DEPENDENCE OF ACTINIDE SOLID STATE CHEMISTRY AND PHYSICS ON THE CHANGING ROLE OF THE 5f-ELECTRONS

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Abstract: It is well established that the chemistry, physics, and material science of the actinides do not reflect perfectly a series of elements with a regular increase in the number of localized f-electrons (f-orbital occupation). This situation results from the changing role of the 5f-electrons across the series. Therefore, a full understanding of the properties of the individual elements necessitates an understanding of the series as a whole. The changing influence of the f-electrons is reflected in many of the actinide's properties. Systematic comparisons of selected high-temperature and high-pressure behaviors of actinide materials are discussed to demonstrate the variable nature and roles of the f-electrons, as well as their susceptibility to experimental parameters. Keywords: Actinide Solid State Science; Actinides; 5f-Electrons; High-Pressure Behavior; Cohesive Energies; Enthalpies of Vaporization; Vaporization of Oxides.

1. INTRODUCTION

Some fifty-five years ago it appeared that the Periodic Table of elements had been established fully and consisted of 92 elements. Since then some 16 new elements have been discovered, which not only completed the actinide series but also introduced the transactinide series.

The two f-element series comprise some 28% of the known elements in the Periodic Table. It is acknowledged that the actinide series is the most complex of the two f-series; indeed, the actinide metals alone tend to be the most complex of any metals in the Periodic Table. There is a tendency for scientists to align their interests with either the 4f-elements or the 5f-elements, rather than with the f-elements as a whole. The radioactive nature and scarcity of many of the members, diminishes the incentive to study these elements. Also, an interest in actinides is often limited to a few that have applications in nuclear energy and/or weapons. However, a full understanding of the properties of an individual actinide, or its compounds, necessitates the understanding of the series as a whole, and perhaps an understanding of both f-series of elements.

In principle, the properties of the two f-series should reflect a regular increase in the number of their f-electrons (f-orbital occupancy) when progressing across them. If this process was rigidly followed, elements in each series would be expected to have similar solid state behavior and properties. This arrangement is best approached in the 4f-series, although differences still prevail between these elements. In the actinide series, the 5f-electrons of the earlier members are involved in bonding at room temperature and pressure (itinerant 5f-electrons) and this gives rise to the unique bonding and the complex crystal structures that are well established for them. The transplutonium members of the series tend to be more like the 4f-series, although there are interesting differences result from the greater spatial extension of the 5f-electrons as compared to the 4f-electrons.

Just as the different nature of the divalent lanthanide metals, Eu and Yb, in the lanthanide series should not be overlooked but used to gain an overall understanding of this series, the behavior of all the 5f-elements should also be considered to gain a "big-picture" of the series with regard to f-electron systematics.

Comparisons of the high-temperature and/or high-pressure behaviors of actinide materials demonstrate the variable nature of the 5f-electrons, and their susceptibility to experimental parameters. Two significant
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facets of the high-pressure behavior of the actinide metals are the resistance of the earlier members to structural change, and the inducement of 5f-electron itinerancy in the transplutonium members. The high-temperature vaporization behaviors of actinide metals also demonstrate clearly significant changes in metallic valence across the series, which arises from this variable nature of the 5f-electrons. The changing role of the 5f-electrons is also observed in actinide compounds; for example, in the vaporization of oxides.

Systematic comparisons of chemical and physical properties of the actinides are discussed here to emphasize the changing influence of the 5f-electrons across the series, and how experimental parameters may affect the role of the 5f-electrons in the actinides.

2. General Behavior and Properties

The actinide metals have widely varying physico-chemical properties compared to most other groups of metals in the Periodic Table. This arises in part due to the diffuse nature and extended wavefunctions of the delocalized 5f electrons of early members, and the increasing magnitude of the promotion energies for the 5f electrons of higher members of the series. These factors and their ramifications on actinide properties have been discussed elsewhere [1-3].

It is often informative to compare the lanthanides and actinides in terms of their electronic configuration and the role played by f-electrons. A simple but informative comparison can be made by assigning metallic valencies based on the number of bonding electrons, and examining these assignments in terms of position in the series and the expected electronic configuration. Using this process the actinide metals can be placed in three categories based on their metallic valency; that is, divalent; trivalent; or greater than trivalent. These three actinide groupings are shown in Fig. 1, where they are compared to a similar classification for the 4f-series of elements. The actinides which display itinerant 5f-electrons at normal temperature and pressure (Pa-Pu) plus Th (which does not have an f-electron) are placed in the greater-than-three valency group. In the second group are the normally trivalent metals Ac, Am-Cf, Lr. The third class of actinides, first encountered at Es and extending through No, are listed as divalent metals (like Eu and Yb in the lanthanide series).

Even though the transplutonium elements tend to be more lanthanide-like (e.g., localized f-electrons) at normal temperature and pressure, a significant difference between the two series is observed with the divalency of the Es-No members. The reason for the divalency of these elements is not obvious from their relative positions in the two series; except for No, where a 5f^14 state provides a comparable situation to that for Yb. The divalency of Es, Fm, and Md is attributed to the large promotion energy needed to provide the third conduction (bonding) electron, which is not offset by the additional crystal energy that is gained. Their divalency is a matter of energetics.

Thus, in addition to the first pivotal position at Pu (the last actinide having f-bonding at normal conditions), there is a second pivotal change in the series at Es (which presumably extends through No) with the introduction of divalent metals. Most of the above mentioned solid state properties and these two pivotal positions in the series reflect a changing role of the 5f electrons; from being itinerant to localized; and from the change in their promotion energies [1].

3. Structural and Other Considerations

The trends observed with crystal structures and atomic volumes of the actinides strongly reflect this changing role of the 5f electrons (and the metallic valency) across the series. Excluding the special cases of Ac and Th (absence of f-electrons; d-electron bonded metal), the Pa-Pu metals are characterized by
half of the lanthanide series. The divalent structures of the lighter lanthanides rather than the hcp structures observed in the second half of the lanthanide series. The divalent metal, Es, exhibits a fcc structure [4,6] as does divalent Yb metal. The divalent metals, Fm, Md, and No, for which structural data do not exist, may also crystallize in such an fcc structure.

It is apparent that the actinides, Pa-Pu, which have itinerant f-electrons form more complex structures than do the transplutonium elements, which have localized f-electrons. It is important to note that the four trivalent transplutonium metals, Am-Cf, exhibit isostructural alpha phases (which are also isostructural with several of the lanthanides), while the alpha forms of Pa-Pu elements, even neighboring members, are not isostructural.

The high-temperature phases of the Th-Pu metals tend to form more symmetrical structures with temperature (cubic); the transplutonium metals, Am-Cf, also have high temperature cubic structure but it is fcc (at least initially) rather than bcc, as exhibited by their lanthanide counterparts. There is evidence from dilatometry [7] and differential thermal analyses that Am [8] and Cm [9] do form a third bcc (gamma) phase just prior to melting but X-ray confirmations have not been acquired for these bcc structures. Summaries of the lattice parameters and structure types for the actinides [4] and for the transplutonium metals [5] are available.

Values for the lattice parameters of the beta (fcc) forms of the transplutonium metals acquired by quenching from high pressures [9], have resolved apparent discrepancies that appeared to exist between the atomic volumes of the alpha and beta forms. Previous parameters acquired from thermal quenched samples of the high temperature beta phase of Cm, Bk, and Cf were too large; the pressure-quenched parameters now give excellent agreement between the alpha and beta forms. Subsequent data on the beta forms of Cm [9] and Cf [10] obtained recently from thermal treatments have confirmed these smaller parameters.

An interesting aspect of the changing role of the f-electrons across the actinide series is that it often varies with the particular material being considered. The elements themselves are the most affected and the more ionic materials seem to be the least affected. This can be illustrated comparing the structural properties of the metal, monopnictides, and oxides. With the metals, as discussed above, the atomic volumes of the actinides are essentially all smaller than those of the lanthanides; the most significant differences occur with the lighter (Pa-Pu) actinides. With the monopnictides (e.g., nitrides, bismuthides; mainly isostructural NaCl type structures), the lattice parameters
of the early actinide members are smaller than those of the lanthanides (probably due to "additional" bonding) but those of the transplutonium compounds are nearly identical or slightly larger than with the parameters for their lanthanide homologs. With the sequioxides, the relationship between the lattice parameters is more consistent, but the parameters for the actinides sesquioxides are all slightly larger than those for their lanthanide electronic homologs. The important point is that systematic comparisons of such properties show the changing role in bonding in the actinide series as a function of the material as well as position in the series.

This changing role of the f-electrons should also be important in the alloying behavior of these elements. It would be expected that the itinerant f-electron metals would be more compatible in alloying with other f-bonded metals, as compared to localized f-electron metals. Localized f-electron metals should alloy better with other localized f-electron metals of the same metallic valence. Alloying should be more probable when the solute and solvent have the same metallic valences, bonding, and structures types. Divalent metals would not be expected to have a significant solubility in the trivalent metals. An interesting case arises with Pu metal, as it has available several almost equivalent electronic levels; for example, the population of different levels is affected by temperature. Thus, Pu metal may be able to "adapt" to alloying with other metals better than the other f-bonded actinide metals.

4. Vaporization of the Actinides

One of the important bulk properties of an element is its enthalpy of vaporization, which can be a measure of its cohesive energy. The magnitude of a metal's enthalpy can be used to assign a metallic valence; that is, the number of electrons that are involved in its conduction band. This valence is useful for systematic comparisons between the elements and also reflects the changing nature of the f-electrons across the actinide series.

One of the most common methods to determine a metal's enthalpy of vaporization is to measure the equilibrium partial pressure of its atomic vapor as a function of temperature. These partial pressures are determined often by Knudsen effusion, and this technique has been used for many of the pure actinide metals through Cf [11], and for alloys of Es [12] and Fm [13]. An enthalpy of vaporization has been estimated for Md [14] based absorption data using tracer quantities of the element [15].

Comparisons/assessments of actinide enthalpies of vaporization can be accomplished by simply establishing a grid network which employs the enthalpies of vaporization of the lanthanides, Ba, and Hf as reference values [13]. Grid lines drawn at about 45, 100, and 140 kcal mol\(^{-1}\) (188, 418 and 586 kJ mol\(^{-1}\)) form regions of divalent, trivalent, and greater-than-trivalent, metallic valencies. By plotting the enthalpies for the actinide metals such a grid, it is possible to assign a grouping of metallic valences (see Fig. 2).

![Fig. 2. Enthalpy of Vaporization of the f-Elements.](image-url)

For the early members of the actinide series (neglecting Ac for which an experimental value is not available) such an analysis suggests metallic valencies of greater than three (enthalpies greater than the trivalent lanthanides), in accord with the greater bonding afforded by the itinerant f-electrons. The enthalpies for these early members then establishes one grouping for the actinides (Th-Pu). The inclusion of Pu in this group must also be based on other factors, (its high viscosity in molten form, high boiling point, etc.). The magnitude of its enthalpy of vaporization could suggest a trivalent metal in its liquid state (from which it vaporizes); its
The principal effect of pressure on the actinide metals is to decrease the separations between the atoms and between their orbitals; the opposite effect that is obtained by raising the temperature. Given the pressures and temperatures available in the laboratory, a far greater magnitude of change can be acquired with pressure. Many materials can be reduced from one third to one half of their original volumes by pressures attainable in the laboratory, which can bring about interesting changes in bonding and structure.

Given that the early members of the actinides already have itinerant f-electrons and complex bonding at room pressure, it is not surprising that these "rigid" structures may be the least affected by applying pressure; or that very high pressures would be needed to force changes. From studies with diamond anvil cells that have been published to date [17,18] this is basically the behavior that has been observed with the Pa-Pu elements under pressure. Very recently, a new study of Th [19] up to 300 GPa of pressure has shown that it undergoes a phase change at 100 GPa from its fcc structure to a tetragonal structure (which may be similar to, or the same as, the structure of Pa). The implication of this structural change is that the 5f band of Th, which is normally above the Fermi level, has now become involved in the metal's bonding under pressure.

In contrast to the behavior of the lighter actinides, the first four transplutonium elements exhibit 2 to 3 structural changes, and ultimately adopt the alpha-uranium structure under pressure. The formation of the latter structure has been interpreted as signifying that partial f-electron delocalization has occurred in these metals, and the 5f-electrons are now partially involved in the metallic bonding. That is, an experimental parameter, pressure, has affected their f-electrons so as to force them to become itinerant f-electrons.

The structural sequence observed with the transplutonium metals with increasing pressure is: dhcp-fcc-distorted fcc (trigonal)-orthorhombic. Both Am and Cf form this distorted fcc phase while Bk and Cm metal do not. Data do not exist for the pressure behavior of actinides above Cf (see Fig. 3). This above pressure sequence is qualitatively the same as observed with the lanthanides (hcp-Sm type rhombohedral-dhcp-fcc-distorted fcc-low symmetry structure), although the initial structure may be different. The significant point is that the lanthanides may also have their f-electrons forced into bonding by pressure, and then exhibit structures known for, or that are similar to, those for the f-bonded actinides. Thus, under pressure; Ce [20] and Sm [21] eventually form b.c. tetragonal structures (like Pa, or Th at high pressure); Pr forms the alpha uranium structure [22]; and Nd forms a low-symmetry, monoclinic structure [23].
The bulk modulus of a metal can be extracted from its pressure behavior (e.g., from the relative atomic volume as a function of pressure). This modulus indicates the resistance of the metal to compression and reflects the rigidity/strength of the metallic bond. It can be used for group classification of metals. The greater the number of bonding electrons, the smaller the compressibility, the greater the rigidity, and the larger the modulus. The moduli are larger for the Th-Pu actinides than for the transplutonium metals, which are comparable to those for the trivalent lanthanide metals. Much smaller moduli are found with divalent Eu and Yb.

Thus, the changing role of the f-electrons in the actinide series is reflected in structural behaviors under pressure and in the magnitudes of bulk moduli. The susceptibility of these f-electrons to an external parameter, pressure, further emphasizes the dependence of the chemistry and physics of the actinides on the behavior of their 5f-electrons.

6. High-Temperature Behavior of Oxides

Actinide oxides display a variety of oxidation states with the highest binary stoichiometry in the series being achieved with UO₃. The variation in oxidation states for the actinide oxides results from the close proximity of the 7s, 6d, and 5f electrons. The largest number of electrons used for bonding in the oxides are incurred with the Pa-Pu group, as found with their metals. After Np, the highest binary oxide that forms is the dioxide; if Ac is excluded, Pu becomes the first actinide to exhibit a sesquioxide (see Fig. 4). The highest oxidation state displayed by an actinide is frequently not observed in its binary oxides.
There has been only a limited number of studies of the vaporization/decomposition of transplutonium sesquioxides. For Pu$_2$O$_3$, the vaporization/decomposition process has been reported to proceed mainly via the generation of PuO [25, 26]. Even with PuO$_2$, the major species is PuO with very small amounts of PuO$_2$ also being vaporized. Even less information is available for the Am$_2$O$_3$ system [26], although additional unpublished data also exist on it [10, 27]. The process for this oxide is mainly by generation of atomic Am vapor and oxygen. With Cm$_2$O$_3$, the actual vapor species have not been established directly by mass spectrometry but inferred from correlations of the data [28]. Vaporization/decomposition is believed to proceed via generation of CmO and oxygen vapors. We have recently initiated studies of some of the higher transplutonium sesquioxides. With Cf$_2$O$_3$ [29], one observes atomic Cf vapor and oxygen as the products; preliminary work with Es$_2$O$_3$ [10] suggests its behavior is similar to that of Cf$_2$O$_3$. It is expected that for the sesquioxides of higher actinides (e.g., Fm-No) that their vaporization will also generate atomic actinide vapor while Lr$_2$O$_3$ would be expected to generate LrO$_2$.

Which volatile product is observed for the vaporization/decomposition process of the sesquioxides can be linked to the changing role of the 5f-electrons; not merely to oxidation states, but to the 5f-electrons in the elements. The magnitude of the dissociation energy for the monoxides, which determines whether atomic or monoxide species are the major product, reflects inversely the magnitude of the promotion energies for the $f^9s^2$ to $f^{n-1}d^{2}z$ transitions in the elements.

Thus, the greater the promotion energy, the smaller the dissociation energy of the monoxide, and the greater will be the likelihood that the sesquioxide will vaporize/decompose to yield atomic vapor. Thus, although one might expect that Eu$_2$O$_3$ and Yb$_2$O$_3$ (which are known to have divalent oxidation states) might readily form monoxides upon vaporization, instead they form Eu and Yb atomic vapor. The monoxides of these two elements have the lowest dissociation energies and the highest promotion energies in the lanthanide series. The behavior of the transplutonium sesquioxides also seem to fit this scheme. In Fig. 5 the monoxide dissociation energies for the lanthanide [24] and the lighter actinide [26] oxides are plotted as a function of their positions in each series. The extrapolated line for the higher transplutonium elements is in accord with the recent experimental observations for Cf$_2$O$_3$ and Es$_2$O$_3$[10].

Fig. 5: Dissociation Energies of f-Element Sesquioxides,

7. Concluding Statements

From the above discussion, it is clear that a great deal of the solid state chemistry, physics, and material science of the actinides is dependent on the changing role of the 5f-electrons across the series. Indeed, the actinides do not reflect perfectly a series of elements that regularly increases the f-orbital occupation across the series. As a result of this changing role of the 5f-electrons, which can be sensitive to experimental parameters, complex and rapidly changing behaviors are often observed. Thus, the 5f electrons may be considered as "pseudo-active" electrons. Most importantly, a full appreciation and understanding of the behaviors of individual actinides necessitates an understanding of the series as a whole.

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