assume that these numbers are also approximately correct for 5f-electrons, then the α → δ-Pu transition involves a change in f-level occupancy of ~1 electron, as does the γ→δ-Pu transition. γ- and ε-Pu probably have the same number of 5f-electrons; the β→γ-Pu transition probably involves a change in f level occupancy of a small fraction of an electron.

Plutonium has eight outer electrons which we divide into two groups, valence and 5f-electrons. We suppose that the valence electrons primarily determine the alloy chemistry of Pu and that the f-electrons participate in bonding to a lesser extent. The ease with which Pu appears to be able to change from one 5f configuration to another suggests that Pu in dilute solid solution in other metals might try to adopt the valence of the solvent metal. From this viewpoint, the apparent size of Pu in hexagonal α-Sc(Pu) alloys suggests the hypothesis that Pu in δ-Pu is approximately trivalent. In ε-Pu, Pu is then tetravalent, and in α-Pu, pentavalent. These assignments differ from those of Zachariasen[4] but follow a similar trend.

The unusual lattice parameters observed in the α- and δ-Pu alloys (reported here) can then be thought of in the following way. A trivalent impurity in Pu encourages neighboring Pu atoms in the lattice to become trivalent. Since trivalent or "delta-like" Pu is much larger than pentavalent α-Pu, the isopressed α-Pu alloys should show large positive deviations from Vegard's Law. If so, then why is this not observed in the case of Sc or Zr substitutions? Examination of

the P-T phase diagram for elemental Pu indicates that ~2 kbar is sufficient to suppress δ-Pu, which we are arguing is the approximately trivalent form of Pu. It can be estimated via simple elasticity theory that a large solute atom such as Sc or Zr in the α-Pu lattice will exert a pressure on neighboring Pu atoms of the order of tens of kilobars. A very different behavior for small and large solute atoms is therefore expected on our model, since this local pressure effect will hinder the valence change of neighboring Pu atoms in the lattice.

Summary

The atomic volumes of δ-Pu(Sc) and of isopreased, nonequilibrium α-Pu(Al) and α-Pu(Ti) solid solutions are anomalous in that substitution of Sc, Al, or Ti atoms for Pu atoms in the crystal lattice causes large volume expansion, even though the Sc and the δ-Pu have the same atomic sizes and the Al and Ti have smaller sizes than the α-Pu. The effect is greatest for the trivalent solutes, Sc and Al, and less for the tetravalent solute, Ti. On the other hand, atomic volumes of isopressed α-Pu(Sc) and α-Pu(Zr) alloys follow approximately Vegard's Law and there is no effect due to differences in the solute valencies. In this case, the trivalent Sc and tetravalent Zr have atomic sizes larger than the α-Pu. These results are discussed on the basis of an heuristic model for the valence of Pu in its various phases.

† Work performed under the auspices of the U. S. Department of Energy.

* Vegard's Law states that there is a simple linear relation between the lattice parameter and the composition in atomic percent for solid solutions.

** The atomic volume is defined as the volume of the unit cell in $Å^3$ divided by the number of atoms in the cell.

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HIGH PRESSURE X-RAY DIFFRACTION STUDY OF ACTINIDES AND THEIR COMPOUNDS BY ENERGY DISPERSIVE METHODS

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Actinides and actinide compounds were studied in diamond anvil cells at pressures up to 40 GPa. Energy dispersive x-ray diffraction methods were used; the x-ray sources were either a tungsten anode fine focus sealed x-ray tube working at 59 kV and 31 mA, or the storage ring DORIS at the German electron synchrotron DESY, Hamburg[1,2].

Diffracted intensity sufficient to record spectra within periods ranging from ten minutes to some hours was obtained, in the case of the tungsten tube, by use of a conical slit for the diffracted radiation. This allows the complete diffraction cone at a fixed Bragg angle θ to be collected at a large surface intrinsic germanium detector. With synchrotron radiation, the incident beam is in general intense enough to compensate for absorption by the diamonds (6 mm total thickness) and the sample. A linear diffracted beam and a small surface detector, with resultant higher resolution, can be used in this case.

The pressure was determined from the lattice parameter of an added 'marker' substance (sodium chloride or cesium chloride) or from the wavelength shift with pressure of the R_1 fluorescence line of an added ruby splinter ('ruby pressure gauge'). The ruby fluorescence was excited with a laser or with the synchrotron radiation itself.

The variation of lattice parameter and relative volume of thorium metal was measured up to 35 GPa. Thorium keeps its face-centered cubic structure in the whole range of pressures. Fitting the results to a second-order Birch equation yielded a bulk modulus B_0 of 58 GPa and a pressure derivative B_0' of 4.2 [3].

α-uranium metal was studied up to 6.6 GPa and showed no phase transformation in this pressure range. Single-peak fitting of the uranium data gives a bulk modulus B_0=128.6 GPa and elastic constants (TPa^{-1}) ε_{11}=3.627, ε_{22}=2.191, ε_{33}=1.956.

Several series of measurements were made for stoichiometric UO_2 at pressures up to 40 GPa. This compound reproducibly transforms to a low symmetry high pressure structure and shows a marked hysteresis on pressure release before retransforming completely to its ordinary fluorite type structure. The transformation is sluggish and extends over the range 29 to 38 GPa on pressure increase; when pressure is released, the pure high pressure structure is conserved down to 15 GPa.

The diffraction pattern of the high pressure UO_2 resembles the lead chloride structure type. No final structure type assignment can be given at present, as line overlapping in the spectra available up to now prevents an exact comparison with calculated spectra. The formation of the $PbCl_2$ type is favored at high pressure because it is about 8% denser than the fluorite type. It is observed as a high pressure allotrope of other fluorite type compounds, and exists for uranium and thorium dichalcogenides (β-US_2, β-USe_2, ThS_2, $ThSe_2$) at ordinary pressure. Assuming the lead chloride type leads us to U-U distances which are below the transition range of the Hill plot[4], while f.c.c. UO_2 is above that range. This would be in agreement with the observation of a phase transition, given that the cation coordination in lead chloride is higher than in fluorite.

Fig. 1 gives the variation of lattice parameter and relative volume with pressure for f.c.c. UO_2. The data measured with CsCl and NaCl marker are in good agreement. Some data to 12 GPa communicated by J.M. Fournier[5] agree with the present measurements. Bulk modulus calculations from the present data confirm the value given by Wachtman et al.[6] ($B_0 \approx 210$ GPa).

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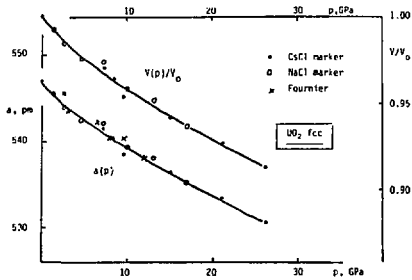

STRUCTURE RELATIONSHIPS IN AMERICIUM METAL*

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As a function of applied pressure americium metal exhibits four phases in the pressure region of 0 to 20 GPa. The four phase regions are shown in the compression curve of Fig. 1. Phase I has the double-hexagonal close-packed structure; Phase II is face-centered cubic; Phase III is an exotic double-body-centered monoclinic material and Phase IV displays the α-U structure type. Data points for Phase I were taken from the work of Refs. 1,2; for Phase II from Refs. 2,3; for Phase III from Ref. 4; and for Phase IV from Ref. 5.

A relatively simple structural relationship exists beteen the four phases of americium that occur as a function of applied pressure. Phase I has the double-hexagonal close-packed structure and exists from 0 to approximately 4-6 GPa. The dhcp structure is characterized by a layer stacking sequence whose shorthand representation is given as ABACABAC... where each letter represents both a layer and a position within the layer relative to a hexagonal coordinate system. Phase II has the face-centered cubic structure and exists from 4-6 GPa to 10 GPa. The fcc configuration of atoms may also be thought of as a rhombohedron which in turn may be referred to a hexagonal coordinate system. Relative to the hexagonal axes the fcc structure is characterized by a layer stacking sequence whose representation is ABCABCABC.... The application of pressure to dhcp "squeezes out" the long-range order of the 4-layer dhcp structure allowing the slightly simpler 3-layer stacking of the fcc to form.

Phase III is a double-body-centered monoclinic material and exists from approximately 10 to 15 GPa. Its derivation from a fcc structure may be described as follows. In the fcc lattice let a body-centered monoclinic sub-cell be defined with dimensions of $a_m = a_c/\sqrt{2}$, $b_m = a_c$, $c_m = a_c/\sqrt{2}$ and $\beta = 90^\circ$. Let two of these cells be stacked one on top of the other in the b axis direction; the resulting cell is double-body centered and the symmetry is consistent with space group #11, $P2_1/m$. The application of pressure distorts this special cubic subcell to true monoclinic symmetry and moves the two interior atoms away from their special body-centered positions. The structure of Phase III americium is illustrated in Fig. 2a. The atoms with the same numerical y values form distorted pseudo-hexagonal layers that are displaced relative to one another and the ideal spherical packing of a fcc material.

The relationship of Phase III (monoclinic) to Phase IV (orthorhombic) is illustrated in Figs. 2 and 3. In Fig. 2a we show the structure of Phase III americium viewed down the +b axis. Four unit cells are shown. In Fig. 2a let every fourth layer (i.e., those atoms at y = 3/4) be shifted to coincide in projection with the atoms at y = 1/4. This motion divides the b axis in half and yields Fig. 2b where projection along one unit of the haived b axis is shown. In Fig. 3a we show a small distortion of the arrangement of Fig. 2b. In Fig. 3b an othorhombic unit cell is outlined in the configuration of Fig. 3a. If the orthorhombic origin of Fig. 3b is moved -1/4 c the normal representation for the α-U structure type is obtained. The application of pressure to Phase III results in a shift of every fourth layer of atoms, and with minor adjustments of lattice constants and atom positions, yields the α-U structure type of Phase IV.

In summary, the application of pressure to americium metal results in the formation of four phases. Starting with a dhcp structure the material transforms

to a fcc structure as a long-range 4-layer stacking sequence is converted to a slightly simpler 3-layer stacking sequence. The next transformation is from a fcc to an exotic monoclinic structure that is in turn a slight distortion of a combination of two small body-centered cells that are derivable from the fcc configuration. A shifting of every fourth layer of the Phase III monoclinic structure yields the predominate zig-zag features of the α-U structure type for Phase IV of americium. Thus, the change in crystal structure that occurs in the transformation between each of the phases results from simple shifts in layer stacking sequences with minor adjustments in lattice constants and atomic positions.

* This work was performed under the auspices of the U. S. Department of Energy.

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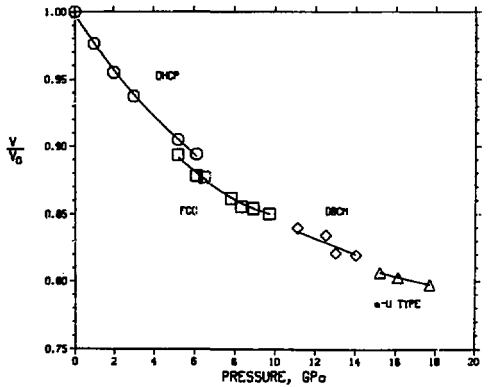

Fig. 1. Compression of americium metal. (○) phase I, hexagonal; (□) phase II, cubic; (◇) phase III, monoclinic; (△) phase IV, orthorhombic.

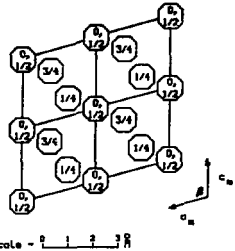

Fig. 2a. The structure of phase III projected on the 010 plane of the monoclinic cell. Four unit cells are shown.

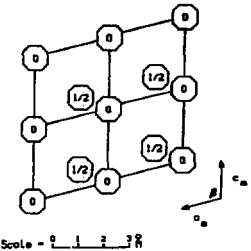

Fig. 2b. The configuration resulting from Fig. 2a. when atoms at y = 3/4 are shifted to coincide in projection with atoms at y = 1/4 and the b axis is halved.

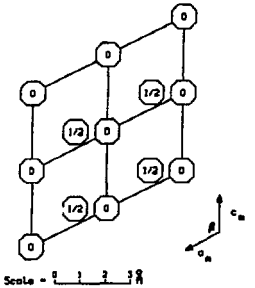

Fig. 3a. A slight distortion of the arrangement of Fig. 2b.

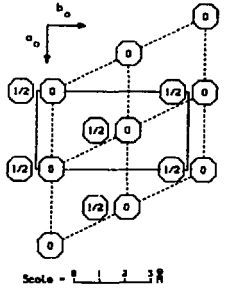

Fig. 3b. An orthorhombic unit cell (solid outline) obtained from the configuration of Fig. 3a. (dashed outline). If the orthorhombic origin is moved -1/4 a the normal representation for the orU structure type is obtained.

HIGH PRESSURE STUDIES ON CURIUM

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Crystal structure of curium metal at 1 atmosphere pressure and room temperature has been studied by many investigators. Cunningham and Wallman (1964) reported a hexagonal structure for curium with a = 3.496Å, c = 11.331Å with a volume of 29.98Å^3. However, Smith, Hale, and Thompson (1969) reported a closed packed cubic structure for curium with a = 4.1382Å and a substantially lower volume of 21.04Å^3. This discrepancy on volume was explained by them on the grounds that the cubic close packed form is $^{+4}$ as opposed to +3 in the hexagonal close packed form. Spirlet and Müller (1973), Reul (1975) and Stevenson and Peterson (1979) all have reported a dhcp structure for curium.

High pressure phase transformation data for curium has not been attempted previously. In order to understand the crystallographic behavior of curium at high presures and also to elucidate the similarities between the heavier actinides and the light lanthanides, we undertook the high pressure study of curium in a diamond-anvil apparatus.

The curium sample used in this study is mainly of the isotope ^{248}Cm. Spectral analysis of it did not show any major contaminants. Curium was vapor deposited onto molybdenum substrate and the sample in the final form was 0.07 to 0.10 mm thick foil. A small sliver was cut from the foil in an open hood and then coated with Canada balsam thinned with xylene in the hope that the coating would inhibit oxidation and potential contamination. All experiments were carried out in a diamond-anvil high pressure apparatus of the kind described by Bassett et al. (1967). A 99.99% pure molybdenum foil of 0.0254 mm thickness was pre-pressed between the diamonds, and the sample was loaded onto the indentation thus formed. In this procedure, the xylene plus Canada balsam solution acted as pressure medium and the molybdenum foil acted not only as a gasket but also as an internal pressure standard. Even though molybdenum is a poor choice as an internal pressure calibrant with curium, our selection was restricted because curium was vapor deposited onto a molybdenum substrate.

In a few runs, pre-pressed stainless-steel gaskets were used and the sample was loaded into the gasket hole (ca.120 mm) along with a 1:4 ethanol and methanol mixture. A small ruby chip was placed on top of the sample which served as the internal calibrant along with the molybdenum which is a substrate for curium. In both cases an external fiducial molybdenum pieced on the back of the diamond, was used to measure the sample to camera distance.

X-ray patterns were made at various pressures from 1 atm to 20.0 GPa pressure. Pressures are based on the accuracy of the measured Mo lattice constants. However, we noticed considerable spread in the pressures determined from different molybdenum lines within a given run. At present, we are in the process of continuing this study with different substrates for curium, in order to alleviate this problem. The typical exposure times ranged from 120-180 hours. In a given run, lattice constants calculated from different diffraction lines varied by as much as 0.5 to 2.0%.

The curium sample used has a dhcp structure at 1 atm with a = 3.490 ± 0.006 and c = 11.308 ± 0.018Å. These values agree reasonably well with the data reported in the literature. At lower pressures, we could identify 6-8 reflections for curium, however, at high pressures (12.0 GPa and above), we could see a maximum of four reflections only. Because of the limited number of reflections and the quality of x-ray films, the lattice parameters derived from our data have larger standard deviations.

Preliminary volume compression data for curium are obtained up to 6.5 GPa pressure. We observed 15% volume compression for curium at 6.5 GPa.

The ccp phase described by Smith, Hale, and Thompson has a V/Vo of 0.7 relative to the dhcp phase of this study. In view of the fact that the dhcp phase has now been shown to be stable to 6.5 GPa with a V/Vo of 0.846, it is unlikely that the ccp phase is a correct description for pure curium.

We did not find any indication for a structural transformation up to this pressure. However, data for runs around 18.0 GPa suggest a possible structural change. At this time, we cannot convincingly confirm it due to the limited number of reflections. Skriver et al. (private communication) from band calculations predict phase transformation for curium at pressures higher than 20.0 GPa.

We are very thankful to Ken Hulet and Ron Lougheed from the Nuclear Chemistry Division of our Laboratory for providing us the ^{248}Cm sample.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

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CRYSTAL STRUCTURE OF AMERICIUM IN THE PRESSURE RANGE, 11 - 13 GPa*

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Phase transformations in metallic americium at high pressure were recently summarized by Akella, Johnson, Thayer and Schock (1979) and by Akella, Jonnson, and Schock (1980) as follows: at atmospheric pressure and room temperature, Am is double-hexagonal close-packed (=dhcp)(McWhan, Cunningham and Wallman (1962)); between 5.0 ± 1 GPa and 10.0 ± 1 GPa, the crystal structure is face-centered cubic (=fcc). The transformation, dhcp to fcc, is accompanied by little change in atomic volume for Am. Above 10.0 and extending to ∿ 15 GPa, a third modification was observed. A fourth phase at still higher pressures was indicated. Roof et al (1980) have described this latter phase as being of the orthorhombic α-U type.

We report here the crystal structure of Am as derived from our x-ray diffraction studies for the pressure region 10 to at least 13 GPa. This structure is monoclinic and corresponds to a simple distortion of the α-U structure. Our results for the atomic volume of Am in this pressure region are in disagreement with values reported by Roof, et al (1980) (see below).

Attempts to fit the powder-pattern to various prototype crystal structures previously reported in the literature were unsuccessful, although a vague resemblance to the α-U structure was noticed. The data were next put through various automated computer-indexing programs that determine unit-cell dimensions and crystal system solely from powder-diffraction data.

The most promising solutions were obtained from Smith and Kahara's (1975) computer-indexing program, QTEST, with an error setting of $\Delta Q(Q=1/d^2)$ of 0.0040 $Å^{-2}$. Refined values of the lattice constants for a centered monoclinic cell containing 4 Am are given in Table 1. (The unit cell is set with the unique axis as c to allow comparison to α-U.)

Table 1. Lattice constants vs pressure for monoclinic unit cell of Am. Cell is C-centered, contains 4 atoms with the unique axis as c.

Pressure, GPa	a, Å	b, Å	c, Å	γ, °	Atomic Vol., $Å^3$
11.0	3.101(9)	6.212(19)	4.625(14)	93.5(1)	22.3
12.0	3.105(11)	6.187(21)	4.653(16)	93.7(1)	22.3
13.0	3.038(6)	6.258(12)	4.573(9)	93.5(1)	21.7

*"Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Ntl Laboratory under contact number W-7405-ENG-48."

The dimensions of this unit cell are similar to those obtained for the metastable α"-phase found in certain quenched uranium alloys. For example, Stewart and Williams (1966) give unit cell dimensions for uranium, 10 at. % Mo: a = 2.866, b = 5.752, c = 4.940 Å; γ = 92.3°; at. vol. = 20.34 $Å^3$ (as compared with an at. vol for α-U of 20.81 $Å^3$). Atomic positions are ± (x, y, 1/4) and ± (1/2 + x, 1/2 + y, 1/4) with x = -0.036 and y = 0.102. For Am with this structure, we place the atomic positions as x = -0.05 and y = 0.102.

The α"-structure can be easily derived from an hexagonal close-packed arrangement by small atomic displacements so as to increase one interaxial angle beyond 90° (Stewart and Williams (1966)). Thus, a prototype exists for the structure reported here, although Am would be the first pure element to possess this structure.

Volume compression data are shown in Fig. 1. According to these data, the transformation in Am from fcc to an α"-U structure-type is accompanied by a discontinuity in atomic volume of ∿ 3.5%.

We note also that the atomic volumes reported here for 11-13 GPa are smaller than those Roof et al (1980) reported at still higher pressures.

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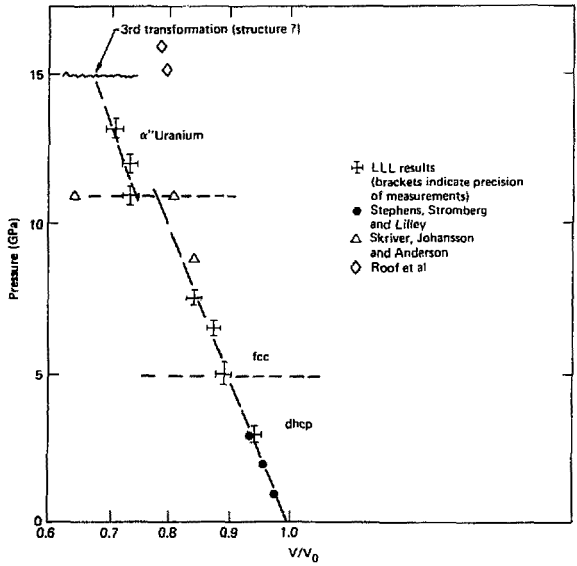

Figure 1. Volume compression of Americium.

CHARACTERIZATION OF SOME METALLIC STATE PROPERTIES OF HEAVY ACTINOIDS BY THERMOCHROMATOGRAPHY

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As elements beyond einsteinium are not available in weighable quantities, it is necessary to employ some indirect techniques to characterize their metallic state properties. In the present work we used data on the thermochromatographic behavior of atomic actinoids in columns of polycrystalline titanium and molybdenum, as well as the experimental evidence that for known alkali, alkaline earth and rare earth metals in tracer quantities, the deposition temperatures or the enthalpies of adsorption evaluated from the latters correlate with metallic valency. In order to secure the free atomic state of actinoids in the gaseous phase, they were applied on the column by evaporation from molten lanthanum at 1425°K and some calcium vapor was introduced into the carrier gas (helium). The columns used consisted of a quartz tube with an inner tantalum foil lining, that prevented diffusion of oxygen from the tube walls into the carrier gas, and a titanium foil lining, or with a solc molybdenum foil.

On the titanium column, under certain conditions the elements Na, K and Rb formed adsorption zones at temperatures of 400-500°K, Yb at 750°K, Ra at 800°K, calcium vapor condensed at about 1000°K, and Eu and Sm yielded two peaks on the thermochromatogram: one coincident with the calcium condensate and the other at a higher temperature of 1120°K. The actinoids Cf, Es, Fm and Md formed zones close to that of Yb.

On the molybdenum column, the behavior of the alkali metals, Ra and Eu was the same as titanium, while Yb and Sm yielded peaks at 1200-1300°K. Cf was also adsorbed in that range, while Es, Fm and Md gave peaks at 700-800°K, the same as on titanium.

The position of Cf, Es, Fm and Md zones on the titanium columns relative to other elements provides evidence that these actinoids are divalent metals and are adsorbed in divalent state. For molybdenum one can expect higher energy of adsorption interaction than for titanium. So the formation of high temperature peaks of Eu, Yb and Cf on molybdenum (as well as of Eu on

titanium) suggests that in this case the divalent metals are adsorbed in trivalent state[1]. As Es, Fm and Md are adsorbed in divalent states even on molybdenum, one may conclude that their f energy levels are lower with respect to the Fermi level than in the case of Cf and even lower than for Eu and Yb. The measured evaporation rate of Cf from molten lanthanum appears to be intermediate between those of Eu and Yb. This fact shows that californium is divalent. The trivalent metals Sc, Tb and Am did not evaporate to a measurable extent at the injection port temperature.

Based on the deposition temperatures measured as a function of flow rate and retention time, using a sort of the Arrhenius plot[2], the enthalpy and entropy of adsorption of Cf on titanium were evaluated as -162 ± 8 J/mole and 144 ± 11 J/mole k, respectively (at 800°K).

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MECHANISM OF URANIUM OXIDATION FROM THERMOGRAVIMETRIC MEASUREMENTS*

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The oxidation of uranium has been studied in oxygen and water vapor in the absence and presence of oxygen, as a function of reactant pressure and temperature between 60° to 180°C. Thermogravimetric measurements were performed using pure gas reactants under static conditions, and nitrogen or argon as inert carriers in a flow system.

The kinetics of the oxidation reaction was found to obey a law of the form $(\Delta W/A) = kt^n + c$, where $(\Delta W/A)$ is the weight gain in mg/cm^2; k is the reaction rate constant in mg/hr-cm^n; t is the time in hours; and, n and c are constants. For the oxidation in dry oxygen n was 0.805, while the value of c was 0.2 mg/cm^2. The oxidation of uranium in oxygen-free (< 5 vppm) water vapor followed a linear law with n = 1 and c = 0. On the other hand, the oxidation process in humid air could be best described by an initial linear region (n = 1) followed by an accelerating period and a final linear region.

The activation energy for oxidation for the various environmental conditions used are summarized in Table 1. Note that the activation energy for the oxidation process in humid air is the highest, followed in decreasing order by that in oxygen and then that for water vapor alone.

Table 1. ACTIVATION ENERGY FOR THE OXIDATION OF URANIUM (P_{TOTAL} = 1 ATM)

OXIDATION CONDITIONS	TEMPERATURE RANGE, °C	ACTIVATION ENERGY kJ/MOLE (KCAL/MOLE)**
P_{H_2O} = 7.97 kPa (60 TORR) - H_2 CARRIER	62 - 100	41.79 ± 3.43 (9.99 ± 0.82)
P_{O_2} = 6.26 TO 41.60 kPa* (47.10 - 313.03 TORR)	120 - 177	70.97 ± 2.41 (16.96 ± 0.58)
P_{H_2O} = 7.97 kPa (60 TORR) - AIR/INITIAL	81 - 139	98.07 ± 7.96 (23.44 ± 1.90)
P_{H_2O} = 7.97 kPa (60 TORR) - AIR/FINAL	81 - 139	78.51 ± 4.97 (18.76 ± 1.19)

* PRESSURE INDEPENDENT IN THIS RANGE

** 95% CONFIDENCE LIMITS

The effect of oxygen on the water uranium reaction was studied at a constant water vapor pressure of 13 kPa (97.8 torr) and oxygen partial pressures from 0.101 Pa (7.6 x 10^{-4} torr) to 63.73 kPa (479 torr). A decrease in oxidation rate by a factor of ∿ 12 was found between oxygen

partial pressures of 1.01 Pa (7.6×10^{-3} torr), and 10.1 Pa (7.6×10^{-2} torr). Above the latter value an increase in oxygen concentration did not have a significant effect on the corrosion rate.

The pressure dependence of k for the reaction of uranium with oxygen-free water vapor and humid air was investigated at a constant temperature of 100°C. These data were fitted to the equation $k = aP^{1/n}$, where P is the water vapor pressure in kPa, and "a" and 1/n are constants. The results are shown in Figure 1. For water vapor alone 1/n = 1/2.1 while for humid air a change from a positive to a negative slope is evident for both initial and final linear oxidation regimes, indicating a possible change in the oxidation mechanism.

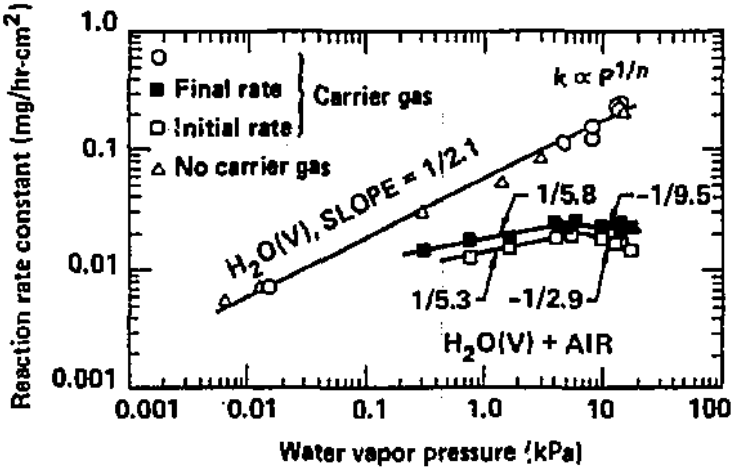

Figure 1

The interpretation of our results has taken into account the complex defect structure[1,2] and electrical properties of uranium oxides. Assuming that: (1) Vacancy migration predominates in UO_{2-x}, $UO_{2.0}$ and U_4O_9, and that interstitial migration predominates for UO_{2+x}[1]; (2) the reaction rate constant is proportional to the predominant electrical conductivity of the oxide in question ($k \propto \sigma$, where σ is the electrical conductivity), then since $\sigma = AP^{1/n}$, $k \propto P^{1/n}$, where P is the pressure of the gaseous reactant and A and 1/n are constants.

Based on the dependences of k on $P(H_2O)$ and $P(H_2O + air)$, the activation energies, and the oxide stoichiometries determined experimentally by x-ray diffraction we have shown that:

1. A single defect cluster $2(O_I^a V_O O_I^b)^{-m} + mh^+$ rich in interstitials controls the oxidation in $H_2O(v)$ and dry oxygen. (O_I = oxygen at an interstitial site, V_O = oxygen vacancy, h = hole; m = 1 for H_2O and has not been determined for oxygen). Oxygen transport takes place via the "interstitialcy mechanism."[3]

2. For $H_2O(v)$ + air in the water vapor region from 0.3 to 6 kPa, the pressure dependence of k (1/n ∿ 1/5) and the oxide composition (∿ $UO_{2.20}$) indicate that the interstitial-rich cluster $2(O_I^a V_O O_I^b)^{-4} + 4h^+$ controls the oxidation.

At $H_2O(v)$ pressures between 6 and 17 kPa (1/n = - 1/9.5) a change in *mechanism takes place and a vacancy-rich cluster of the type 2* $(V_O^{\bullet\bullet}O_i V_O^{\bullet\bullet})^{4+}$ + 8 e^- controls the oxidation (U_4O_9).

3. The activation energies for "interstitialcy" controlled oxidation are lower chan those for a "vacancy-rich" process in the high $P(H_2O)$ regime [E (H_2O) < E (O_2) < E (H_2O + air)]. This finding is consistent with theoretical predictions.[3]

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* Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract Number W-7405-ENG-48.

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KINETICS FOR THE REACTION OF HYDROGEN WITH A PLUTONIUM-1 W/o GALLIUM ALLOY POWDER*

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A number of experimental studies have been carried out to describe the physicochemical properties of the plutonium-hydrogen system. Earlier studies have described in detail the equilibrium behavior and thermodynamic properties of plutonium hydride. Much less information is available on the kinetics of the reaction of hydrogen with plutonium. Some kinetic data for the reaction of hydrogen with plutonium coupons have been reported by Bowersox[1,2] and Colmenares et al.[3] However, many of the early experimental kinetic data were influenced by oxide films on the metal coupons which increased the importance of hydrogen diffusion and hydride nucleation on the reaction kinetics. Additional work is required in order to fully understand the kinetics of plutonium hydriding as well as the factors which influence the kinetics.

This paper describes the results from an investigation of the hydriding kinetics of plutonium-1 W/o gallium alloy powder. Metal powder was used because it could be prepared with a clean surface and any bulk hydrogen diffusion effects would be minimal. Experiments were carried out over a temperature range of -29 to 355°C and at hydrogen pressures of 20 Pa to 67.95 kPa. Actual measurements were made with a recording vacuum microbalance.

The reaction model used to describe the reaction of hydrogen with plutonium metal powder has been described previously.[4] This model assumes that once hydrogen is adsorbed on the surface, diffusion into the bulk is very rapid and not rate determining. Thus, the reaction takes place uniformly throughout the particle and not strictly at the metal/hydride interface. The general reaction equation is:

$$W_t = W_m \left[1-\left[1+k(n-1)\, M_o^{(n-1)} t\right]\right]^{1/1-n} \qquad (1)$$

where W_t = hydrogen reacted in time, t
W_m = total hydrogen reacted
k = rate constant
n = order of the reaction
M_o = milligram atoms of metal initially available

In the special case where the reaction is first-order (n=1) equation (1) becomes

$$W_t = W_m \left(1-e^{-kt}\right) \qquad (2)$$

This equation was used throughout this study to evaluate rates of reaction.

Hydriding of plutonium metal released significant amounts of heat. With the experimental set-up being used, this heat could not be dissipated and the net result was an increase in sample temperature. Net effects of large temperature fluctuations on the hydriding rates were evaluated using the Arrhenius equation for hydrogen pressures of 0.667 and 26.6 kPa. Figure 1 shows the typical Arrhenius plot of the first-order rate constants as a function of reciprocal temperature. The

calculated activation energies, E_a were negative for both the 0.067 and 26.6 kPa data; e.g., -0.03 kJ/mol (-0.006 kcal/mol) at 26.6 kPa. These negative activation energies have no theoretical meaning in themselves but they do indicate that the reaction between hydrogen and plutonium requires minimal activation. It can be concluded from these results that temperature has virtually no effect on the rate of reaction and the inability to maintain isothermal conditions is of little consequence.

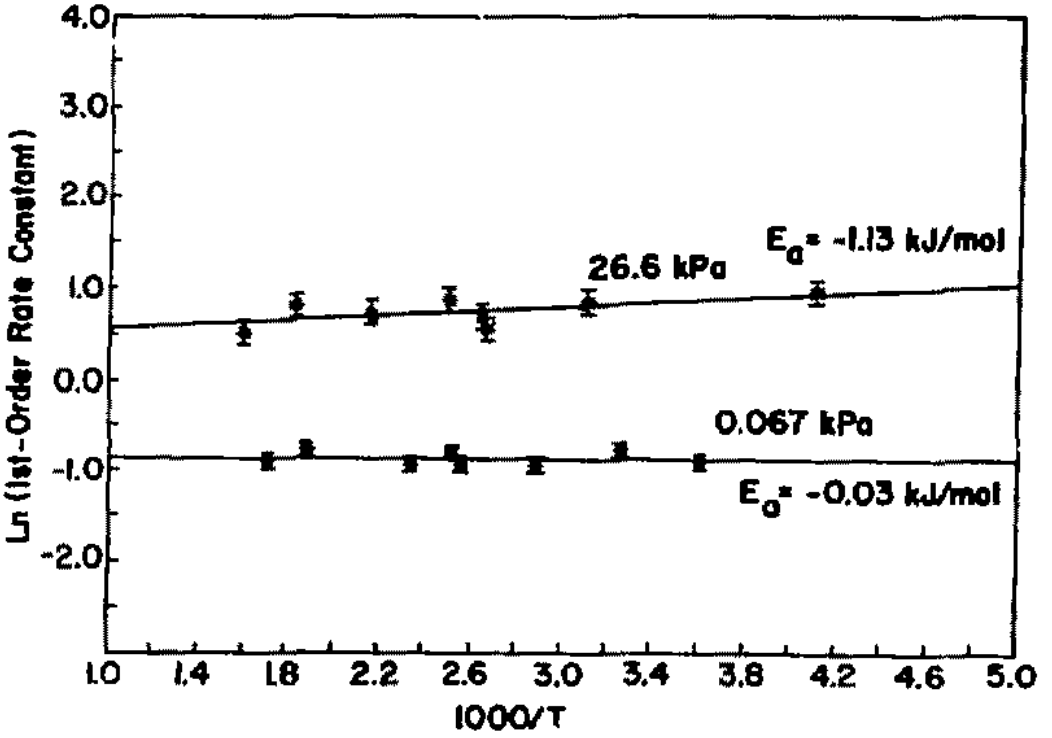

Figure 1.

Data from all runs at various pressures were analyzed using the equation:

$$k_{hyd} = k_o P^n \qquad (3)$$

where k_{hyd} is the first-order rate constant, P the hydrogen pressure in kPa, k_o is a constant and n is the order of the hydrogen pressure dependence. A plot of the data using this equation revealed a discontinuity at about 1 kPa (8 torr) which indicated the pressure range 0 to 1 kPa (0-8 torr) n is equal to 0.45 while for pressures greater than 1 kPa n is 0.11.

In the low pressure region the rate is proportional to $P^{\frac{1}{2}}$. For pressures greater than 1 kPa the pressure dependence of the reaction is proportional to $P^{0.11}$ or very nearly equal to zero. This type of behavior is similar to the Langmuir adsorption isotherm and suggests that hydrogen adsorption may play a major role in the overall hydriding kinetics.

A Langmuir model can be tested for the hydriding of plutonium powder by using the equation:

$$\frac{P^{\frac{1}{2}}}{k_{hyd}} = \frac{1}{k_2 K^{\frac{1}{2}}} + \frac{P^{\frac{1}{2}}}{k_2} \qquad (4)$$

Plotting $P^{\frac{1}{2}}/k_{hyd}$ against $P^{\frac{1}{2}}$ gives a straight line with the slope $1/k_2$. Such a plot is shown in Figure 2. From an evaluation of the date k_2 was found to be 2.69 min^{-1} and K was equal to 0.66 kPa^{-1}. Using these constants hydriding rates have been predicted over the pressure range 0 to 100 kPa. Predicted rates obtained from equation (4) were in good agreement with the experimental values from 0 to 70 kPa.

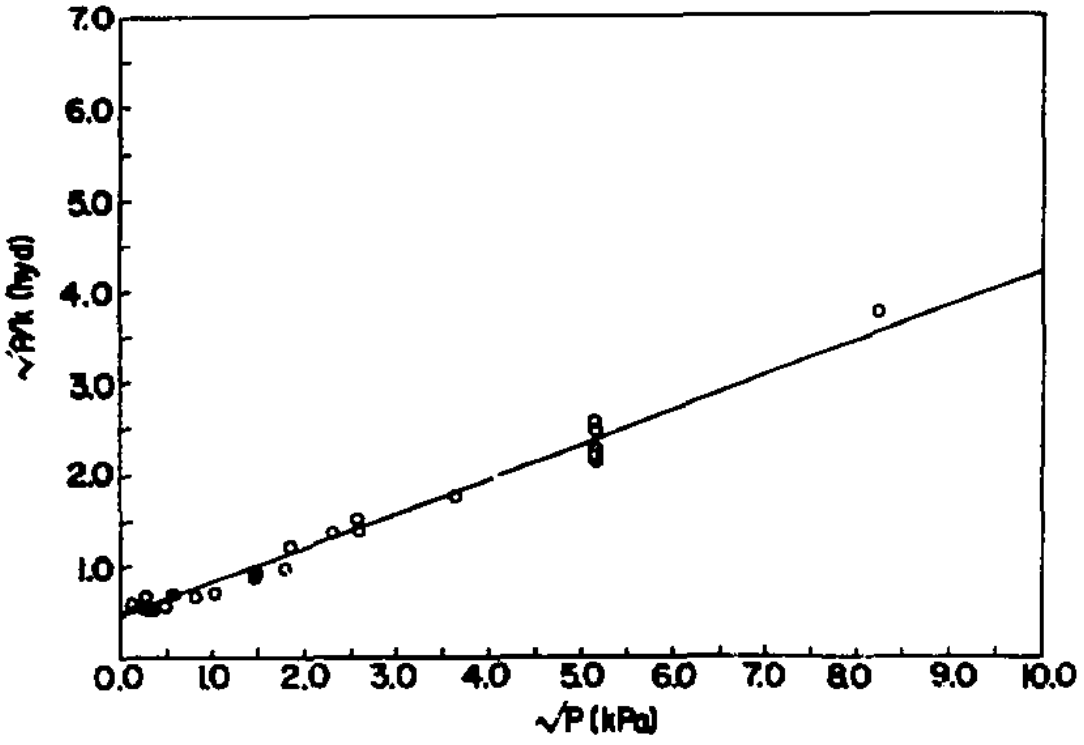

Figure 2.

*Research performed under the auspices of the U. S. Department of Energy.

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THE PLUTONIUM + HYDROGEN SYSTEM: EQUILIBRIA OF THE STABLE HYDRIDE PHASES*

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Tensimetric measurements have verified previous results indicating the existence of two stability regimes in the Pu + H system.[1] The phase diagram suggested by these findings differ from that proposed in earlier studies.

The stable regime is entered by rapid reaction of alpha-phase Pu and high purity H_2 at temperatures greater than 500°C. A 25g metal sample is placed in a stainless steel vacuum-pressure system, heated in vacuum to 100-200°C and then exposed to a H_2 charge which is sufficient to convert the sample to trihydride and leave residual H_2 concentration in excess of 0.05 mol ℓ^{-1}. The hydride composition attained upon cooling the products to 25°C is $PuH_{3.00 \pm 0.01}$.

Pressure-composition isotherms have been measured by successively removing hydrogen from the system. The variation of the partial molar free energy of hydrogen in equilibrium with the solid hydride, PuH_x, along the 440 K isotherm is shown by the lower curve in Figure 1. The previously determined partial molar free energy of hydrogen in equilibrium with the metastable PuH_x solid solution is shown by the upper line.[1] This cubic phase is obtained by slow reaction of the elements at temperatures less than 200°C. The enhanced stability of the high temperature product is evident. The presence of three distinctively different slopes in the free energy curve indicates the existence of three hydride phases in the $2.5 < x < 3.0$ composition range. Evidence for the existence of a fourth phase near $x = 2.77$ is marginal. At 440 K the ΔG° difference between the trihydride phases is approximately 6 kcal mol^{-1}. At $x = 2.35 \pm 0.05$ and lower compositions, ΔG° is zero and two stability regimes cannot be distinguished.

Although structures of the newly discovered hydride phases have not been fully determined, X-ray diffraction data have shown the coexistence of cubic ($a = 5.341(3)$Å) CaF_2-type and hexagonal ($a = 3.779(5)$, $c = 6.771(8)$Å) LaF_3-type phases. These structures are assigned to those found in the $2.35 < x < 2.77$ and $2.77 < x < 2.95$ regions, respectively. The measurement of reliable diffraction data across the composition range is complicated by the fact that unknown changes in sample composition occur from H_2 loss during preparation. However, the tensimetric and diffraction data both suggest that the PuH_2 + PuH_3 system is similar to the SrF_2 + EuF_3 system in which a continuous solid solution, $(Sr,Eu)F_x$, is observed over the $2.78 < x < 3.00$ range.[2] For $2.78 < x < 2.95$, the fluoride has the hexagonal LaF_3-type structure; for $2.95 < x < 3.00$, the phase is orthohombic YF_3-type.

Entry into the stable hydride regime at high temperature is attributed to structural rearrangement of the cation lattice. At low temperatures metals are unable to rearrange from the cubic array of

the CaF_2-type dihydride and hydrogen enters available lattice sites (octahedral or octahedral-related) as x increases. At high temperature, sufficient kinetic energy is available for structural rearrangement. Examination of the metal positions in the cubic and hexagonal hydrides shows that their cations have closest-packed coordinates which are accurately described as ABC and AB layers, respectively, and that these layers are coherent. A microdomain mechanism is proposed for the cubic to hexagonal conversion. The LaF_3- and YF_3-type structures are related by a simple displacive transition.

Previously reported kinetic data suggested that the $2.0 < x < 2.4$ region of the Pu + H system is similar to that of the MF_x(M = Sm, Eu, Yb) systems. Although additional data are needed to fully define the Pu + H diagram, thre present results suggest that the $2.78 < x < 3.00$ region is modeled by that of the $(Sr,Eu)F_x$ system.

* This work was performed under U. S. Department of Energy contract DE-AC04-76DP03533.

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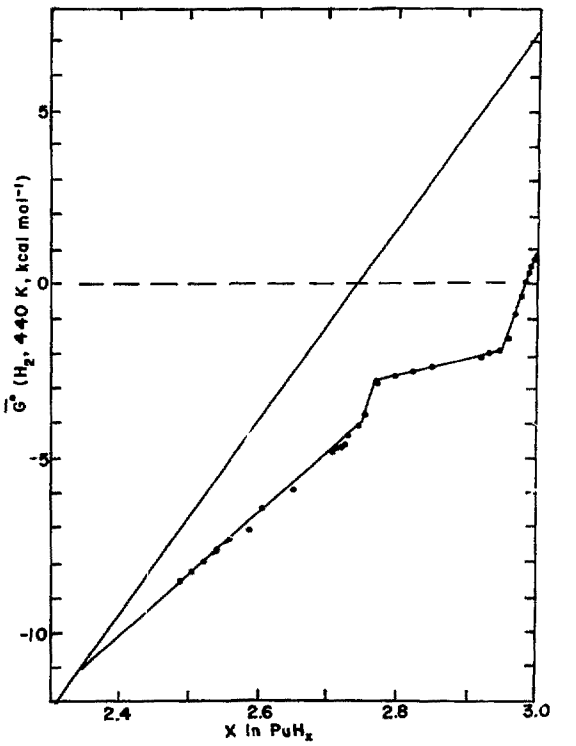
Figure 1. Variation of the partial molar free energy of hydrogen with x in the Pu + H system at 440 K.



COMPARISON OF THE REACTION BEHAVIOR, VALENCIES AND ATOMIC RADII OF ACTINOIDS AND OTHER TRANSITION METALS

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Examination of binary and ternary metal, carbide and nitride systems reveals close relationships in the reaction behavior of actinoids with that of the other transition metals. The phase behavior of light actinoids (Th up to Np) follows that of the transition metals of the d-series of the 4th and 5th groups. In the heavy actinoids (Pu and those following) a type of behavior similar to that of rare earth is observed. The relationships between lattice constants, atomic radii and valency conditions show a uniform picture for the transition metals, including the actinoids, if a specific system of atomic radii is used as a basis. Empirical realtionships obtained when linking atomic radii, valency conditions and lattice parameters observed furnish useful forecasts at to the existence of compounds and the formation of mixed phases. Problems of classifying actinoids in the Periodic Table of Elements are outlined with respect to the reaction behavior and formal valency. Empirical relationships between atomic radii, valency states and the existence of certain compounds as well as the information these parameters furnish and the applications they allow are discussed (cf. also /1/).

Table 1 lists the atomic radii used, Fig.1-6 show examples of relationships between lattice constants of various compounds and the atomic radii of the metals involved, the valency states serving as a parameter (cf./5,6/).

Table 1: Metal radii(coordination number 12) of the transition metals for the relationships shown in Fig. 1-6 (cf. /2,3,4/)

	nm		nm		nm
Sc (3)	0.164	Tm	0.175	Am (3)	0.186
Sc (4)	0.152	Yb	0.174	Am (4)	0.172
Y	0.177	Lu	0.174	Cm (3)	0.186
La	0.188	Th	0.180	Cm (4)	0.171
Ce (3)	0.185	Pa (4)	0.177	Bk (4)	0.170
Ce (4)	0.167	Pa (5)	0.164	Ti	0.140
Pr	0.183	U (4)	0.175	Zr	0.155
Nd	0.182	U (5)	0.162	Hf	0.153
Sm	0.180	U (6)	0.154	V	0.135
Eu	0.180	Np (4)	0.173	Nb	0.145
Gd	0.180	Np (5)	0.161	Ta	0.145
Tb	0.178	Pu (3)	0.187	Ru	0.134
Dy	0.178	Pu (4)	0.172	Rh	0.135
Ho	0.177	Pu (5)	0.160	Pd	0.138
Er	0.176				

If one analyzes the relationships outlined above and other, similar relations between the occurrence of intermetallic phases, structure and bonding conditions (as expressed by atomic distances), one can recognize a uniform pattern of behavior within two regions, one consisting of the trivalent metals, the other of those of the 4th and 5th groups. Cerium, in some respects Sc (cf. /7/), and the actinoids in the transition range of increasing localization of 5f-states frequently exhibit the behavior shown by both groups. With respect to their phase behavior, the lighter actinoids follow the transition metals of the d-series in the 4th and 5th groups. The empirical relationship between radii, valencies and lattice constants of phases within each of these groups turn out to be slightly different. In both cases, these relationships confirmed the system of radii for the actinoids as defined by Zachariasen.

Even if there is little theoretical backing of the radii in intermetallic phases of transition metals, they can yet be used as very welcome quantities in computation, e.g., for estimating valency states and the influence of steric and electronic parameters on the occurrence of specific phases, or in verifying experimental data and detecting inconsistencies. A number of new compounds were detected in the light of the relationships outlined above.

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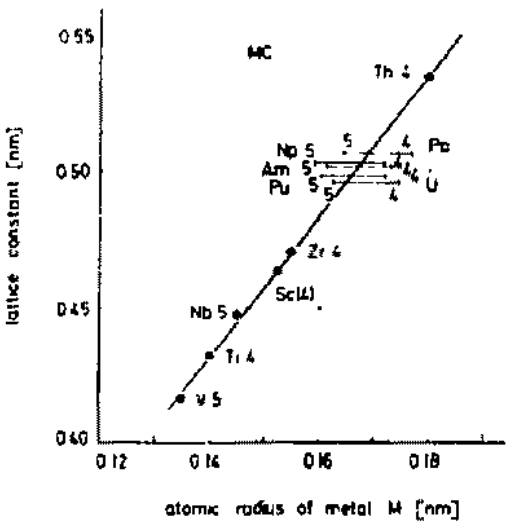

Fig. 1

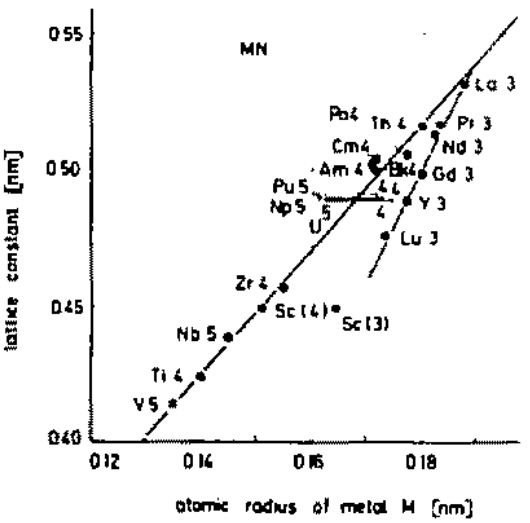

Fig. 2

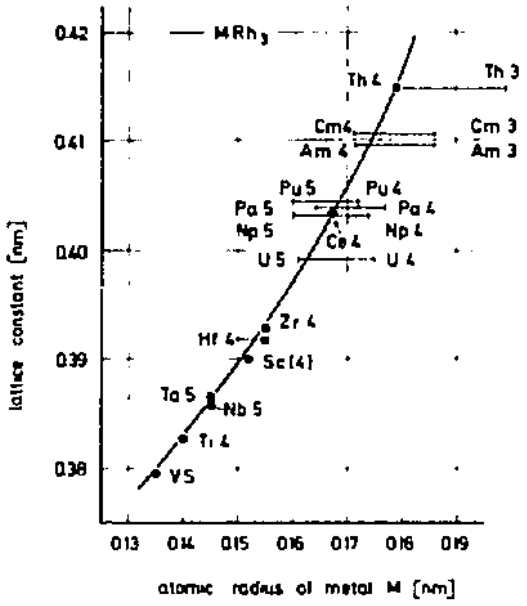

Fig. 3

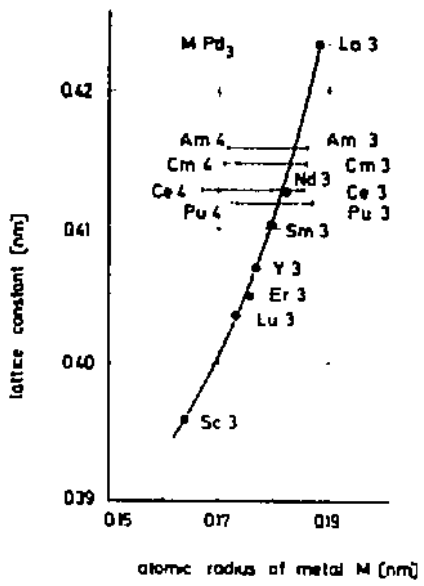

Fig. 4

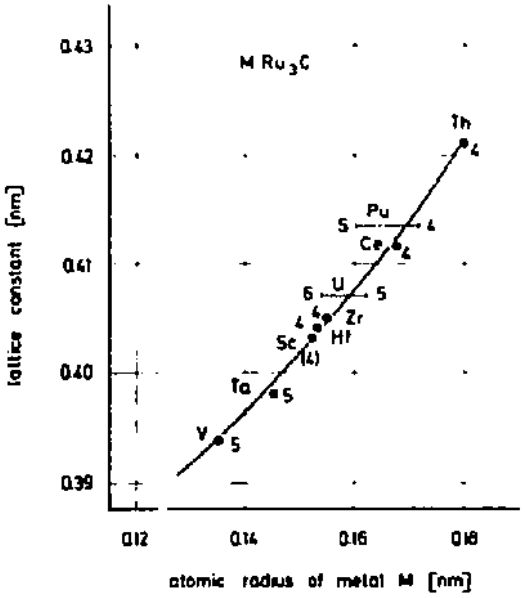

Fig. 5

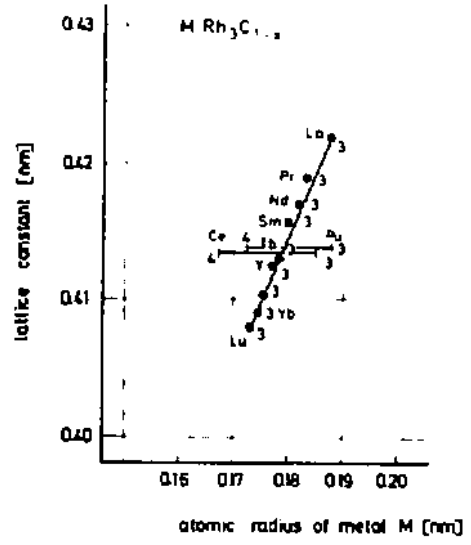

Fig. 6

HEAT CAPACITY OF UP-USe SOLID SOLUTIONS

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Heat capacity measurements in the low temperature range (5-300 K) are reported on three compositions in UP-USe solid solutions : $UP_{0.95}\ Se_{0.05}$, $UP_{0.9}\ Se_{0.1}$, $UP_{0.82}\ Se_{0.18}$.

A magnetic phase diagram based on neutron diffraction and magnetic susceptibility data has recently been published (1). This diagram shows that for $UP_x\ Se_{1-x}$ solid solutions, the simple antiferromagnetic type I structure characteristic of x = 1 is replaced by a type IA structure, then by more long-range order structure when x is decreased. For x < 0.7, the ferromagnetic structure characteristic of USe sets in.

The specific heat curves Cp(T) display at all compositions typical anomalies characteristic of the onset of magnetic ordering (T_N = 108.5, 98.3, 97 K respectively) in general agreement with the data of (1). On cooling down, all three compounds show several other peaks for Cp(T). For x = 0.95, at 38.5 K the transition must be due to the type I-type IA transition. For x = 0.9 and 0.82, peaks at 58.6 and 62 K respectively are evidences of the "step-like" transition reported by (1) and (2) for the type IA structure. This transition is associated with a moment-jump without any structure change (1,3). For x = 0.95 and 0.9, peaks at about 30.5 K may be due to UO_2 contamination or, for the former composition to bulk phase phenomenon associated with the type I-IA transition. Then, for both compounds, peaks at about 22 K, are likely to be due to the moment-jump in type I phase, typical of UP-rich compounds.

Room temperature values of the thermodynamic data compare well to the values obtained for the terminal compositions (4,5). The same constatation holds for the overall values of the entropy of ordering which are still surprisingly low.

A detailed analysis of the magnetic entropies and energies associated with the various anomalies is given for all compounds.

The electronic heat capacity coefficient γ is derived both in the low and high temperature range. Typically at low temperature γ = 35mJ/mole. K^2 with negligible high temperature value. This behaviour is analysed in a very narrow 5f band model located close to the Fermi level.

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U_2N_2Te - RECONCILED INTERPRETATION OF HEAT CAPACITY AND MAGNETIC DATA

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U_2N_2Te is tetragonal with a La_2O_2Te type structure (1) (space group I 4 m m m). The substitution of U by Th leads to an isomorphous non-magnetic compound. Magnetization measurements have shown U_2N_2Te to have unusual magnetic behaviour (2) with a Curie point at 71 K but no saturation reached under 140 kOe at 4.2 K. Neutron diffraction studies (3) have revealed a ferromagnetic ordering with the moment direction at an angle of about 70° with the tetragonal axis. These properties have been explained by Troc et al (2) in terms of crystal-field interaction on the $5f^2$ electrons of U^{4+} ions.

Low-temperature specific heat measurements on U_2N_2Te and Th_2N_2Te have been undertaken in a double aim. The magnetic entropy curve could give an estimate of the multiplicity of the low-lying levels. Then, further experiment under magnetic field (70 kOe) would show the field effect on the Curie temperature and the magnetic entropy. Experiments have been carried out on three different samples with the same qualitative results. Th_2N_2Te was used to extract the lattice component of the specific heat.

The magnetic data and heat capacity results are used in a tentative interpretation based on the crystal field model and the molecular field approximation. The experimental data to be interpreted are : the paramagnetic moment $\mu_p = 2.7\mu_B$, the ordered moment $\mu_f = 2.5\mu_B$ and its increase with the applied magnetic field (to $2.78\mu_B$ at 140 kOe), the angle of μ_f with the basal plane $\theta \leq 20°$, the shift of Tc up in external magnetic field (8 K at 70 kOe) and the entropy of magnetic ordering $S_{mag} \simeq 1R$ (8.0 - 8.5 J/mol °K). In U_2N_2Te the uranium ion is surrounded by 4 nitrogen and 4 tellurium anions forming a tetragonal antiprism of C_{4V} point symmetry. The contribution to the crystal field potential coming from the nitrogen square is highly dominating. A simplified model with the uranium (4+) ion of pure $^3H_4$ ground term turns out to be adequate. The point charge model (PCM) gives a splitting scheme with three levels (Γ_3, Γ_5 and Γ_1) far remote from others (> 1000 cm^{-1})

and the total splitting of the $^3H_4$ term being equal to 3600 cm^{-1}. The Γ_5 and Γ_1 eigenfunctions are rich in $|\pm 1\rangle$ and $|0\rangle$ components, respectively. The first three levels lie within a 0-300 K energy interval.

Detailed analysis of the experimental data allow us to reconstruct the lowest part of the uranium ion splitting diagram in U_2N_2Te independently and sufficiently univocally. According to the best fit the Γ_5 doublet rich in $|\pm 1\rangle$ component (over 80 %) is the lowest state. The most probable sequence of the singlets is - Γ_1 (at ∿ 100 K) and Γ_3 (at ∿ 300 K). The Γ_1 singlet is rich in $|0\rangle$ component (over 80 %).

Γ_3 (300 K) $\quad \frac{1}{\sqrt{2}}|2\rangle + \frac{1}{\sqrt{2}}|\bar{2}\rangle$

Γ_1 (100 K) $\quad \gamma|0\rangle + \varepsilon|4\rangle + \varepsilon|\bar{4}\rangle \qquad (\gamma > 0.9)$

Γ_5 (0 K) $\quad \beta|\pm 1\rangle + \alpha|\mp 3\rangle \qquad (\beta > 0.9)$

This reconstructed scheme of levels corresponds pretty well to the PCM scheme. These three levels are assumed to form a close system and their eigenfunctions are treated as "zero approximation" ones in the molecular field matrix.

The paramagnetic susceptibility and the effective paramagnetic moment are only slightly dependent on the detailed structure of the lowest levels. μ_p varies from 2.90 to 3.15μ_B with a most probable value of 2.95μ_B. Such system of levels produces rather large perpendicular and small parallel magnetic moment giving as a result an angle between the easy direction and the basal plane $\theta = 15 \pm 5°$.

The molecular field theory give

$$\frac{\mu_B H_m}{kT_c} = 0.80 \pm 0.05$$

which corresponds to $H_m = 850 \pm 50$ kOe . The ordered magnetic moment is calculated by diagonalization of the Zeeman energy $\vec{\mu}(\vec{H}_m + \vec{H}_{ext})$ matrix.

μ_f varies from 2.5 to 2.8μ_B and increases with applied magnetic field (by 0.05 - 0.1μ_B at 140 kOe). The present approach predicts also some shift up of Tc in external magnetic field (by ~ 10 % at 140 kOe). The entropy of magnetic ordering is calculated following the Grunzweig-Genossar (4) approach. For the considered systems of levels this entropy is close to R.

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NUCLEAR PHYSICS, THERMODYNAMIC PROPERTIES, SOLUTION CHEMISTRY, AND APPLIED CHEMISTRY

LIGHT-PARTICLE EMISSION DURING THE SPONTANEOUS FISSION OF ^{256}Fm AND ^{257}Fm*

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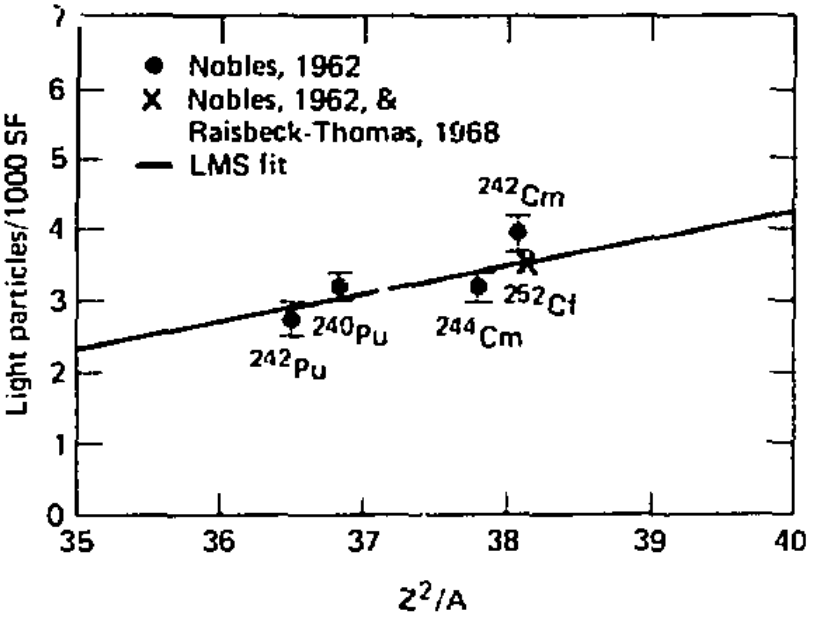
We have made preliminary measurements of light particles emitted during the spontaneous fission (SF) of 2.6-h ^{256}Fm and 101-d ^{257}Fm in order to determine whether the potential energy available for this process is diminished by the formation of colder, more spherical fragments at scission. The SF properties of ^{256}Fm and ^{257}Fm are clearly transitional between the "traditional" asymmetric, low-kinetic energy fission of the lighter actinides, and the symmetric, high-kinetic energy fission of ^{258}Fm and ^{259}Fm.

Much experimental and theoretical work has been undertaken over the past two decades to characterize the phenomenon of light-particle emission during fission.[1] Most closely studied has been ^{252}Cf, which is found to emit a light particle once in every 285 binary SF events. More than 90% of the time, the emitted light particle is an alpha particle, followed in abundance by tritons, protons, ^{6}He, and deuterons.[2] The results of these studies suggest that ternary and binary fission are quite similar except for the expenditure of some energy in the formation and acceleration of the light particle which is predictably reflected in lower fragment energies and masses, and less fragment neutron and gamma-ray emission.

The rate of light-particle emission increases somewhat linearly with Z^2/A, which is the ratio of electrostatic to surface energy in the liquid-drop model of fission. This trend, illustrated in Fig. 1, might be expected, at least for those nuclides which exhibit the "normal" asymmetric mode of fission, since the fraction of energy available for fission which appears as fragment kinetic energy generally decreases with increasing Z^2/A. A larger amount of potential energy is, therefore, available for producing the more elongated, pre-scission nuclear shapes apparently necessary for the emission of light particles.

This trend of increased light-particle emission with increasing Z^2/A might be expected to continue on up through the heaviest actinide, if it weren't for the anomalous fission behavior of ^{258}Fm and ^{259}Fm. For these isotopes, most of the available energy for fission appears as fragment kinetic energy because the fragments themselves are relatively spherical and unexcited, owing this stability to their proximity to the doubly-magic nucleus ^{132}Sn. Since the emission of a light particle appears to cost the nucleus at least 25 MeV in potential energy, there is likely to be a large decrease in the light-particle emission rate for the SF of ^{258}Fm and ^{259}Fm due to a lack of deformation energy available for this process. The study of light-particle emission rates in ^{258}Fm and ^{259}Fm would be an impossible undertaking, due to the short half-lives and low availability of these isotopes; therefore, we are studying light-particle emission during the SF of ^{256}Fm and ^{257}Fm, where an anomaly in the emission rates might first be detected.



Our experimental apparatus consists of two counter telescopes mounted facing one another inside a vacuum chamber. The SF sample, mounted on 0.2-mg/cm^2 graphite foil, is placed between them. Counting data is accumulated by a small computer and stored on a floppy disk for subsequent off-line analysis. The ^{256}Fm is obtained from the bombardment of ^{254}Es by 34-MeV alpha particles at the 88-in cyclotron at the Lawrence Berkeley Laboratory to produce 76-min ^{256}Md, which subsequently decays by electron capture to ^{256}Fm. The ^{257}Fm was obtained from the Transuranium Element Production Program of the U. S. DOE. We used ^{252}Cf to calibrate our counting systems, assuming values of the light-particle emission rate from the literature.[2]

The initial results indicate that the rate of alpha particle emission during the SF of ^{256}Fm and ^{257}Fm is some 40 to 50% higher than for ^{252}Cf SF, which is in opposition to our expectation of a rate equal to or somewhat lower than that of ^{252}Cf.

*This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

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ALTERNATIVE APPROACHES TO THE SYNTHESIS OF SUPERHEAVY ELEMENTS: COMPLETE FUSION AND DAMPED COLLISIONS

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Recent experimental results on dynamical aspects of heavy-ion fusion and damped collisions are reviewed with special emphasis on the potential of these alternative approaches to produce superheavy elements. For fusion reactions it was suggested that the condition for fusion, i.e. capture inside the conditional saddle point[1], requires dynamical deformations of target and projectile in the entrance channel if very heavy compound nuclei are to be formed. Experimental results[2] on fusion of ^{208}Pb with ^{26}Mg, ^{27}Al, ^{48}Ca, ^{50}Ti, ^{52}Cr, and ^{58}Fe, are presented in Fig. 1, where they are compared with the prediction of a one-dimensional proximity model of capturing spheres[3] (full lines) and with predictions of Swiatecki's two-dimensional model[4] (dashed lines).

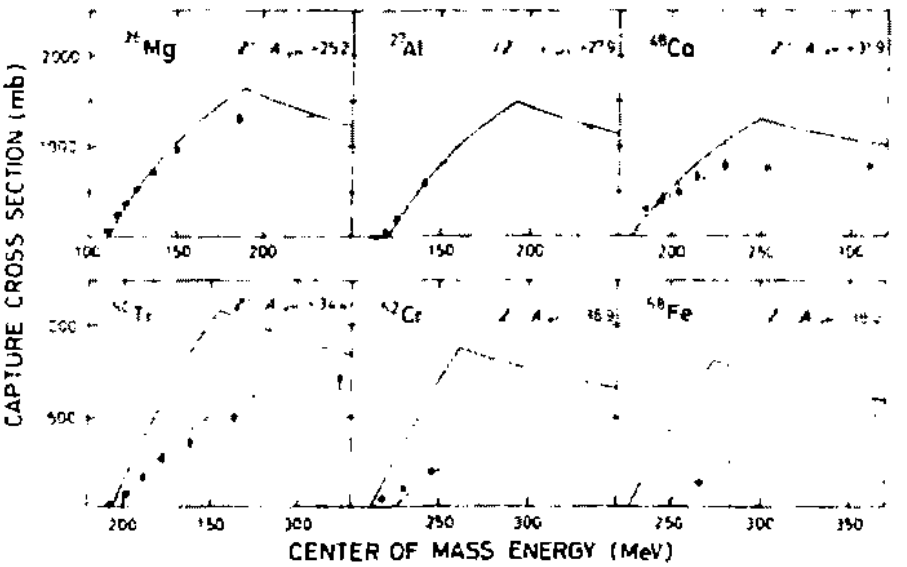

Fig. 1

Together with data[4] on fusion of ^{110}Pd with ^{136}Xe, and of ^{160}Gd with ^{86}Kr, these data show consistently that the "extra push" of kinetic energy above the barrier required to fuse two heavy nuclei sets in when the entrance channel model parameter[1] exceeds $(Z^2/A)_{eff.} = 32.5$. An "extra push" results in extra excitation energy of the superheavy compound nucleus and, thus, drastically reduces its survivability.

However, at the same time, there is clear experimental evidence[2], see also Fig. 1, for the fact that the macroscopic model[3] is not adequate to reproduce the fusion cross sections for heavy systems very close to (or below) the barrier. The exciting gain in the fusion cross sections below the barrier[5] (and the associated reduction in the compound nucleus excitation

energy) has been discussed[5,6] in terms of barrier penetration, static deformation and zero-point motion of low-lying collective surface vibrations. At present, it is not clear whether these microscopic effects can be used to advantage for the production of super-heavy nuclei or whether the limitations of the macroscopic dynamics[1] of nucleus-nucleus collisions predominate for target-projectile combinations necessary to form compound nuclei near Z=114.

Analyses of the statistical spin component, K_0, as deduced from γ-multiplicities[7] or from fission fragment anisotropies[8], indicate that the capture of the projectile proceeds across a very compact shape corresponding to the non-rotating liquid drop saddle, even for systems as heavy as Z=110, and that K_0, accordingly, is very large.

This is contrary to the results[9] on sequential fission of the heaviest transfer products in $^{238}U+^{238}U$ and $^{238}U+^{248}Cm$ collisions where one observes no increase in K_0 as Z approaches the value 110. This may reflect a genuine physical difference in the two production modes. In fusion reactions the colliding nuclei have to merge inside the conditional saddle point. The system then stays behind the saddle until the mass asymmetry is completely relaxed ($\sim 10^{-20}$ sec).[2,7] In damped collisions of ^{238}U and ^{248}Cm nuclei at dissipated energies of > 150 MeV (Ref. 9) fragment elongations outside the appropriate saddle point configurations might be associated with the required large mass transfer. An intriguing question is whether the same large mass transfer can be achieved at much lower dissipated energies and much smaller fragment elongations so that statistically equilibrated heavy fragments are formed. At least for fragments up to Z=101 formed in the low-energy tails of the broad Q-value distributions this seems to be the case: The measured cross sections for surviving heavy actinides[10] in the $^{238}U+^{238}U$ and $^{238}U+^{248}Cm$ reactions, see Fig. 2, are consistent with the decay by multiple-chance fission of fully equilibrated primary fragments.

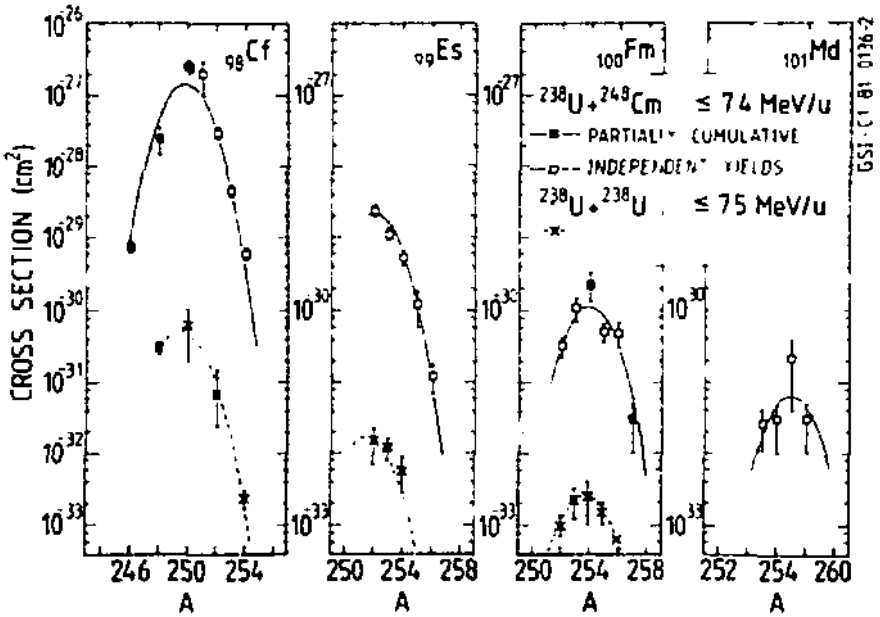

Fig. 2

The minimum excitation energies of these products scale nicely with a one-body dissipation plus particle-hole excitation model by Dakowski et al.[11] The same model predicts minimum excitation energies of 25 MeV for Z=114 in the $^{238}U+^{248}Cm$ reaction if fragment deformations are absent.

In summary, there are conceptual problems both with the complete fusion approach and with the damped collision approach to the synthesis of supheavy nuclei, that deserve further study. These are i) the possibility to fuse sufficiently heavy nuclei without "extra push" at or even below the barrier, and ii) the question of fragment deformation in the low-energy tails of the Q-value distributions in damped collisions.

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THE ELECTRON BINDING ENERGIES IN ATOMIC SYSTEMS WITH 107 < Z, +Z₂ < 188

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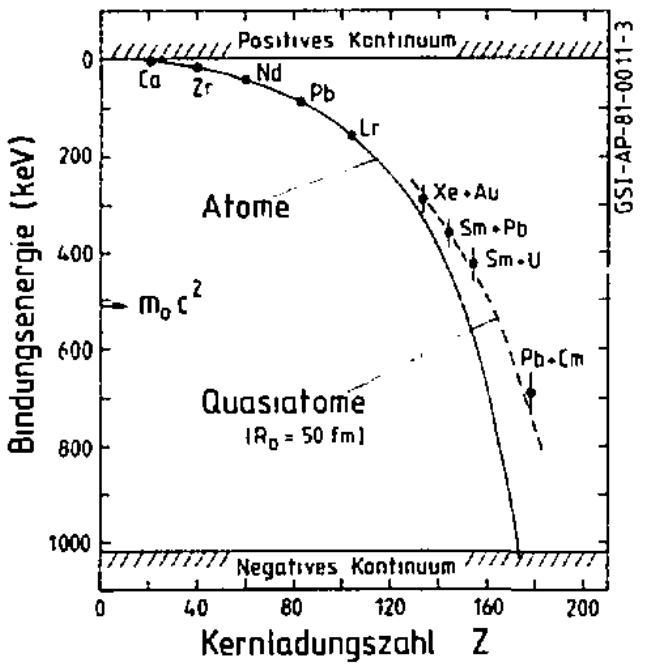
The possibility to accelerate very heavy ions opened the field of atomic collision studies of these ions (Z_1) on heavy targets (Z_2). Collision times being larger than electron orbiting times guarantees the adiabatic adjustment of the electron binding energy to the potential of the approaching heavy nuclei. At the turning point of the trajectories for energies 1 MeV/u < E/A < 5 MeV/u the nuclei are far within the K-shell radii of an atom with a hypothetical atomic number (Z_1+Z_2) corresponding to the combined system. The electrons for a short time period are bound as in an atom with (Z_1+Z_2). If ionisation occurs during this time period the binding energy of the quasiatom and its wavefunctions determine the ionisation probability. It has been shown ionisation to occur predominantly in the quasiatoms /1/. The study of ionisation probabilities and the finding of a scaling law for the ionsation of K-shell electron /2/ opened a way to determine the binding energies in the innermost shells of atoms with atomic numbers beyond the natural ones. The accuracy of the method is moderate, about 5 %. We will report on determinations of K- and L-binding energies for systems with 130 < (Z_1+Z_2) < 188. The experimental method and theoretical basis of our analysis is presented. Binding energies up to 700 keV have been verified experimentally (Fig. 1). The predicted diving of electrons into the Dirac-sea at (Z_1+Z_2 = 173) up to now is waiting for experimental confirmation.



The binding energies of K-electrons as a function of atomic number. The binding energies of the 1sσ-electrons have been measured at R_0 = 50 fm for the quasiatomic systems indicated. The K-binding energies for some elements are given as points. The full lines are calculated by Soff et al. /3/.

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DECAY OF 13.9-MIN ^{241}Np

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A nuclear spectroscopic study of ^{241}Np revealed several new γ-ray transitions which aided in the interpretation of the level structure of ^{241}Pu. A new decay scheme is proposed.

Sources of ^{241}Np were prepared by the ^{238}U(α,p) reaction (irradiation with 32-MeV α particles) and by the ^{244}Pu(n,p3n) reaction (irradiation with 30-160 MeV neutrons[1]). The neptunium was chemically separated in a series of steps which involved elution of unwanted activities, with 4.5M HNO_3 and 12M HCl, from a DOWEX MP-1 anion exchange column. Neptunium was then eluted with an HCl-HF solution and purified further by fuming with $HClO_4$ to volatilize Ru and Tc, reduced to Np^{+4}, and finally coprecipitated with LaF_3. In some of the uranium irradiations the Np^{+4} was also purified by extraction from 1.0M HCl into 0.5M TTA in xylene followed by back extraction into 9M HCl.

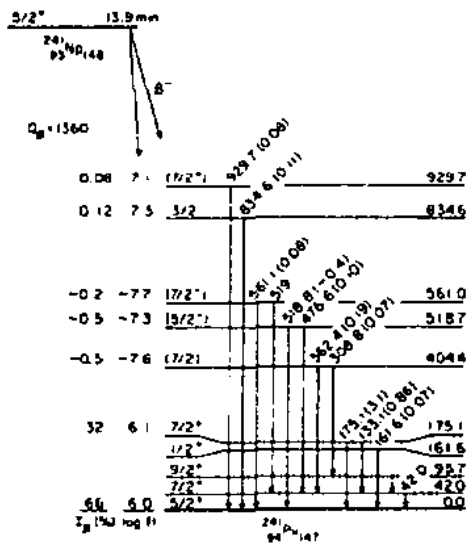
The γ-ray spectra were measured as a function of time with high resolution Ge(Li) detectors, and the analyses were performed by means of the INTRAL and SAMPO codes. Intensities of γ rays per disintegration were determined from almost weightless sources mounted on 10 μg/cm^2 plastic films whose absolute β-ray emission rates were measured with a 4π proportional counter. The half-life of ^{241}Np was determined to be 13.9 ± 0.2 min by means of least squares decay analyses of the 175.1-keV γ-ray peak. All of the γ transitions are shown in the Table with their respective energies E_γ in keV and their intensities I_γ given as γ rays per 100 decays.

Gamma Rays from Decay of ^{241}Np

E_γ	I_γ	E_γ	I_γ
42.0 ± 0.1	0.10 ± 0.03	476.6 ± 0.2	0.10 ± 0.01
133.1 ± 0.1	0.86 ± 0.05	518.8 ± 0.1	0.44 ± 0.03
161.6 ± 0.2	0.07 ± 0.01	561.1 ± 0.2	0.08 ± 0.03
175.1 ± 0.1	3.1 ± 0.2	834.6 ± 0.2	0.11 ± 0.03
308.8 ± 0.2	0.07 ± 0.02	929.7 ± 0.2	0.08 ± 0.02
362.4 ± 0.1	0.19 ± 0.02		

Based on these data and on previously identified levels[2] in ^{241}Pu, the decay scheme shown in the Figure was constructed. The fraction of β$^-$ feeding to the various levels, and the corresponding log *ft* values, were estimated from a balance of transition intensities. The multipolarities for the γ-ray transitions were assumed as M1, except that the 476.6-, 518.8-, and 561-keV γ rays were taken as E1, and the 161.6-keV γ ray as E2. Then the theoretical total conversion coefficients were used to determine the various γ-transition intensities. The ratio $I_\gamma(175.1)/I_\gamma(133.1)$ for depopulation of the 175.1-keV level is 3.6, a value which is in good agreement with the ratio of 3.4

reported recently by Dickens and McConnell[3] in their work on the α decay of ^{245}Cm. The levels shown at 518.7 keV and 561.0 keV are probably the same as the 520-keV and 560-keV levels, respectively, seen by Braid et al,[4] in their study of the $^{241}Pu(d,d')^{241}Pu$ reaction. The 518.8-keV γ rays probably constitute a doublet and depopulate both of these levels.



The (d,d') reaction studies of ^{241}Pu and neighboring odd-A nuclei[5] indicate that $^{241}_{94}Pu_{147}$, with ground state $5/2^+[622]$, exhibits an octupole vibrational state and associated rotational band with $K^\pi = 5/2^-$ and $I^\pi = 5/2^-, 7/2^-, 9/2^-, \ldots$. Evidence from the decay of ^{241}Np indicates that the octupole band in ^{241}Pu starts from the 518.7-keV level. Spin assignments to the 834.6-keV and 929.7-keV levels were made with the help of results from various nuclear reaction studies[2,4]: neutron capture by ^{240}Pu, the $^{242}Pu(d,t)$ reaction, and the $^{242}Pu(^3He,\alpha)$ reaction.

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HYDRATION OF LANTHANIDE AND ACTINIDE IONS : SEMI-THEORETICAL AND EXPERIMENTAL APPROACH

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If one consider a Born Haber cycle envolving solid and gaseous metal, gaseous and hydrated ions one observe that sublimation enthalpy of the metal and formation enthalpy of the aqueous trivalent ions are measured or estimated from experimental data in case of the actinides (1). First ionization potentials are known (2) and consequently hydration enthalpy has been only calculated for trivalent ions (3).

We will first give a general analytical expression $\Delta H_h = f(r, n, z, r\ (water))$ (r being the radius of the considered entity and n the most likely primary hydration number of the ion of charge z). This expression gives calculated values which are close from the 37 experimental data corresponding to halides, alkalis, alkali-earths, trivalent and some divalent and tetravalent lanthanide ions : standard deviations are less than 1 % for each of the six considered families. It takes in account classical terms : Born term, dipolar, quadrupolar and induced dipole interactions. We added three other terms : analytical expression of the interactions(depending from r) between the central ion and the water molecules outside the first hydration sphere, and two parity terms related to the charge of the considered ion and the row of the element in the periodic table. We used the 37 experimental data concerning ions of charge -1 to +4 to compute the 9 unknown parameters aswell as the absolute hydration enthalpy of the proton. The obtained expression has been applied to ΔH_h calculations for M^{2+}, M^{3+} and M^{4+} lanthanide ions. By deducing hydration numbers of actinide ions from those of lanthanides with the same charge we calculated ΔH_h for divalent, trivalent and tetravalent actinide ions. It gives the possibility to deduce ionization potentials of the actinides.

The second approach is to get experimental data on the hydrated radii of the actinide ions. It was interesting to look for a change of the hydration number in the actinide series similarly as proposed for lanthanides (4).

Since the study of heavy actinides is only possible by radiochemistry we undertook transport number measurements, essentially the determination at 25°C of diffusion coefficient in LiCl-HCl or $LaCl_3$-HCl aqueous medium (pH is adjusted at 2.5 in order to prevent hydrolysis of trivalent ions). It has been verified that autodiffusion coefficient are identical with diffusion coefficients measured in the indicated conditions. One obtained in both cases $D^0_{(\mu=0)}(Eu^{3+}) = 5.9.10^{-6}\ cm^2\ s^{-1}$.

Precise D^0 values have also been obtained for some lanthanides from conductivity measurements. Diffusion coefficient of Am^{3+} has been measured and compared with Eu^{3+} data and experiments with mixtures of actinides (americium, curium, californium and einsteinium) make possible a comparison between the D^0 and therefore the radii of the hydrated ions.

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SOME PROBLEMS OF THE CHEMISTRY OF ACTINIDES IN THE LOWER OXIDATION STATES

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One of the fundamental problems of the chemistry of actinides is the problem of similarity of this group of elements with the lanthanide group. Since the first half of actinides holds special position in the actinide row it would be important to find out the likeness between the second half of actinides with the group of lanthanides.

In order to solve this problem it is necessary to compare the regularity of stability change for unusual oxidation states of both groups of elements with an increase in atomic number. Our latest studies proved that the oxidation potentials of the Me^{3+}/Me^{2+} couple change symbatically with an increase in atomic number for the first half of lanthanides and the second half of actinides, and antibatically when comparing the second halves of both groups. A similar picture is true for other unusual oxidation states, such as 4+, and 1+. It should be mentioned that while there is a chemical likeness between actinides and lanthanides in the oxidation states 4+, 3+, and 2+, and therefore, it is possible, based on this likeness, to predict their behavior, a similar comparison would not be possible for monovalent actinides because monovalent lanthanides are not obtained.

By now, mendelevium is the only actinide obtained in the oxidation state 1+. Thus any information on the properties of Md(1+) is of significant scientific value. We showed /1/ that mendelevium can be reduced to the monovalent state in the presence of divalent europium. Using Hertri-Fok radius of *maximal electron density we calculated the ionic radius of* Md (1+) (coordination number = 9, electron configuration $5f^{14}$) equal to 1.20 Å /2/. The same value of the ionic radius was determined by us /3/ derived from the data on the cocrystallization of Md(1+) with NaCl and KCl /1/. Based on this data, we calculated the value of solubility product of MdCl in aquaethanolic solutions. The solubility product as well as the interatomic distance of MdCl lie within the interval between the respective values for NaCl and KCl /3/. Thus Md(1+) with electron configuration $5f^{14}$ is likely to be an analogue for Na^+ and K^+. similar to No^{2+} with the same electron configuration being analogous to Ca^{2+} and Sr^{2+} /4/. Likeness between Md(1+) and Na^+, and K^+ shows also in the fact that Md(1+) does not form stable complexes with Cl^- /1/.

We calculated the hydrotation energy of Md(1+) and determined that the hydrotation energy gain An(1+) in electron con-

figuration $f^n s^1$ can provide stability for Md(1+) as well as for Fm(1+) in water and aqua-ethanolic solutions. This opens up a good outlook for obtaining Fm(1+).

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THE THERMODYNAMICS OF THE COMPLEXATION REACTIONS OF AMERICIUM (III) AND CURIUM (III) WITH AMINOPOLYCARBOXYLATE LIGANDS+

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The stability constants for the complexation reaction of trivalent actinides with various aminopolycarboxylate ligands have been measured at 25° [1]. The thermodynamic data (ΔH, ΔS) available for these reactions is sparse and contains large uncertainties. Because of the importance of these very strong complexing agents in various separation processes for the trivalent actinides from the chemically similar trivalent lanthanides, a systematic study of the thermodynamic parameters which control these reactions seems appropriate.

The aminopolycarboxylate ligands used for the study were iminodiacetic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid. The stability of the first complex of each of

$$M^{+3} + H_xL \rightleftharpoons ML^{+3-x} + xH^+$$

the ligands with Am(III) and Cm(III) was measured using a solvent extraction technique. The organic phase utilized dinonylnapthalenesulfonic acid as the cation exchanger. All aqueous phases were maintained at 0.5 M ionic strength by the addition of $NaClO_4$.

The enthalpies of formation for each reaction were derived from the variation of the stability constants over the temperature range of 5° - 50°. This data was fit by a method of least squares analysis to the van't Hoff isochore. Previous determinations of enthalpy changes for the actinides have been done by this method [2].

The aminopolycarboxylates used in this study were chosen because thermodynamic data for the trivalent lanthanides[3,4] was available in order that a comparison could be made. The thermodynamic data for the complexation of Am(III) and Cm(III) with nitrilotriacetic acid is shown below along with data for Eu(III).

Thermodynamic Properties
(25°; μ=0.5 M $NaClO_4$)

	Eu(III)[3]	Am(III)	Cm(III)
ΔG_1 (kJ/m)	-63.6±0.5	-63.9±0.3	-64.4±0.4
ΔH_1 (kJ/m)	-6.4±0.5	15.6±0.9	21±2
ΔS_1 (J/m °C)	192±2	267±2	288±2

The results, as expected, show that the ΔG values for the actinides are only slightly larger than those values for the lanthanides. The enthalpy changes observed for the actinides are more positive and, therefore, evidence for greater dehydration of the actinide ion during the formation of the complex. Comparison of the entropy changes shows the actinides are more positive by a magnitude which would indicate the loss of an additional two water molecules.

Previous authors[5,6] have discussed the variations of ΔH and ΔS for the trivalent lanthanides and actinides in terms of the "compensation" effect. This interprets the variations in the values of ΔH and ΔS as being dominated by hydration effects. The present results for the complexation reaction of the aminopolycarboxylates and Am(III) and Cm(III) will be discussed in terms of the dehydration mechanism for the trivalent 5f actinide elements.

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THERMODYNAMIC PROPERTIES OF THE GASEOUS LOWER VALENT FLUORIDES AND CHLORIDES OF URANIUM*

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Chemical techniques were developed for generating effusive molecular beams containing the sub-valent fluorides and chlorides of uranium. The gaseous uranium halide beam species were identified and characterized by mass spectrometry, with primary identification based on the measured ionization threshold energies (appearance potentials) of the positive ion species observed. These threshold energies, which are close to the vertical ionization potentials (IP) of the parent neutrals, progressively increase as successive halogen atoms are added to the central uranium atom, varying from values near the IP of uranium for the monohalides to values approaching the IP's of the halogen ligands for the penta- and hexahalides.

A number of gaseous reaction equilibria involving the uranium halide species and certain reference species were studied by high temperature mass spectrometry, using low ionizing electron energies to eliminate overlapping fragmentation effects. The gas mixtures were generated in an effusion oven source, and a characteristic test applied to ascertain that chemical equilibrium was attained. The magnetic-deflection mass spectrometer, the experimental technique, and the methods for interpreting and evaluating the results have been described in previous publications.[1]

Because of major uncertainties in the spectroscopic and molecular constants of the U-F and U-Cl species, the reaction equilibria were studied over wide temperature ranges, and thermochemical data were derived solely from the temperature variation of equilibrium constants (second-law method). A summary of the reaction thermochemistry and derived bond dissociation energies (BDE) is given in Table I. The BDE values in Table I exhibit several significant trends. First, both the U-F and U-Cl data show a dramatic decrease in bond strength as the fifth halogen atom is added to the central uranium atom, with the U-F data showing a further substantial drop with addition of the sixth F atom; the results corroborate the relatively high stability of the tetravalent state of uranium, and indicate that the pentavalent and hexavalent states are attained only at the expense of substantial valence promotion energy. Additionally, the BDE data illustrate that UF_6 is only marginally stable and is, in fact, an effective fluorinating agent. Secondly, the variation in BDE with number of halogen ligands is quite different for the two halide systems, reflecting perhaps a substantial change in ionic-covalent bonding character.

Information about the spectroscopic and molecular constants of the U-F and U-Cl species is relatively sparse, especially that pertaining to the energies and configurations of the low-lying electronic states. However, the reaction entropy data in Table I together with accurate entropies of sublimation of $UF_4(s)$ and $UCl_4(s)$ yield reasonably accurate total entropies of the halide species that can be used to check the assignment these constants. For the U-F species, the results indicate that the electronic contributions are appreciable, and are comparable to those of atomic uranium in the same temperature range. In fact, the experimental entropies of the uranium fluorides

are in good agreement with calculated values based on reasonable rotational and vibrational constants plus the estimated electronic state assignments of Gurvich and co-workers.[2] Corresponding data for the U-Cl molecular species (except for UCl_4) have not yet been analyzed fully. For gaseous UF_5 and UCl_4, where the direct sublimation data yield entropies accurate to within about 0.5 cal/deg mole, the experimental data strongly support a distorted tetrahedral structure of effective C_{2v} symmetry as suggested by electron diffraction data,[3] rather than a regular tetrahedral structure that is more in accord with the photoelectron spectra.[4] Overall, the new thermochemical data define the equilibrium behavior of the gaseous U-F and U-Cl systems over a wide temperature range, and provide useful insights into several aspects of the chemical bonding.

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Table I

REACTION THERMOCHEMISTRY AND DERIVED BOND DISSOCIATION ENERGIES OF URANIUM FLUORIDES AND CHLORIDES

Gaseous Reaction	ΔH°_T Kcal/mole	ΔS°_T cal/deg mole	Derived BDE kcal/mole
$U + BaF = UF + Ba$	-17.8 ± 0.7	-3.0	$D(U-F) = 156$
$UF + BaF = UF_2 + Ba$	4.8 ± 0.6	0.6	$D(FU-F) = 134$
$UF_2 + BaF = UF_3 + Ba$	-8.3 ± 0.4	-9.5	$D(F_2U-F) = 147$
$UF_3 + CaF = UF_4 + Ca$	-19.5 ± 0.6	-14.9	$D(F_3U-F) = 146$
			$D(F_4U-F) = 102$*
			$D(F_5U-F) = 69$*
$U + Cl = UCl$	-98.7 ± 1.5	-22.8	$D(U-Cl) = 99$
$UCl + Cl = UCl_2$	-118.0 ± 1.9	-31.2	$D(ClU-Cl) = 118$
$UCl_2 + Cl = UCl_3$	-113.4 ± 1.2	-31.8	$D(Cl_2U-Cl) = 113$
$CuCl + UCl_3 = Cu + UCl_4$	-9.2 ± 0.3	-8.6	$D(Cl_3U-Cl) = 99$
$UCl_4 + \frac{1}{2}Cl_2 = UCl_5$	-20.3 ± 0.3		$D(Cl_4U-Cl) = 49$

*From previous studies, Reference 5.

Activities of Components in the System $Th(NO_3)_4$-HNO_3-H_2O

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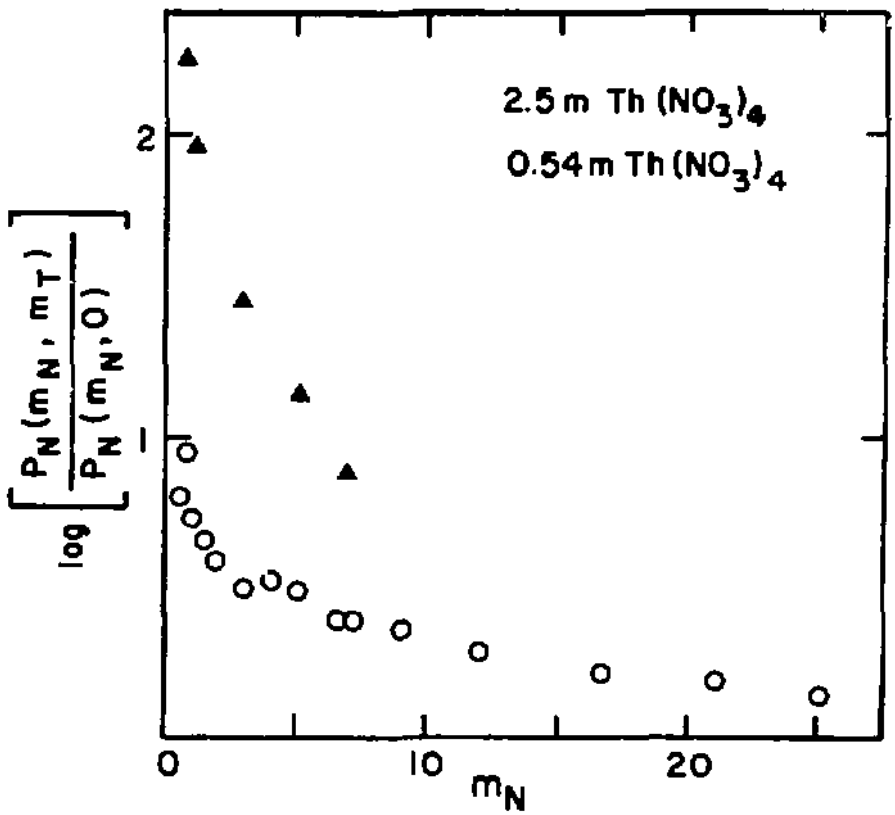
The equilibrium composition of the vapor above thorium nitrate-nitric acid-water mixtures has been studied as a function of thorium nitrate concentration, nitric acid concentration and temperature, using a transpiration technique. At 25°C the thorium nitrate solution concentrations (m_T) which were used ranged from 0.1 to 2.5 molal and the nitric acid concentrations (m_N) from 0.3 to 25 molal. The vapor pressure of the nitric acid ($P_N(m_N,m_T)$) was found to increase with increasing thorium nitrate concentration for a constant molality of nitric acid in the aqueous solutions. At constant m_T the ratio $P_N(m_N,m_T)/P_N(m_N,0)$ becomes larger with decreasing nitric acid concentrations. This is most pronounced for m_N less than 3 molal as shown below.



The water vapor pressures decreased regularly with both increasing nitric acid and increasing thorium nitrate concentrations. At 50°C the concentrations of nitric acid in the vapor could be determined over more dilute solutions that at 25°C, but experimental errors were also somewhat greater. Trends in the results at 50°C were similar to those found for 25°C but at 50°C the ratio $P_N(m_N,m_T)/P_N(m_N,0)$ did not increase as rapidly at low nitric acid concentrations.

Both empirical multiparameter functions and functions based on theories of ionic interactions[1,2] were fitted to the 25°C experimental data. From these, and available literature data for the nitric acid-water and thorium nitrate-water systems at 25°C, expressions were calculated for the variation of water and thorium nitrate activities as functions of the nitric acid and thorium nitrate concentrations using the Gibbs-Duhem equation[3]. The calculated water activities agreed reasonably well with those determined from the experimental water vapor pressures. Values calculated for thorium nitrate activities were, however, strongly dependent on the form of the functions originally used to fit the nitric acid vapor pressure data. Consistent trends were found in the thorium nitrate activities for solutions 0.5 - 10 molal in nitric acid. The analysis of the 50°C data was less satisfactory both because of larger errors in the 50°C measurements and because the behaviour of the binary systems has not been as thoroughly investigated.

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VAPOR PRESSURE AND THERMODYNAMICS OF Bk-249 METAL*

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The vapor pressure of ^{249}Bk metal has been measured over the range 1100-1500 K, using combined Knudsen effusion mass spectrometric and target collection techniques. Vapor pressure data are combined with appropriate estimates for solid free-energy functions and the crystal entropy S^{o}_{298} to calculate enthalpies, entropies and heat capacities from 298 to 3000 K. The vaporizations are described by the equations:

$$\text{Log}_{10}\ P(\text{atm}) = -(15737\pm264)/T + 5.84\pm0.22 \quad [\text{solid, } 1107 - 1319\ K]$$

$$\text{Log}_{10}\ P(\text{atm}) = -(15047\pm203)T + 5.27\pm0.14 \quad [\text{liquid, } 1345 - 1528\ K]$$

from which we calculate

$$\Delta H^{o}_{298}\ (\text{2nd law}) = 74586\pm1192\ \text{cal/mol} \quad [\text{solid}]$$

$$\Delta H^{o}_{298}\ (\text{2nd law}) = 73331\pm 891\ \text{cal/mol} \quad [\text{liquid}]$$

and

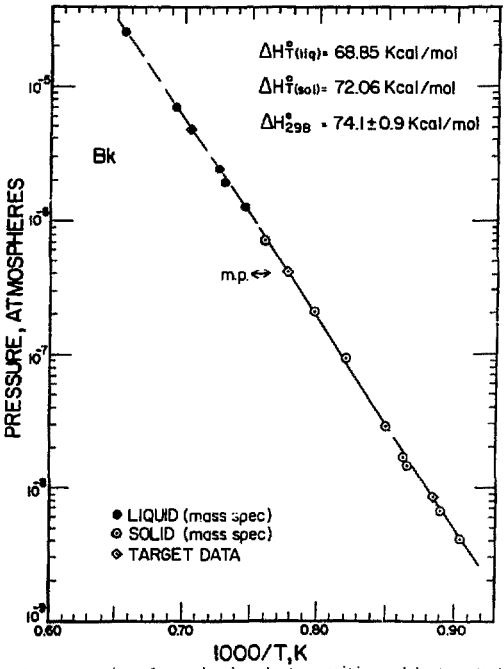
$$\Delta H^{o}_{298}\ (\text{3rd law}) = 74,168\pm60\ \text{cal/mol} \quad [\text{solid and liquid}].$$

Seven milligrams of high-purity berkelium-249 metal were loaded into a single crystal tungsten cup, which was inserted into a tungsten effusion cell. The apparatus and techniques have been described previously.[1] Six liquid data points and ten solid data points were obtained with the mass spectometer before sample exhautsion. In addition, three target exposures were taken to calibrate the data line. These results are plotted in the figure. The related data are shown in the table.

Data were taken in random temperature jumps throughout the range. No apparent scatter or residual cell effects were seen during this process. The target values were analyzed by combined windowless soft-beta and pulse-analyzed alpha counting; the californium daughter growth also allows a post-analysis check of the validity of the Bk-data. The early data points contained a varying signal from the ^{249}Cf daughter, which gradually disappeared during the experiment. Correction for the Cf contribution was made from the target analysis.

The data clearly show a change in slope in the neighborhood of 1300 K. From the pressure equations we calculated a heat of melting of ~3200 cal/mol and an entropy charge of 1.9 cal/mol-deg. This heat may or may not include a dhcp-fcc transition, which in any case occurs near the melting point. Early work[2] indicated a temperature of melting of 986°C; some recent preliminary results show a possible higher temperature.[3] We have arbitrarily chosen a melting temperature of 1050°C, showing (on the figure) a fair possible range. In any case the exact location (±100°C) does not materially affect the values calculated or the conclusions drawn. From the data, we estimate a boiling point of 2860±50 K.

The crystal entropy S^{o}_{298} was calculated using Nd as a model, according to the correlation of Ward and Hill.[4] Since Bk develops its full paramagnetic moment,[5] we used the magnetic entropy of the f^{8} trivalent ground-state configuration for this calculation. Gas phase data were taken from the work of Conway, et al.[6] who list 102 odd and 72 even levels between 3700 and 12,000 cm^{-1}. The calculated crystal entropy S^{o}_{298} = 18.7±0.3 cal/deg-mol. Free-energy



functions, entropies of vaporization, heat capacities and heat contents were calculated by the self-consistent method described for our work with californium.[7]

Our choice of Nd as a model was based on similarity of crystal structures, phase transitions, melting point and heat of vaporization. Using the Johansson correlation,[8] which shifts Pu, etc. under Ce, etc. in terms of similar physicochemical properties, Pm would have been the proper homolog; however, there are as-yet essentially no published thermodynamic data for this metal. A preliminary measurement on a very small sample of Bk gave an anomalously high heat $^{H}_{T}$ = 91 kcal/mol, which was probably due to the sample size and use of a Ta container, which has since been found to interact with the Bk. Empirical predictions for the heat of sublimation based on spectroscopic data and the calorimetric heat of

T, K	P, atm	-Log10 P	H°_{298}, Third Law, cal/mol
Solid			
1107	4.02×10^{-9}	8.39577	74,120
1124	6.62×10^{-9}	8.17914	74,113
1128[1]	8.54×10^{-9}	8.06854	73,798
1155	1.44×10^{-8}	7.84164	74,315
1169	1.66×10^{-8}	7.77989	74,238
1176	2.85×10^{-8}	7.54510	74,031
1219	9.04×10^{-8}	7.04383	73,852
1258	1.95×10^{-7}	6.70997	73,978
1282[1]	4.01×10^{-7}	6.39686	73,728
1319	7.04×10^{-7}	6.15243	74,287
Liquid			
1345	1.24×10^{-6}	5.90658	74,168
1373	1.87×10^{-6}	5.72816	74,412
1390	2.44×10^{-6}	5.61261	74,145
1421[1]	4.70×10^{-6}	5.32790	74,367
1443	7.09×10^{-6}	5.14935	74,263
1528	2.59×10^{-5}	4.58670	74,400

[1] Denotes also target data point.

Ref. 9,10 predicted a value of 70-76 kcal/mol; our results confirm these predictions. Our final value for the heat of vaporization H°_{298} = 74.1±0.9 kcal/mol is the average of our second and third law data.

Work performed under the auspices of the U. S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division.

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ENTHALPY OF FORMATION AND MAGNETIC SUSCEPTIBILITY OF CmO_2 AND Cm_2O_3 [a]

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Stoichiometric curium dioxide has been prepared from ^{248}Cm (containing 0.17 at. % ^{244}Cm) by careful calcination of pure curium(III) oxalate at 550-600°C, followed by prolonged heating at 300°C. Monoclinic curium sesquioxide was prepared by hydrogen reduction of the dioxide at 825°C. The purity of these compounds has been verified by X-ray powder crystallography and by thermogravimetric analysis.

The magnetic susceptibility of milligram-scale samples of each compound was measured on a Faraday balance at temperatures between 2 and 298 K. Following the magnetic measurements, the enthalpy of formation of each compound was determined by solution calorimetry.

Susceptibility data on ^{248}Cm oxides are compared with earlier values obtained on ^{244}Cm and ^{248}Cm oxides in terms of expected magnetic moments for Cm(III) and Cm(IV) and in terms of nonstoichiometry of CmO_2 caused by incomplete oxidation or by radiation damage. The thermochemical data on the oxides are interpreted in terms of the aqueous reduction potential E (Cm^{4+}/Cm^{3+}) and in terms of the stabilities of other lanthanide and actinide dioxides and sesquioxides.

a Work performed under the auspices of the Office of Basic Energy Sciences, Division of Nuclear Sciences, U.S. Department of Energy under contract N° W-31-109-ENG-38 ; the Institut Interuniversitaire des Sciences Nucléaires (Brussels) ; and a collaborative Research Grant from the North Atlantic Treaty Organization.

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STABILITIES OF TERNARY ALKALINE EARTH - ACTINIDE (VI) OXIDES M_3AnO_6 [a]

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The complex oxides Ca_3UO_6, Sr_3UO_6, Ba_3UO_6, Ba_3NpO_6, and Ba_3PuO_6 were prepared by solid-state syntheses at temperatures up to 1200°C. X-ray powder photographs show that Ba_3NpO_6 and Ba_3PuO_6 have lower symmetry than was reported earlier ; the X-ray data on the other complex oxides confirm previous structural studies. Spectrophotometric, volumetric and gravimetric analysis, isotope-dilution mass spectrometry, and alpha counting have been used to characterize these compounds.

Samples of these compounds were reacted in solution calorimeters in appropriate dilute acids to determine their enthalpies of formation. In most cases, the reported results are derived from two or more preparations. These complex oxides all have similar crystal structures (distorted, ordered perovskite) with actinide(VI) ions in octahedral oxide coordination. The enthalpies of formation, coupled with lattice-energy calculations, have been used to estimate the stabilities of hexavalent actinides in these perovskites in comparison with the binary oxides and other species, and to calculate enthalpies of formation of the HO_6^{8-} complex ions.

a Work performed under the auspices of the Office of Basic Energy Sciences, Division of Nuclear Sciences, U.S. Department of Energy, under contract N° W-31-109-ENG-38 ; the Institut Interuniversitaire des Sciences Nucléaires (Brussels) ; and a collaborative research grant from the North Atlantic Treaty Organization.

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COMPARISON OF THE AFFINITY OF TRIVALENT ACTINIDE AND LANTHANIDE FOR NITROGEN AND SULFUR DONORS

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This work is part of an investigation of the differences and analogies of the trivalent actinides and lathanides complexes in liquid phases. Aqueous or organic complexes of the two series with nitrogen and sulfur donors ligands will be described.

It appeared that nitrogen ligands form stronger complexes with the actinides even if the values of the ionic radia were in favor of lanthanide more stable species. For example Am(III) with $r = 1.06$ Å give a 1:1 complexe with 1-10 orthophenanthroline for which $\beta_1 = 10^{2.68}$ when Eu(III) of which $r = 0.93$ Å give a weaker complexe with $\beta_1 = 10^{1.88}$. In order to compare the ability of several ligands to complexe selectively the 4f or the 5f ion of a given pair we reported in Table I the value of S_F of Am(III)-Eu(III) couple. S_F is a selection factor defined as :

$$S_F = 2(\Delta G_{Ac} - \Delta G_{Ln}) / (\Delta G_{Ac} + \Delta G_{Ln})$$

ΔG_{Ac} and ΔG_{Ln} are the free enthalpy changes for the formation of the actinide and lanthanide 1:1 complexe.

Table I : S_F for the Am(III)-Eu(III) pair for selected oxygen, nitrogen and nitrogen-oxygen donors

Ligand	Complexe	S_F	Most probable number of ligand(other than N)-metal bonds	Most probable number of N-metal bonds	References
F^-	MF^{3+}	-0.084	1	0	(1)
$CH_3CO_2^-$	$M(CH_3CO_2)^{2+}aq$	0.03	2	0	(2)
EDTA *	$M(EDTA)^-$	0.09	4	2	(3) (4)
N_3^-	MN_3^{2+}	0.93	0	1	This work
phen *	$M(phen)^{3+}$	0.69	0	2	This work
TPTZ *	$M(TPTZ)^{3+}$	0.38	0	3	This work

* We used the above abreviation for the following ligands
DTPA = diethylene triaminopentaacetic acid, phen = 1-10 orthophenanthroline, TPTZ = 2-4-6 tripyridyltriazine.

It can be seen that the higher S_F factors are obtained with the nitrogen donors.

Dialkyldithiophosphoric acids $((RO)_2PSSH)$ have been chosen as sulfur donors complexing agents. We observed aqueous complexes for tetravalent or hexavalent

actinide but no soluble species for pentavalent actinide or trivalent actinide and lanthanide. So it was not possible to compare directly the stability of Am(III) and Eu(III) aqueous complexes with dialkyldithiophosphate.

However Am(III) and Eu(III) showed a very different behavior when extracted by mixtures of di2ethylhexyldithiophosphoric acid (HDEHDTP) and tributylphosphate (TBP). The distribution coefficients of Am(III) and Eu(III) as a function of the reactants ratio are shown figure 1.

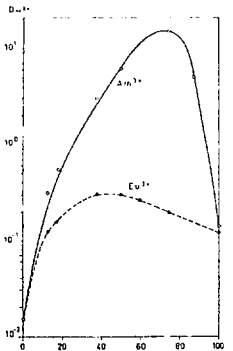

FIGURE 1

DISTRIBUTION COEFFICIENTS OF Am^{3+} AND Eu^{3+} IONS
BETWEEN AQUEOUS SOLUTIONS 0.05M IN HNO_3 AND (HDEHDTP + TBP) 1 M IN DODECANE

It can be seen that the two ions are extracted via different synergistic effects. From these curves and complementary extraction data it can be deduced that the complexes in the organic phases are respectively : $Am(DEHDTP)_3$ TBP and $Eu(DEHDTP)\ (NO_3)_2.(TBP)_2$. This difference illustrates the greater affinity of actinide for sulfur donors ligands.

In conclusion, we have to point out that contrary to what is observed with oxygen donors for which the formation constants of actinide and lanthanide complexes are governed by the ionic radia of the metal ; the nitrogen and sulfur donors show a significant higher affinity for the actinides even if the radius of lanthanide are smaller.

These features suggest that the covalent part of the nitrogen or sulfur actinide bond is sufficient to counter balance the smaller size of the heavier lanthanide. They imply also that the covalent part in nitrogen or sulfur bonds to lanthanide are smaller than the covalent contribution in the homologuous actinide complexes.

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ELECTROCHEMICAL AND SPECTROSCOPIC STUDIES OF ACTINIDES IN CARBONATE-BICARBONATE BUFFERS*

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The electrochemical and spectroscopic properties of actinides in carbonate and bicarbonate solutions are under investigation.

For uranium, the reduction of U(VI), which exists primarily as the triscarbonatodioxouranate(VI) ion $UO_2(CO_3)_3^{4-}$, is observed by cyclic voltammetry. In carbonate solutions (0.1-1.0 M), an irreversible one-electron reduction leads to stable U(V) species. Spectroscopic studies are consistent with the presence of only one U(V) species, the spectrum of which is remarkably featureless. Electrochemical reduction of the U(V) species is not achieved in carbonate solutions. In bicarbonate solution (1 M), U(VI) is reduced to U(V) at potentials comparable to those for carbonate solutions, but at the lower pH values the U(V) species disproportionates to U(IV) and U(VI). Spectroscopic results are consistent with the presence of only one U(IV) species, the spectrum of which shows similarities to other U(IV) species in basic solution.

For neptunium, results are nearly identical throughout the pH range 8.3-11.2, i.e., in bicarbonate or carbonate. At a potential much less negative than that required to reduce U(VI) to U(V), Np(VI) is reduced quasi-reversibly to Np(V). Spectroscopic results are consistent with the presence of only one Np(VI) and one Np(V) species. One difference in the spectrum of Np(V) in carbonate versus bicarbonate occurs at 997 nm. In bicarbonate this peak has a much larger extinction coefficient than in carbonate. Reduction of Np(V) to Np(IV) occurs near the limit of useful potential range for mercury. Although accurate coulometric data are unattainable, comparison of spectroscopic properties clearly indicates that Np(IV) is produced.

For plutonium, results to date indicate that Pu(VI) is reduced quasi-reversibly to Pu(V) at a slightly more negative potential than the corresponding reduction of Np(VI). This system is currently under investigation and results will be reported as they become available.

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SPECTROELECTROCHEMICAL STUDIES OF THE ACTINIDES: RECENT RESULTS ON Np AND Am IN AQUEOUS CARBONATE SOLUTION*

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Spectroelectrochemistry at optically transparent electrodes (OTE's) in conjunction with cyclic voltammetry has been applied to the study of the Np(VII)/Np(VI) and Am(IV)/Am(III) redox couples in aqueous alkali metal carbonate solutions. The strong complexation provided by carbonate ions affects the formal reduction potentials of these redox couples and stabilizes the higher oxidation states. The absorption spectra and redox potentials of the Np(VII)/Np(VI) couple in Na_2CO_3 solution and the Am(IV)/Am(III) couple in $(NH_4)_2CO_3$, Na_2CO_3-$NaHCO_3$, K_2CO_3 and Cs_2CO_3 media are reported.

Heptavalent neptunium can be prepared by electrolytic oxidation of Np(VI) in 0.25-1.5 M Na_2CO_3-0.2 M NaOH.[1] The stability and absorption spectrum of Np(VII) in carbonate solution make the Np(VII)/Np(VI) redox couple amenable to spectroelectrochemical investigation.

A concentrated solution (> 1 M) of ^{237}Np(VI) was prepared in 1 M $HClO_4$ and an aliquot introduced into 2 M Na_2CO_3. This 10^{-2} M Np(VI) solution was adjusted to pH 13 by addition of NaOH, and cyclic voltammetry was then performed at a platinum wire microelectrode. The cyclic voltammogram displayed a reversible wave for the Np(VII)/Np(VI) redox couple, and the formal reduction potential ($E^{o'}$) was found to be 0.46 ± 0.01 V in this medium. [All potentials given here are referenced to the normal hydrogen electrode (NHE)]. This Np(VI)-Na_2CO_3 solution was subsequently placed in a platinum screen OTE in the light beam of a spectrophotometer. An absorption spectrum of the yellow-green Np(VI) solution was recorded (Fig. 1) prior to electrolytic oxidation, and spectra were then recorded as a function of time during the potential-step electrolysis. The spectrum of dark green Np(VII) in Na_2CO_3 solution is shown in Fig. 1. The $E^{o'}$ for the Np(VII)/Np(VI) redox couple in this medium is presently being determined spectroelectrochemically to provide a more accurate value than that obtained via cyclic voltammetry.

Tetravalent americium is unstable with respect to disproportionation in most mineral acid solutions, because of the high value, about 2.4 V[2], of the Am(IV)/Am(III) potential. It is possible to prepare stable Am(IV) in strongly complexing aqueous solutions such as concentrated alkali metal fluorides[3], concentrated phosphoric acid[4,5], and acidic sodium pyrophosphate solutions.[4] Our recent work stabilizing Pr(IV) and Tb(IV) in concentrated aqueous alkali metal carbonate solutions suggested the possibility of stabilizing Am(IV) in this same medium.[6]

Solutions of from 10^{-1} to 10^{-2} M ^{243}Am(III) were prepared in various carbonate solutions (2 M $(NH_4)_2CO_3$, 2 M Na_2CO_3-$NaHCO_3$, 5.5 M K_2CO_3, and 5 M Cs_2CO_3) by dissolving freshly precipitated $Am(OH)_3$ into these carbonate solutions.

Cyclic voltammograms of Am(III) in Na_2CO_3 solution were recorded at a platinum microelectrode as a function of pH. The pH was adjusted by bubbling CO_2 through the solution. At p. 9.7 a reversible voltammogram of the Am(IV)/Am(III) redox couple was obtained from which an $E^{o'}$ value of 0.92 ± 0.01 V was

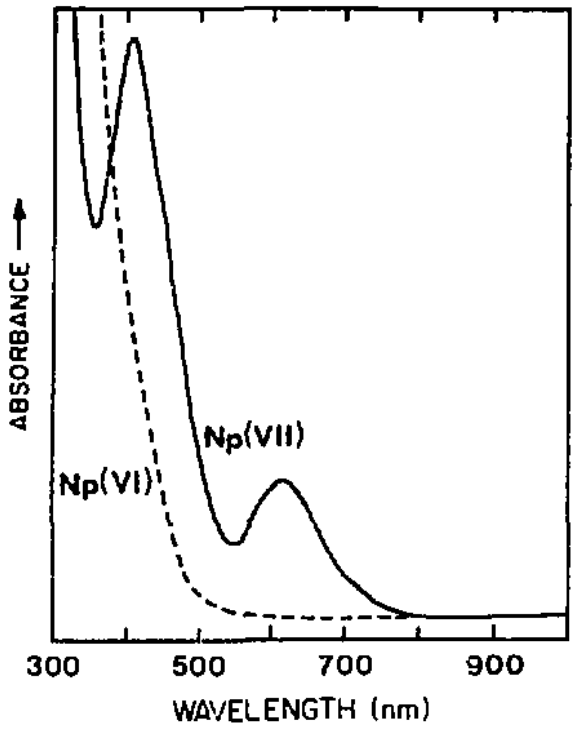

FIGURE 1

determined. The same solution was placed in an OTE of reticulated vitreous carbon (RVC). An absorption spectrum of the Am(III) solution was recorded prior to electrolysis (Fig. 2). A potential of 0.60 V was applied to the cell and increased to more positive values until a change in the spectrum was noted. The solution first turned golden-yellow and then red-brown. The absorption spectrum of the product, Am(IV), is shown in Fig. 2.

The assignment of oxidation state IV to the oxidized americium species was based on electrochemical and spectroscopic evidence and determination that only a one-electron transfer was involved, as shown by spectrophotometric and potentiometric titrations with $K_4Fe(CN)_6$ in 2 M Na_2CO_3 solution .

Assuming the shift in reduction potential provided by complexation with carbonate ions is 1.7 V more positive than that in non-complexing solution,[6] the standard reduction potential for the Am(IV)/Am(III) couple can be calculated. This value is 2.62 ± 0.01 V which agrees well with that recently reported.[7]

It is expected that concentrated alkali metal carbonate media may be exploited as a means to generate and stabilize other, less-stable, higher oxidation state actinides such as Cm(IV) and Cf(V).

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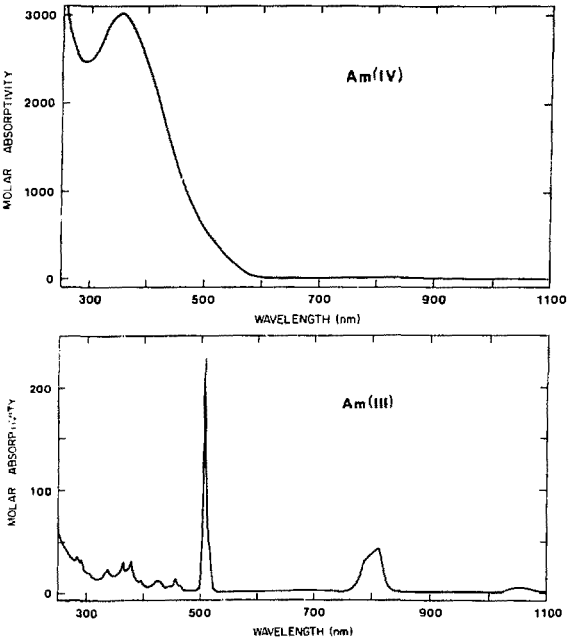

FIGURE 2

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APPLICATIONS OF SPECTROELECTROCHEMICAL TECHNIQUES TO STUDIES OF THE ACTINIDES*

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Simultaneous application of electrochemical and spectroscopic techniques (spectroelectrochemistry) to the generation and characterization of less-stable oxidation states of the actinides is described. An electrochemical reaction can be monitored by passing light directly through an optically transparent electrode (OTE) and the solution adjacent to it. This provides a convenient method for obtaining spectra, redox potentials, electron-exchange numbers, and reaction rates of electrogenerated species. Because of the simplicity and sensitivity of the technique and the advantages of using small sample volumes (less than 1 mL), spectroelectrochemistry is well suited to studies of actinide redox couples.

New electrode materials such as reticulated vitreous carbon (RVC)[1] and porous metal foam (PMF)[2] have been employed as OTE's for actinide studies. RVC is a three-dimensional network of glassy-carbon struts with a large surface-to-volume ratio which allows for rapid and complete electrolysis throughout the solution in and around the electrode matrix. RVC exhibits high optical transparency, is an inert electrode material, and is not easily damaged by radioactive solutions. PMF is similar in structure and appearance to RVC, but the PMF matrix, being metal, is a superior conductor of electricity. In addition, PMF is more versatile than RVC in that it is easier to plate platinum or mercury onto PMF for extended potential range capabilities.

Simple OTE's were made by sandwiching a thin slice of RVC or PMF between quartz microscope slides (Fig. 1) and placing epoxy on three edges as described elsewhere.[3,4] The OTE was dipped into a small reservoir of actinide solution, and by means of a suction tube at the top of the cell, a portion of the solution was drawn up into the electrode matrix. An SCE reference electrode and a platinum wire counter electrode were placed in the bulk solution reservoir, and the entire assembly was placed in the sample compartment of a spectrophotometer for spectroelectrochemical studies.

A more elaborate OTE cell design was utilized in our recent work. It consists of a Teflon cell holder which positions a quartz cuvet in the sample beam of a spectrophotometer. The Teflon cell holder is equipped with a lid which supports the OTE, SCE reference, and platinum wire counter electrodes. When the lid is lowered the electrodes are immersed in the solution. Two different quartz cuvets were used with the cell holder, a 0.5-cm path length cuvet (0.75 mL) and a 2.0-cm path length one (1.0 to 1.5 mL).

Spectroelectrochemical studies of the actinides Np through Cm were performed in a gloved box modified with an appendage, fitted with quartz windows, which slides into the sample compartment of a Cary Model 14-H spectrophotometer. Electrochemical measurements were performed with an EG&G PARC Model 173D/179D/175 potentiostat/coulometer/universal programmer.

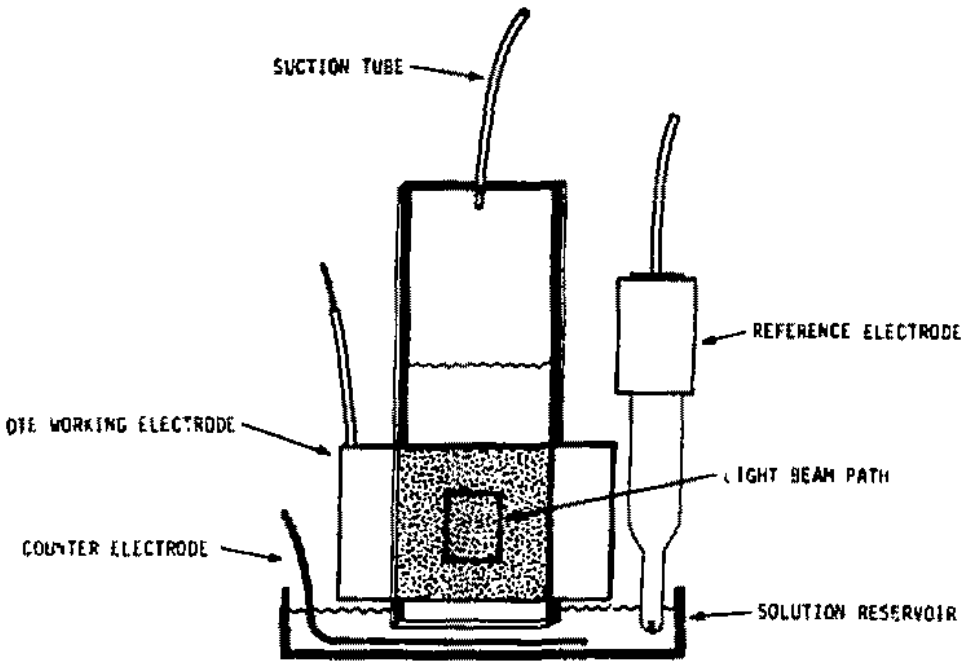

FIGURE 1

The Np(VI)/Np(V) redox couple in 1 M $HClO_4$ is used here as an example to demonstrate the spectroelectrochemical method for determination of the formal reduction potential ($E^{\circ\prime}$) and the number of electrons exchanged (n) for the reaction

$$NpO_2^{2+} + e^- \rightleftharpoons NpO_2^+.$$

The relationship between the applied potential (E) and the concentrations of neptunium species is described by the Nernst equation,

$$E = E^{\circ\prime} + \frac{0.059}{n} \log \frac{[NpO_2^{2+}]}{[NpO_2^+]},$$

and the relationship between the absorbances of the neptunium species and their concentrations is expressed by Beer's law,

$$A = \varepsilon b\,[NpO_2^{2+}] \qquad \text{and} \qquad A' = \varepsilon' b\,[NpO_2^+].$$

Combination of these expressions relates the applied potential to the ratio of the absorbances of the electroactive species:

$$E = E^{\circ\prime} + \frac{0.059}{n} \log \frac{(A/\varepsilon)}{(A'/\varepsilon')}.$$

Experimental data were obtained by placing the NpO_2^{2+} starting solution in an OTE. A potential to ensure retention of Np(VI) was applied to the cell, and

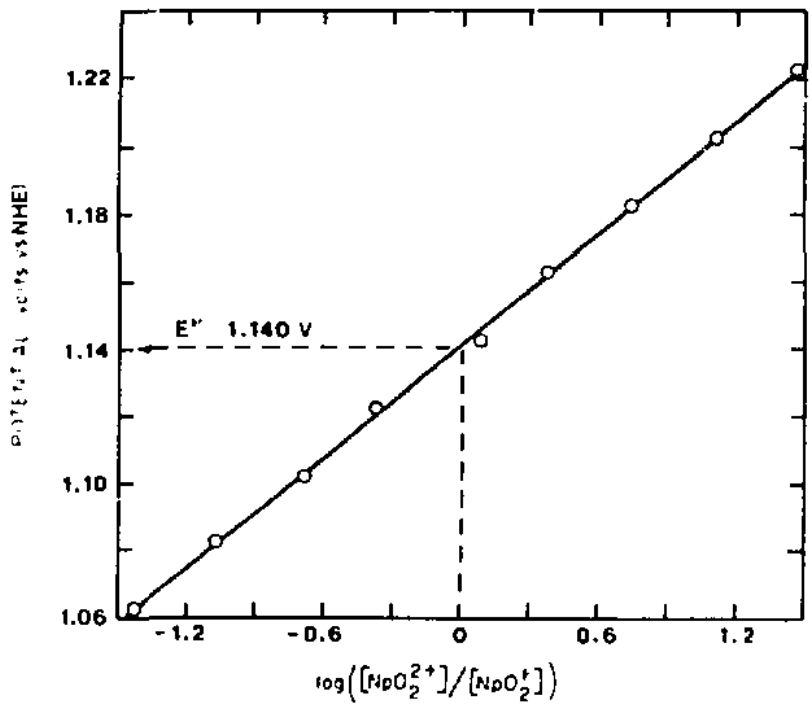

FIGURE 2

an initial spectrum of NpO_2^{2+} was recorded. More negative potentials were then applied to the cell to generate NpO_2^+, identified on the basis of its characteristic absorption spectrum. After equilibrium was established at each applied potential, an absorption spectrum was recorded. A plot of the applied potential versus the ratio of concentrations of the Np species (expressed as absorbance values) yielded a straight line (Fig. 2) with slope equal to 0.059/n and y-intercept equal to $E^{o'}$. The $E^{o'}$ value determined for the Np(VI)/Np(V) redox couple in 1 M $HClO_4$ was 1.140 ± 0.005 V (n = 0.93), in excellent agreement with the accepted value of 1.137 V.[5]

Important advantages of this method include (a) current measurement is not required, (b) the same solution can be recycled for many experiments, (c) attainment of equilibrium is readily determined by noting constant absorbance with time, and (d) the path length of the cell, b, and knowledge of the molar absorptivity, ε, of the redox species are not required if the proper monitoring wavelength is selected.[3] Additional advantages of this technique, as well as descriptions of other spectroelectrochemical methods applicable to actinide studies, will be presented.

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** National Council o Scientific Research - Lebanon.
† On leave from Tohoku University, Sendai, Japan.
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REDOX PROPERTIES OF URANIUM IN AN ACIDIC ROOM TEMPERATURE MOLTEN SALT

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There has been an active interest in the electrochemistry of uranium and the other actinides in molten salts [1,2]. This work describes the redox-properties of uranium in the $AlCl_3$ + n (n-butyl)pyridinium chloride (BPC) room temperature molten salt system, described by Osteryoung et al. [3,4]. Experiments have been restricted to the acidic region (mole ratio $AlCl_3$: BPC > 1). The results are compared with those obtained in a previous study of the electrochemistry of uranium in acidic $AlCl_3$ + NaCl melts at 175°C [5].

Fig. 1 shows a voltammogram for the reduction/oxidation of UCl_4 solutions in 2:1 melts at a glassy carbon rotating disc electrode (35° C; 150 rpm). Cathodic scans exhibit an almost reversible wave (at low rotation rates) for the reduction U(IV) → U(III); anodic scans show two irreversible waves for the oxidations U(IV) → U(V) and U(V) → U(VI). The height of each wave increases linearly with the uranium concentration as shown in fig. 2 (i : reduction wave; i' : sum of both oxidation waves). The oxidation wave U(V) → U(VI) has not been observed previously in acidic $AlCl_3$ + NaCl melts [5]; in the room temperature melt, this wave is found at potentials more positive than the thermodynamic limit of the solvent and stable solutions of hexavalent uranium cannot be prepared. In 2:1 melts, solution of pentavalent uranium also reacts to some extent with the solvent; at 30° C the standard potential of the U(V)/U(IV) couple is estimated as 1.9 V (vs. Al). The standard potential of the U(IV)/U(III) couple determined by coulometric titration, is given by $E^0 = 1.146 - 5.25 \times 10^{-4}\ T(V)$ (at 30° C; $E^0 = 0.987$ V).

If the acidity of the melt is decreased, the waves U(IV) → U(III) and U(IV) → U(V) shift to less positive potentials; the wave U(V) → U(VI) merges with the decomposition of the solvent.

For the reduction wave, the variation of half-wave potentials with melt composition is shown in fig. 3 (the dotted lines have slopes of 62 and 186 mV/decade change of pCl^-, respectively). The results can be explained by the reaction

$$UCl_x^{(4-x)} + e^- \rightarrow U^{3+} + x\ Cl^- \qquad (1)$$

where x varies from 1 to 3 as the composition of the melts changes from 2:1 to 2:1,05 $AlCl_3$:BPC mole ratios (addition of more BPC causes UCl_4 to precipitate; UCl_3 is also insoluble in melts that are only slightly acidic). Reaction (1) has been proposed already for the reduction of UCl_4 solutions in $AlCl_3$ + NaCl melts [5].

The variation of half-wave potentials with melt composition for the wave U(IV) → U(V), at 150 rpm, is shown in fig. 4. Since this wave is irreversible, its position is dependent on rotation rate and no definite conclusions can be drawn from the data of fig. 4; it is worthwhile to mention however that stable solution of U(V) can be prepared in melts with a 1,7:1 to 1,2:1 $AlCl_3$:BPC composition range

At present, spectral studies are undertaken to characterize the different valence states of uranium in these room temperature molten salts.

* This work was supported by the I.I.K.W., Belgium

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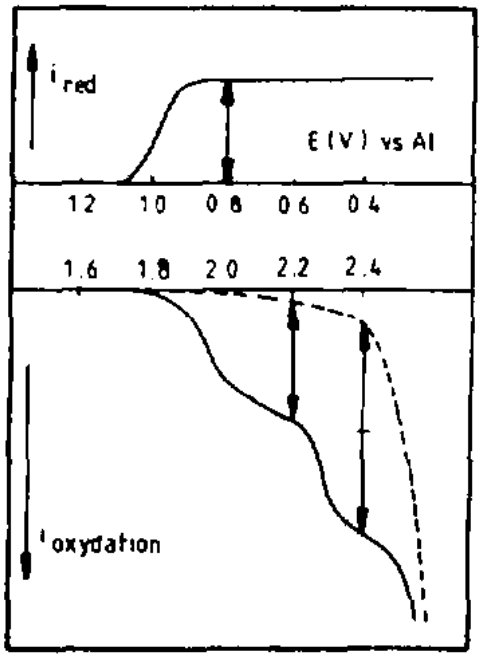

Fig 1

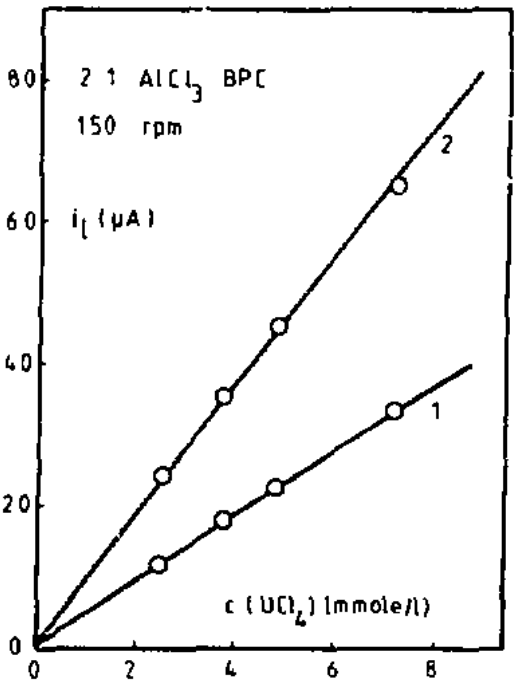

Fig.2

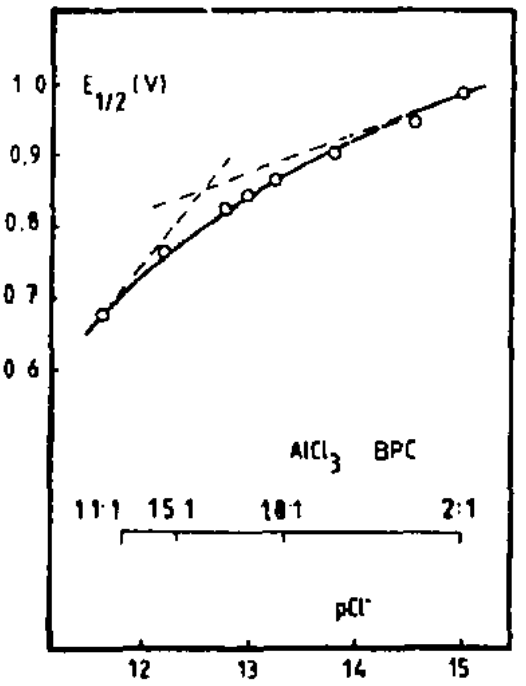

Fig.3

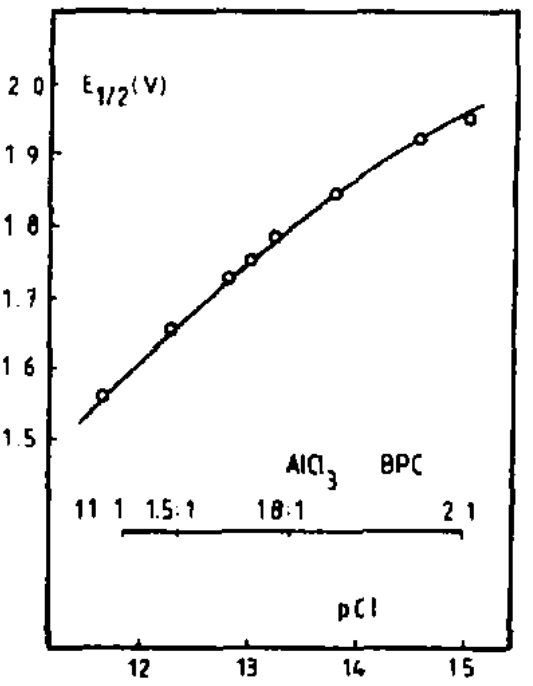

Fig : 4

THE CHEMISTRY OF PLUTONIUM (III) - AQUEOUS CARBONATE*

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Evidence of plutonium (III) carbonate complexes was observed first when plutonium (III) hydroxide and sulfate were dissolved in potassium carbonate solutions[1]. Plutonium (III) "carbonate" was made by adding an excess of ammonium carbonate to a hydrochloric acid solution of plutonium (III)[2], but the precipitate was not analyzed. Plutonium (III) carbonate was also reported prepared by precipitating plutonium (III) sulfate with ammonium hydroxide and reacting the precipitate with carbon dioxide[3]; this compound was not analyzed, but was found to be insoluble in water and carbonic acid and soluble in 45% sodium carbonate.

A systematic study was reported to characterize compounds precipitated by the addition of alkali metal carbonates to dilute hydrochloric acid solutions of plutonium (III);[4] the precipitate was suggested as impure $Pu_2(CO_3)_3$ which redissolved at $Pu:M_2CO_3$ ratios of 1.0:30 to 36, when M=Cs and Rb, but did not redissolve at maximum $Pu:M_2CO_3$ ratios of 1.0:42 and 1.0:75 when M=K and Na, respectively. Preparation of a more crystalline compound was achieved by precipitation at elevated temperatures and was characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis, and X-ray diffraction as $Pu(OH)CO_3 \cdot xH_2O$ or $Pu(OH)_3 \cdot Pu_2(CO_3)_3 \cdot xH_2O$.[5]

This paper will attempt to elucidate the complex chemistry of plutonium (III) in aqueous carbonate media as well as to identify the solid compounds precipitated. The explanation will be based on the above studies as well as unpublished results from the authors' laboratory.

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INTERACTION OF PU(VI) WITH BICARBONATE

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To describe the behavior of plutonium(VI), PuO_2^{2+}, in natural water systems it is necessary to know the extent of hydrolysis and of complexation by HCO_3^-/CO_3^{2-}. Additional interaction with both inorganic (e.g. F^-, SO_4^{2-}, etc.) and organic (e.g. humates, amino acids, etc.) ligands may occur should these be present but hydroxide and HCO_3^-/CO_3^{2-} anions are always present.

Gel'man, et. al., (1) reported stability constants for the formation of $PuO_2(CO_3)(OH)_2^{2-}$, $PuO_2(CO_3)(OH)^-$ and $PuO_2(CO_3)_2^{2-}$. However, their method of measurement of the solubility can result in large uncertainties. We have studied the reaction at pH 8.3 between plutonium(VI) and bicarbonate in 0.1 M ionic strength solution by titration calorimetry. The titrations were conducted using Pu-242 in the 4 ml volume Peltier-cooled minicalorimeter at F.S.U. (2). The techniques used in the titration calorimetry experiment have been described previously (3). The heat of dilution of the $PuO2^{+2}$ solution was very small, indicating that the Pu(VI) existed in either monomeric or quite stable oligomeric form.

Analysis of the data, using $\beta_1 = 463$ from previous work (4) gave the values listed in the table.

Thermodynamic Parameters for
Complexation of Pu(VI) and Bicarbonate[a]

T = 25.0°C; I = 0.10 M ($NaClO_4$); pH ≈ 8.3

complex	β	ΔG(kJ·m^{-1})	ΔH(kJ·m^{-1})	ΔS(J·K^{-1}·m^{-1})
1:1	463 ± 60	-15.2 ± 0.4	-1.46 ± 0.5	+46 ± 3
1:2	(2.3 ± 0.5) X 10^4	-25 ± 1	-56 ± 5	-105 ± 50

At pH 8.3, 90-95% of the Pu(VI) exists as the dihydroxy species, $PuO_2(OH)_2$. From literature data, thermochemical cycles can be constructed which support $PuO_2(CO_3)_2^{-2}$ as the 1:2 species; i.e.,

$$PuO_2(OH)_{2(a)} + 2HCO_{3(a)}^- = PuO_2(CO_3)_{2(a)}^{-2} + 2H_2O$$

Assignment of the reaction forming the 1:1 species is more uncertain. However, it seems likely that the species is a bicarbonate complex such ad $PuO_2(OH)(HCO_3)$ or $PuO_2(OH)_2(HCO_3)^{-1}$ rather than $PuO_2(CO_3)$ or $PuO_2(OH)(CO_3)$.

From the log ß values of the table, we estimate that Pu(VI) in trace level concentrations exists predominantly in the form of the mono-bicarbonate complex in marine waters although the fraction present as $PuO_2(OH)_2$ is not insignificant. However, 10% or less is present as $PuO_2(CO_3)_2^{-2}$ in constrast to U(VI) which is considered to be mostly $UO_2(CO_3)_2^{-2}$ is sea water (6).

This research was supported by contracts with the U.S.D.O.E.

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STUDIES ON TRIVALENT AND TETRAVALENT NEPTUNIUM AND PLUTONIUM WITH COMPUTER CONTROLLED VOLTAMMETRY*

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Thermodynamic data for aqueous actinide systems in trace and ultra-trace concentrations are needed as input parameters for chemical modeling of nuclear waste in geologic repositories.[1] Computer controlled voltammetry is a relatively new analytical technique that can be used at these levels for the determination of stability constants[2-4] of tri- and tetravalent neptunium and plutonium systems.

Preliminary studies have been carried out on the performance of various electrodes (dropping mercury, hanging mercury drop, mercury film rotating disk, glassy carbon, gold film rotating disk, platinum rotating disk) with the application of different waveforms (linear scan, differential pulse, differential pulse anodic stripping voltammetry). The detection limits were determined for various conditions.

Np(IV,III) in acidic solutions gave reproducible responses on stationary Hg electrodes. The Np(IV)/Np(III) couple can be considered as quasi-reversible with the transport of the electroactive neptunium species to and from the electrode surface controlled by a diffusion-limited adsorption or desorption process. No electrochemical response was observed with Np(IV) carbonate solutions with Hg electrodes, which suggests the reduction potentials are more negative than -1.9V, requiring fairly large stability constant(s) for the complex(es) of Np(IV) with carbonate ions.

Pu(III) and Pu(IV) solutions in 1M HCl did not produce any response on a glassy carbon electrode with linear sweep voltammetry contrary to a previous report.[5] In addition, no response was obtained with the application of a square wave to a platinum disk electrode in a solution of 9.5×10^{-5} M Pu(IV) in 1M HCl.[6] Differential pulse and differential pulse anodic stripping voltammetry gave excellent response and precision on the platinum disk electrode with peak potentials in agreement with values obtained by coulometry.[7] The Pu(IV)/Pu(III) couple appears to be electrochemically reversible in 1M HCl. The mode of transport, as with Np(IV)/Np(III), is a diffusion-limited adsorption process.

Pu(IV) in 1M carbonate solutions gave good signals using differential pulse polarography at the hanging mercury drop electrode. Peak potentials are in excellent agreement with oscillopolarographic data.[8] Lowering the carbonate concentration by use of 1M $NaHCO_3$ shifted the Pu(IV) peak to a distinctly less cathodic potential than in 1M Na_2CO_3. Differential pulse polarography at a platinum disk electrode, applied to solutions of Pu(IV) in 1M Na_2CO_3, showed well-formed peaks for the Pu(IV)/Pu(III) charge transfer. Again, sensitivity appears to be limited by a diffusion-controlled adsorption process.

The results of complexation studies of Pu(III),IV) carbonate systems, which are currently under investigation, will be presented.

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PREPARATION AND PROPERTIES OF PENTAVALENT AMERICIUM IN PHOSPHORIC ACID SOLUTIONS

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A convenient method was developed for the preparation of Am(V) in phosphoric acid solutions based on electrochemical oxidation of Am(III) to Am(VI) with subsequent electrochemical reduction of Am(VI) to Am(V).

The electrolysis at the anode potential 2.02V provides within 1 hour practically complete (> 99.5%) oxidation of Am(III) to Am(VI) in the mixtures containing 0.02-0.1 M $HClO_4$ and $\geqslant 10^{-3}$ M phosphoric acid. The reduction of Am(VI) to Am(V) reaches at the second stage of the electrolysis at the anode potential 1.27V for 30 minutes.

Am(V) is stable in diluted phosphoric acid and is slowly reduced to Am(III) by the radiolysis. It disproportionates into Am(VI) and Am(III) at the concentration of phosphoric acid > 2 M, the rate of the disproportionation increases proportionally to $[H_3PO_4]^2$. The apparent order of the disproportionation reaction in relation to the concentration of Am(V) is equal to ca.1 at 25°C, it increases with the temperature rise. This phenomenon can be explained by the participation of Am(V)-phosphate complex ions in this reaction.

Am(V) instantly interacts with Am(IV) in 5.5-10 M phosphoric acid being oxidized to Am(VI), direct experimental evidences for this reaction were obtained for the first time. A method for the coulometric determination of americium was developed using Am(VI)/Am(V) couple; this method permits to determine over 30 micrograms of americium with 1.5-2% error in the presence of twofold and threefold amounts of Cm, Pu and hundredfold amounts of La, Ni, Al, Cu, Cr and other elements.

ACTINIDE COMPLEXATION WITH HYDROPHILIC LIGANDS. LACTATES OF Am(III) AND U(IV)*

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The TBP,HDEHP and HTTA extraction systems were analyzed for their use in the study of complex chemistry and new information about the thermodynamics of the lactate complexing of Am, Eu and U(IV) was derived. Furthermore it was found improbable that the extraction mechanism of the Talspeak process involves extraction of any An or Ln lactate containing species.

In our study of the complexation of the actinides with hydrophilic ligands we are presently studing the carbonate, phosphate and carboxylate systems. Of special interest is the situation at near neutral conditions and the separation of actinides from Purex waste. The investigations are carried out by solvent extraction techniques using HDEHP(bis,2-ethyl-hexyl-phosphoric acid), HTTA(2-thenoyl-trifluoroacetone) and TBP(tributylphosphate) and by electromigration. Here, we are reporting the results on the lactate complexing, which is of importance for geological (groundwater), biological and industrial applications. Firstly we present the extraction systems, the extraction mechanisms and extracted species. Secondly we present the obtained stability and thermodynamic constants for the lactate complexes of Am, Eu and U(IV).

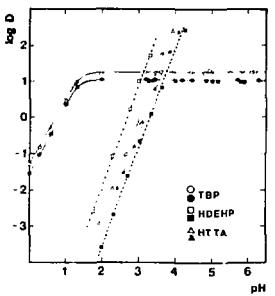

Fig. 1. Extraction systems for complex studies. Distribution of Am (unfilled symbols) and Eu as a function of pH. 1 M (Na,H)ClO$_4$. The initial organic phases were; 100% TBP; $5 \cdot 10^{-3}$ M HDEHP in n-heptane; 0.5 M HTTA in toluene.

The extraction of Am, Eu and U (III,IV,VI) with the three reagents TBP, HDEHP and HTTA were thoroughly studied with respect to ionic strength, pH, reagent concentration, reproducibility, mass balance and extraction of lactic (^{14}C) acid. It was concluded that HDEHP and especially TBP behaved very reproducibly and in accordance with the expected behaviour whereas we had some

problems with HTTA. Relatively poor reproducibility was obtained and the reagent and hydrogen ion concentration dependencies became somewhat lower than expected, especially with n-heptane. TBP has the advantage of being independent of pH in a wide range, pH 2-7, Fig. 1, but has the drawback of being laborious to quantitatively interpret at very high concentrations, in comparison with the perchlorate, of complexing ligand.

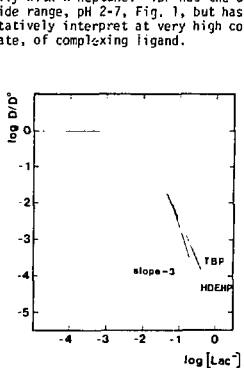

FIG. 1. Stripping of Am by lactate ion at pH 4 - 6. Undilluted TBP (1° pH 2 or 3) and 5.10^{-4} M HDEHP in n-heptane (at pH 4). 25°C. 1 M $NaClO_4$,...ed).

In the presence of lactic acid a reduction of the distribution value D (D = [M](organic phase)/[M](aqueous phase)) is obtained corresponding to the degree of complexing between the metal M and the lactate anion. In Fig. 2 a plot of log (D/D°) versus the lactate anion concentration is shown for Am with HDEHP and TBP. The very similar curvature obtained for the completely different extraction systems suggests that a stepwise complexation occurs in the aqueous phase according to:

$$M^{3+}(Lac)_n^{(3-n)+} + Lac^- \rightleftharpoons M(Lac)_{n+1}^{3-(n+1)}, \quad n=0,1,2,3 \qquad (1)$$

There is no indication of any extraction of a mixed lactate-extraction complex like $Am(Lac)(DEHP)_2$ which was reported resently for the Talspeak process. The deviation at higher lactate concentrations for TBP is due to the change in ionic media as mentioned above.

The pH dependancy of the lactate complexation was analyzed by performing TBP extractions at various constant pH between pH 2 and 6, Fig.3. By considering the effect of pH on the dissociation and distribution of lactic acid one concludes that the complexation proceeds as in eqn. (1). Futhermore, some association with undissociated HLac is indicated.

U(IV) was obtained by electrolytic reduction and followed by measuring the redox potential. Its distribution between TBP and 1 M $NaClO_4$ was determined together with data for U(III) and U(VI). The order of extractibility of the uranium valency states with TBP is; U(VI) U(III) U(IV). Introduction

of lactic acid at pH 2 and 0.001-0.01 M U(IV) gave information on the stability of the formed complexes. Both natural uranium and U^{233} was used after purification from daughter activities.

The temperature influence on the extraction of Am and Eu was investigated in the temperature interval from 5 ^{o}C to 45 ^{o}C allowing determination of the enthalpy and entropy of the complex formation. Preliminery stability and related thermodynamic constants for the lactate complexes of Am and Eu are collected in the table. *Data for the uranium systems are not completed* at present.

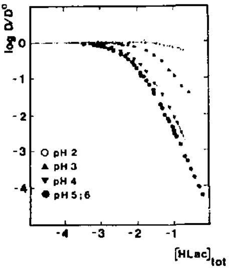

Fig. 5. The pH dependency of the lactate complexing of Am. The distribution D of Am between undiluted TBP and 1 M Na(ClO$_4$,Lac) as a function of total added lactic acid at constant pH. 25^{o}C.

FORMATION AND THERMODYNAMIC CONSTANTS FOR Am AND Eu LACTATES, 25 °C

	log β_1	$\Delta H_{\beta 1}$	$\Delta S_{\beta 1}$	log β_2	$\Delta H_{\beta 2}$	$\Delta S_{\beta 2}$	log β_3	$\Delta H_{\beta 3}$	$\Delta S_{\beta 3}$
Am^{3+}	2.4[illegible] ± [illegible]	[illegible]	−1.4 ± 2.0	4.29 ± 0.35	[illegible]	[illegible]	5.3[illegible] ± 0.3[illegible]	[illegible]	[illegible]
Eu^{3+}	2.4[illegible] ± 0.12	−4.4 ± 0.7	−3.3 ± 2.3	4.19 ± 0.55	+1.2 ± 0.6	15 ± 2	5.90 ± 0.25	[illegible]	[illegible]

ΔH in kcal mole^{-1}, ΔS in cal mole^{-1} deg^{-1}

* This work was supported by the Swedish Natural Science Council.

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SUBLIMATION AND GAS CHROMATOGRAPHY OF β-DIKETONATES OF ACTINIDE AND LANTANIDE ELEMENTS IN THE VAPOURS OF β-DIKETONES

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Sublimation and gas chromatography of β-diketonates and their adducts with donoractive compounds can be used for the separation and isolation of actinide and lantanide elements. Practical application of these methods was limited, however, by difficultes associated with the synthesis of volatile compounds of the microamounts of radionuclides as well as with the decomposition and sorption of coordination-unsaturated chelates in sublimation and gas chromatography because of the interaction with the impurities in the carrier gas and with the equipment construction materials.

It was established /1/ that a large number of metal compounds(hydroxides, salts of readily volatile acids: chlorides, oxychlorides, nitrates, acetylacetonates, tenoyltrifluoroacetonates) reactid in miligram or trace amounts with the vapours of fluorinated and other β-diketones forming volatile β-diketonates which at certain temperatures can be quantitatively extracted into the gas phase. This method was used for the synthesis of volatile hexafluoroacetylacetonates, trifluoroacetylacetonates and pivaloyltrifluoroacetonates of rare earth elements, americium, berkelium (IV) and (III), neptunium, thorium and some transition metals.

The synthesis of volatile β-diketonates of radionuclides at elevated temperatures can be combined with their transport through the gas phase as well as with the gas chromatographic and sublimation separation. The methods of quantitative separation of various couples of the elements were developed on this basis.

Gas adsorption thermochromatography of hexafluoroacetylacetonates of ^{243}Am and ^{239}Np in a glass column with a temperature gradient was used for the separation of these elements. Tenoyltrifluoroacetylacetonates of these elements (prepared by extraction) were placed into a starting zone, and argon saturated with HFA vapours was passed above them at ca.200°C. After the quantitative sublimation hexafluoroacetylacetonates of americium (III) and neptunium (IV) were precipated in the column at ca.100 and 60°C respectively.

The separation of $Th-^{233}Pa$ and $^{95}Nb-^{95}Zr$ couples is based on a fraction sublimation of their hexafluoroacetylacetonates. Protactinium and niobium form non-volatile hydroxosubstituted β-diketonates, whereas thorium and zirconium are quantitatively transferred into the gas phase when being treated with HFA vapours.

The gas chromatography of β-diketonates and their adducts with donoractive compounds in the carrier gas saturated with HFA vapours is used for the separation of actinide and lantanide elements.

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INVESTIGATION OF MECHANISM OF URANIUM SORPTION FROM THE SEA WATER

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The report presents the investigation results of the thermodynamics and kinetics of the sorption concentration of uranium from the artificial and natural sea water using natural and synthetic inorganic sorbents of various types.

Chemical interaction leading to the formation of hard-to-dissolve uranium compounds with the sorbent substance is the general feature of the sorption process studied. Awraami-Yerofeyev kinetic equation depicting the topochemical nature of the transformation in the sorbent phase was used for describing the process.

The rate constants of the topochemical reactions were calculated and semi-empirical relationships between initial uranium concentration in the solution, its distribution factor in the system, thermodynamic stability constant of tricarbonate-uranylate complex and the temperature were obtained. The calculated values are in good agreement with the results of the experiments carried out in the waters of the Pacific Ocean as well as Barents and Caspian seas.

The rate constants of the sorption of uranium and other elements were determined for the sorbents tested in natural conditions. The sorbent on the basis of titanium dioxide with a partially changed anatase structure was found to be the most promising one and is known under the trade name of "Thermoxide-5".

The granulated sorbent possesses a high mechanical strength permitting to use the latter in a fluidized bed in order to prevent from mudding and fouling of the sorbent. The concentrate containing grams of uranium was isolated in optimum conditions at the linear filtration rate equal to 1 m/min and with the grain size ranging from 0.6 to 1 mm.

EXTRACTION OF TRANSPLUTONIUM ELEMENTS BY DIPHENYL-(ARYL)DIALKYLCARBAMOYLMETHYL PHOSPHINE OXIDES

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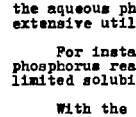
Polydentate neutral organophosphorus compounds attract great interest as efficient extractants of transplutonium elements (TPE) from acid waste nuclear fuel element solutions. High cost of production and refinement of these reagents, their limited solubility in organic solvents or high solubility in the aqueous phase can be the main obstacle preventing from their extensive utilization.

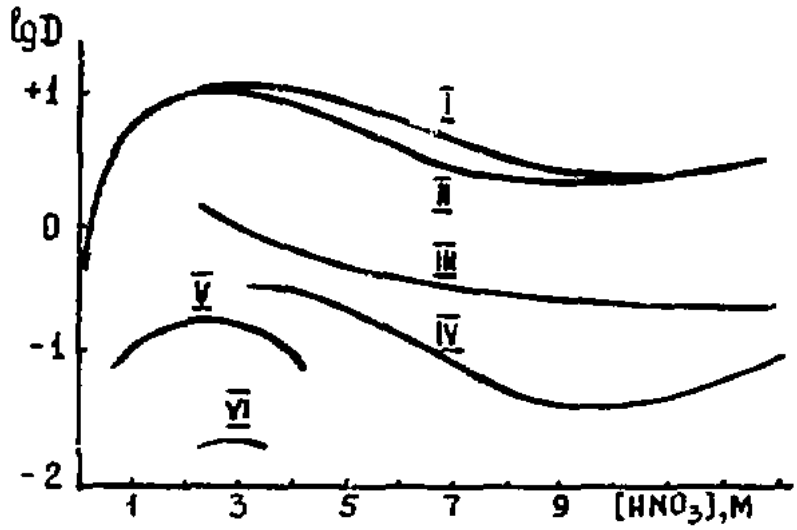
For instance, neutral bi-, tri- and tetradentate organophosphorus reagents posses a high extraction capacity, but a limited solubility in a small number of the solvents /1/.

With the view of the further search for the optimum extractants the following group of the reagents was synthesized and investigated.



$R' = R'' = C_6H_5$,	$R''' = C_4H_9$	(I)
$R' = R'' = C_6H_5$,	$R''' = C_2H_5$	(II)
$R' = R^{IV} = C_6H_{11}$ (cyclo-)	$R''' = C_2H_5$	(III)
$R' = R^{IV} = C_4H_9$	$R''' = C_2H_5$	(IV)
$R' = C_6H_5$, $R'' = C_2H_5$	$R''' = C_2H_5$	(V)
$R' = R'' = C_4H_9O$	$R''' = C_2H_5$	(VI)

We have studied the effect of the substituents, associated with phosphorus and nitrogen atoms, on the extraction capacity of the reagents. The figure below illustrates the relationship between Am(III) extraction by 0.1 M solutions of the reagents I-VI in dichloromethane and nitric acid concentration. The substitution of alkoxyl groups (VI) attached to the P=O groups for alkyl groups (IV) increase substantially the extraction capacity of the reagent. The substitution of butyl (IV) for phenyl radicals (II) also increases the reagent extraction capacity, whereas the substitution of one of phenyl radicals for ethyl radicals markedly decreases this capacity.



The difference in radicals (reagents I and II) associated with nitrogen atoms has no marked effect upon the extraction properties of the reagents, while their solubility is affected.

The solubility of reagents I and II was investigated in organic solvents and in nitric acid solutions.

Reagent I was shown to be the best one, since it possesses the highest extraction capacity, a good solubility in a large number of organic solvents (unlike reagent II) and a low solubility in nitric acid. Its synthesis and refinement presents no problems.

We have investigated the relationship between TPE extraction by reagents I and II in various solvents and the time, the nature of the solvent, the concentration of the acid, salts, reagents and the volume ratio of the phases.

The investigation has shown that reagent I can be used for a rapid quantitative TPE concentrating from highly acidic media with any content of the salts and 1:50 volume ratio of the organic and aqueous phases.

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EXTRACTION OF TETRAVALENT BERKELIUM BY HIGH-MOLECULAR AMINES IN THE PRESENCE OF HETERO-POLYANIONS

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The report presents investigation results of the extraction of tetravalent berkelium by high-molecular amines from 0,1-14 M HNO_3 solutions containing heteropolyanions. Berkelium oxidized by bromate ions in the presence of these anions was found to be quantitatively extracted by primary, secondary, tertiary amines and by quarternary ammonium bases all known to be practically incapable of extracting tetravalent berkelium from nitric acid solutions containing $KBrO_3$ oxidant.

The efficiency of the extraction of berkelium by the amines from nitric acid solutions containing heteropolyanions is somewhat lower with the use of the mixture of $AgNO_3$ and $(NH_4)_2S_2O_8$ (as berkelium oxidant) compared to the oxidation by bromate ions.

The extraction degree of tetravalent berkelium in the presence of heteropolyanions is dependent of the nature of the amine and the initial concentration of nitric acid in the aqueous phase. Decylamine extracts berkelium quantitatively over a wider range of the concentrations of nitric acid (0.5-6 M) compared to dioctyl- and trioctylamine (1 M HNO_3) or to quarternary ammonium bases (0.1-2 M). It should be particularly noted that Bk(III) cannot be extracted under these conditions by high-molecular amines in the presence of heteropolyanions.

$Bk^{4}:NO_3^-$ ratio in the organic phase was found to be six when extracting by decylamine and four when extracting by trioctylamine and quarternary ammonium bases.

Much lower concentrations of amines are required for the maximum extraction of Bk(IV) from nitric acid solutions containing heteropolyanions as compared to the extraction from nitric acid solutions containing bichromate ions in the absence of heteropolyanions. The association of two, three, three and eight molecules of decylamine, dioctylamine, trioctylamine and quarternary ammonium bases respectively with one molecule of berkelium nitrate was established by the relationship between the degree of the extraction of Bk(IV) and the concentration of the amine. Heteropolyanion:Bk(IV) ratio in the organic phase was found to be three in the case of extracting by decylamine and two when extracting by dioctylamine, trioctylamine and by quarternary ammonium bases.

The results obtained permit the conclusion that heteropolyanions do not only stabilize the tetravalent state of

berkelium, but also enter into the composition of the compounds extracted.

The extraction behaviour of a number of TPE, REE and fission elements was studied in the conditions optimum for berkelium extraction, and the majority of the above-mentioned elements was found to be only slightly extractable.

THE EXTRACTION OF URANIUM FROM SEA WATER WITH LEAD SULPHIDE AND GALENA.

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Many studies for the purpose of collecting uranium from sea water have been carried out in recent years and various methods have been proposed. In particular the method of adsorption has been examined for numerous organic and inorganic materials[1-5].

For the recovery of uranium from sea water the adsorbent must posseses some prerequisites which may be summarised as follows:

i) insolubility of the material,
ii) ability to extract uranium with high selectivity and high loading capacity,
iii) easy elution of uranium from the adsorbent

Among the proposed materials the mineral Galena and lead sulphide despite an uncertain solubility in sea water have been reported to be in so far between the most efficient adsorbing materials.

In a recent paper the distribution constant of uranium, was determined for a large series of materials directly from sea water[6], as part of a screening test. However some doubt on the behaviour and reproducibility of the data obtained with lead sulphide and Galena were reported.

In the present communication an investigation on the adsorption equilibrium,pH and temperature effect and adsorption kinetic for the title compounds will be discussed.

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THE PLUTONIUM CONCENTRATION OF SURFACE AIR AT VIENNA IN THE PERIOD 1962 - 1979

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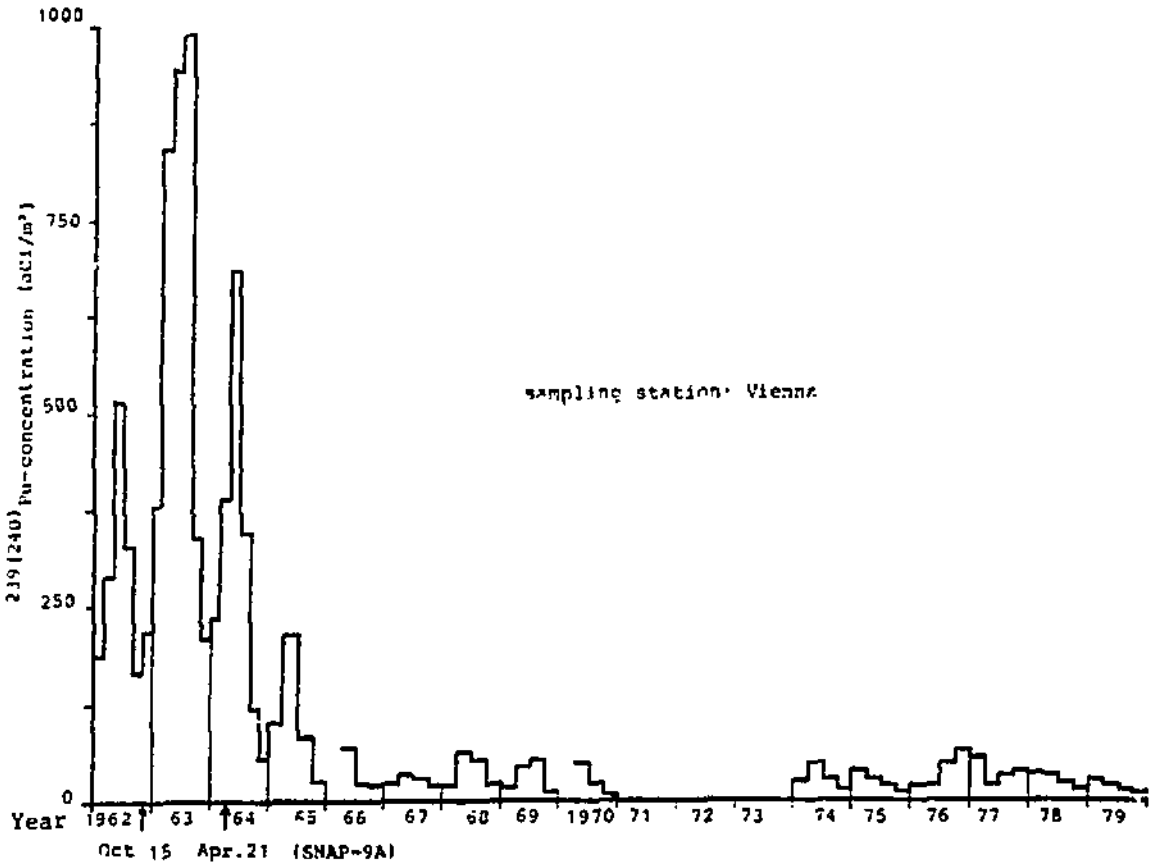
Air filters for the period 1962 - 1979 from a monitoring station in Vienna (Wien/Hohe Warte), which is operating as part of the Austrian network for measuring environmental radioactivity[1], were analysed for plutonium by chemical separation and alpha spectrometry. The procedure used has been described previously[2]. Several filters, all having been exposed for 24 hours, were combined, so that the analysis of each sample gave the average plutonium concentration in air for a period of two or three months.



The $^{239(240)}Pu$ concentration of surface air was found to have reached the highest values (up to 1 fCi/m^3) in the spring of 1963, i.e. some months after the high yield nuclear weapon tests in the fall of 1962. Afterwards the Pu concentration decreased, reaching about 0.03 fCi/m^3 in 1967. This was a result of the Test Ban Treaty coming into force. The annual course of the Pu concentration showed "spring maxima" especially in 1963, 1964 and 1965, such maxima having been observed also for other fallout radionuclides. In 1968 and 1976 the Pu concentration increased again (up to 0.06 fCi/m^3), this being due to French and Chinese weapon tests in the atmosphere. In the last years of the period investigated, the Pu concentration was around 0.01 to 0.02 fCi/m^3.

In 1963 and 1964 the ^{238}Pu activity was between 2 and 6 % of the $^{239(240)}Pu$ activity, such ratios being in agreement with those expected for fallout plutonium from weapon tests. Beginning in 1967 the activity ratio $^{238}Pu/^{239(240)}Pu$ increased to values of 20 to 80 %. This was a consequence of the release of ^{238}Pu when the satellite SNAP-9A burnt up in the atmosphere (in April 21, 1964)[3].

^{238}Pu Concentration of Surface Air at Vienna

Period	^{238}Pu (aCi/m^3)	Activity ratio (%) $^{238}Pu/^{239(240)}Pu$	Period	^{238}Pu (aCi/m^3)	Activity ratio (%) $^{238}Pu/^{239(240)}Pu$
1963/I - II	n.d.[a]	-	1967/I - III	19 ± 3	84 ± 21
III - IV	n.d.	-			
V - VI	25 ± 7	2,5 ± 0,8	1968/I - III	14 ± 2	67 ± 17
VII - VIII	27 ± 7	2,5 ± 0,7	IV - VI	18 ± 3	28 ± 5
IX - X	11 ± 4	2,8 ± 1,2	VII - IX	10 ± 2	19 ± 3
XI - XII	12 ± 5	5,4 ± 2,1	X - XII	4 ± 1	20 ± 10
1964/I - II	21 ± 6	8,7 ± 2,3	1969/I - III	7 ± 2	32 ± 11
III - IV	15 ± 5	4,0 ± 1,3	IV - VI	9 ± 2	19 ± 5
V - VI	n.d.	-	VII - IX	n.d.	-
VII - VIII	10 ± 4	2,9 ± 1,1	X - XII	5 ± 1	35 ± 10
IX - X	n.d.	-			
XI - XII	n.d.	-			
1965 and 1966	n.d.	-			

[a] non detectable

For financial support of this work the authors are indebted to the Austrian Federal Ministry of Health and Environmental Protection.

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WAVELENGTHS OF THE M X-RAY SPECTRA OF URANIUM, NEPTUNIUM, PLUTONIUM, AND AMERICIUM

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The qualitive and quantitative analysis of the actinides are being increasingly important for the characterization of nuclear fuels in the as-fabricated condition and after the irradiation as well as for the analysis of the residues from the reprocessing of burnt fuels. The identification of these elements requires the precise knowledge of the wavelengths and the intensities of the X-ray emission spectra of the M series which have a favourable wavelength region between 200 and 500 pm for the electronprobe microanalysis. X-ray emission spectra of the M lines of thorium, protactinium, and uranium have been reviewed [1]; further measurements on uranium have also been reported [2,3]. The major M lines of the transuranium elements have been analyzed recently in most cases on metallic specimens of neptunium [4,5,6] plutonium [5,7,8,9], and americium [8].

In this study the complete series of the M lines of uranium, neptunium, plutonium, and americium have been measured between 250 and 520 pm. Sintered UO_2, 2% NpO_2 dissolved in a borosilicate glass, sintered PuO_2, and a two-phase AmAl$_4$-Al alloy have been prepared by the hot cell metallographic techniques. The samples were embedded into araldite resin and were polished with 0.25 µm diamond paste. The homogeneity was checked by a autoradiography.

The instrument consisted of an α and γ shielded electronprobe microanalyzer JRXA 50 (Japan Electron Optics Ltd.) which is connected to a shielded cell. The sample loading was carried out inside of the cell from which an automatic and radiation protected transport into the rear of the instrument was guaranteed. The spectra have been analyzed using a linear spectrometer in Johann geometry with a Rowland radius R of 180 mm and a constant take-off angle of 35° between the polished sample surface and the X-ray which is diffracted on the 10$\bar{1}$1 plane of a quartz crystal (2d = 668.62 pm). The distance b between sample and crystal is not constant but varies linearly with wavelength λ and sin θ, resp. The spectra have been recorded continuously with a proportional counter in cps using 20 kV electron accelerating voltage and 100 to 250 nA sample current (fig.1).The high precision analysis has been made by count rate measurements by varying b in steps of 0.05 mm which are approximately equivalent to 0.093 pm. The wavelength measurements were absolute using the relation $\lambda = b \cdot d/R$ and were calibrated for cross-check using the $M\alpha_1$ lines of internal standards, resp. The error in the wavelength measurements is ± 0.1 pm for the stronger lines; it is ± 0.2 pm for intensities lower than 3% of the strongest line of the respective M spectrum.

The measured wavelengths and the relative intensities ($M\alpha_1$ = 100%) of the M series of uranium, neptunium, plutonium, and americium are given in table 1. The $M\alpha_2$ lines could be detected on the high wavelength tails of the $M\alpha_1$ lines for all four elements investigated. However, they were too weak in intensity for a precise wavelength determination. The $M\zeta$ lines of neptunium, plutonium, and americium and the $M_{III}N_{IV}$ and $M_{III}N_I$ transitions of neptunium and americium have been measured for the first time. The results of the remaining lines of uranium, plutonium, and americium agree very well with the literature values. However, the wavelengths of neptunium are throughout 0.1

to 0.5 pm lower than the values cited in literature in spite of the fact that different internal standards (Ce La_1, Ti Ka_1, Ca Ka_1) were used for the analysis of this element.

Table 1. Wavelengths (in pm) and relative intensities ($M_{\alpha 1}$ = 100%) of the M series of the X-ray lines.

line	uranium		neptunium		plutonium		americium	
	λ	r.i.	λ	r.i.	λ	r.i.	λ	r.i.
$M_I N_{III}$	275.4	1	-	<1	258.1	<1	-	<1
$M_{II} N_{IV}$	281.9	2	272.3	1	264.1	1	255.5	3
$M_I N_{II}$	290.7	1	-	<1	-	<1	-	<1
$M_{III} O_{IV,V}$	295.1	5	286.2	2	278.3	3	270.4	3
$M_{II} N_I$	333.1	2	322.2	2	312.7	3	303.0	6
$M_{III} N_V(\alpha_1)$	347.9	13	338.7	3	329.5	6	320.6	7
$M_{III} N_{IV}(\alpha_2)$	352.0	2	342.5	<1	333.7	1	324.9	1
$M_{IV} O_{II}$	357.6	1	-	<1	336.2	<1	-	<1
$M_{IV} N_{VI}(\beta)$	371.6	180	360.8	72	351.0	67	341.3	64
$M_V N_{VII}(\alpha_1)$	391.0	100	380.0	100	370.1	100	360.2	100
$M_{III} N_I$	433.0	0.5	421.5	0.2	412.2	0.2	402.2	0.2
$M_V N_{III}(\alpha_1)$	494.3	0.9	480.4	0.3	467.2	0.2	454.3	0.2
$M_{IV} N_{II}(\alpha_2)$	504.9	0.6	491.3	0.2	478.4	0.2	466.2	0.2

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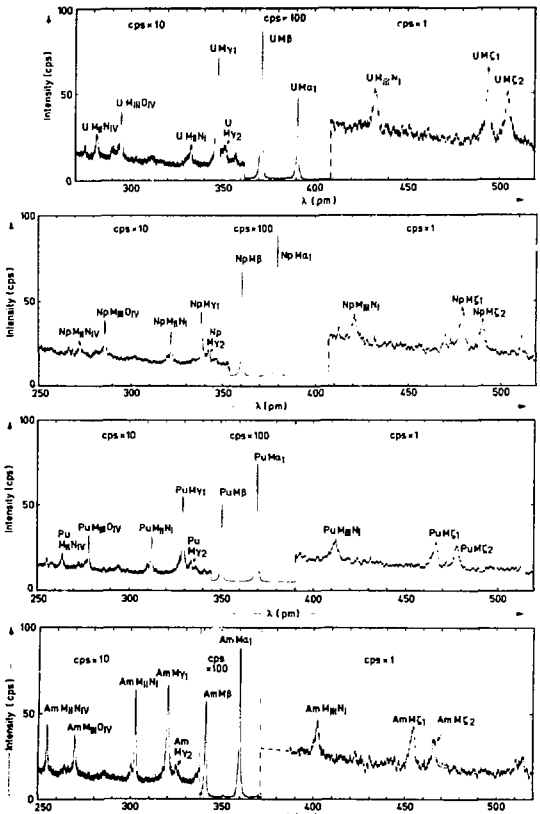

Fig.1 Wavelengths of the M series of the U, Np, Pu, and Am X-ray lines.

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