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Insights into the bonding and electronic nature of heavy element materials☆,☆☆

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Abstract

A long standing issue in heavy element science is what role electrons, especially the f-electrons, play in chemical and physical behaviors. This interest prevails not only for changes found between the two f-electron series and for the different elements in one series, but also for comparing a particular element's behavior in its elemental and combined states. Different types of experimental approaches over the years have been employed to probe and evaluate the nature of bonding and electronic configurations in these materials. In some instances the conclusions arrived from experiment and theory have differed, but theory and experiment have recently become more encompassing, sophisticated and in better accord with one another. Interpretations about the electronic interactions and bonding at ambient or elevated temperatures in the f-elements have been employed for many years and have generated important and guidelines Structural behaviors under pressure and the associated correlations with bonding via experimental methods have become especially enlightening in this regard. These experimental findings also generated increased theoretical efforts to probe these changes and offer new insights. Selected aspects of results obtained to date for f-electron materials using different experimental approaches and conditions will be examined and discussed here with regard to electronic configurations and the potential changes that occur in bonding. A useful approach in this regard is to employ correlations to establish trends as a function of electronic nature and configurations. Findings using this approach will be discussed here and compared to computational results for several materials.
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Keywords: Actinide metals; Alloys and compounds; Structure and bonding

1. Introduction

An important issue in heavy element science is the changing role of the f-electrons, both when progressing from element to element across the series, as well as how experimental variables affect the roles played in the elements' chemistries and physics. It has been well established that the function of these f-electrons can be changed by experimental conditions: temperature and pressure being two of many such variables. It is well recognized that at atmospheric pressure and 273 K the transplutonium elements have localized, non-bonding 5f-electrons and exhibit greater atomic volumes and more symmetrical crystal structures than the four elements accepted as having itinerant 5f-electron character (e.g., protactinium through plutonium). In the case of thorium, it often is considered as reflecting bonding more associated with transition metals (e.g., d–s type bonding) although theoretical considerations have even attribute some fractional 5f character to its bonding. The smaller atomic volumes and more complex crystal structures of the protactinium through plutonium metals result from the greater degree of metallic bonding from involvement of their 5f-electrons. Their structures arise as they offer the lowest energy state for their hybridized electronic bands involved in their bonding, rather than merely reflecting the directional character of atomic 5f-orbitals. The transplutonium elements with localized 5f-electrons display structures observed with the lanthanide and many transition metals. This overall situation is reflected in the well-known change in atomic volume with atomic number and expected f-electron count (Fig. 1).

In the two f-electron series, even larger atomic volumes are observed for the elements having only two bonding electrons

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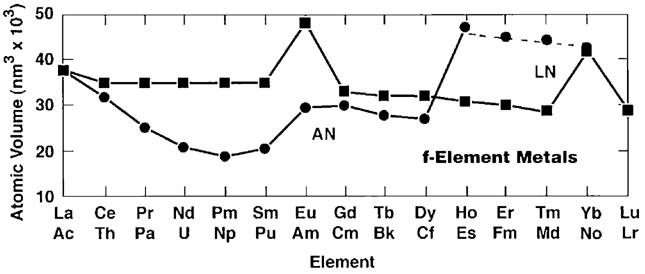

Fig. 1. The atomic volumes of f-elements at atmospheric pressure reflect the interplay between volume and bonding modes. [The extrapolated volumes for Fm, Md and No suggest a volume curve for the divalent metals.].

(europium, ytterbium, einsteinium, fermium, nobelium and probably mendelevium). A dashed line is shown in Fig. 1 to reflect the expected volumes for these three metals. Although experimental volumes for fermium and mendelevium have not been determined, other information supports their divalency. This dashed line can be extended back to europium, and it would then represent a volume curve for the divalent actinides. Therefore, not only are their 5f-electrons localized, but their bonding would involve only two electrons.

The reason is for this divalency is more readily understood at first glance for europium, ytterbium and nobelium, where half-filled or filled f-orbitals are encountered, but less clear for the einsteinium, fermium and mendelevium cases. And, the reason that americium (that might be expected to behave as an electronic homoilog of europium), is not divalent and has a smaller atomic volume is not immediately obvious. These differences are understood by the concept of promotion energies (see subsequent section).

The well-established atomic volume relationship for these f-electron elements displayed in Fig. 1 allows another aspect to be considered—essentially an inverted concept. That is, what would be the bonding consequences of reducing the atomic volumes of these metals with localized f-electrons by pressure? This aspect will be discussed in a section about the effects of pressure.

Topics presented here consider the correlation of electronic states and changes encountered in the gas and condensed phases, when 5f-promotion energies (5f → 6d) may or may not be appropriate for understanding the chemistry/physics and bonding changes, including bonding changes brought about from reduced atomic volumes.

2. Applicable experimental and theoretical approaches

For examining differences between the gas phase and solid phase, it is useful to compare the electronic energy levels of neutral configurations of individual atoms and those expected in the elements in the condensed phase. The levels in neutral configurations of the atoms have been compiled from large amounts of experimental data, most often from vapor discharge lamps [1]. Configurations for the solids are taken from current understandings or are represented here as a generic format for a hybrid-type system representing an overlapping band structure, signified as having an "$5f^x6d^y7s^2$" outer configuration.

The nature and values for many of the actinide enthalpies of vaporization [2–6] and adsorption [7–9] have been published and summarized, and the techniques employed are discussed. The most recent enthalpy of vaporization-type studies were performed on einsteinium and fermium some years ago [10] while the most recent enthaplies of adsorption have been reported for curium, berkelium together with partial data for lawrencium [11], which represents some of the only information for it.

High-pressure techniques with and without synchrotron radiation have been discussed in several publications. A summary of synchrotron techniques for such experimental work is available [12] while specific efforts on americium [13–16] protactinium [17] and curium [18] are published. One overview of such actinide pressure studies has also been given [19].

3. Computational approaches for actinides with localized 5f-electrons

The most recent computational results for total energies of structures and an equation of state for the higher actinide metals addressed here were obtained by density-functional electronic structure calculations. Söderlind [20] and Söderlind and Landa [21,22], used an all-electron full potential linear muffin-tin orbital method (FPLMTO) and Pénicaud [23–25] has employed a fully relativistic, all electron full potential augmented plane wave program for americium. Calculations on curium metal [18] also used an all-electron full potential linear muffin-tin orbital method (FPLMTO), where basis functions, electron densities and potentials were calculated without geometrical approximations. Curium presents a special case, where magnetic interactions are encountered [18] and these must be taken into account in the calculations. A slightly different computation approach has been used for americium by Savrasov et al. [26], which derived the involvement of a different set of orbitals. An extensive discussion of computational approaches was also just published by Kotliar et al., which addresses current problems with computational methods [27]. High-pressure behavior of actinides have also been approached from basic concepts employing analyses of physical properties, compressibility and the distribution of electrons between inner and outer shells by Nadykto and Nadykto [28] and by Nadykto [29] to arrive at electronic structures.

4. Correlations of actinide electronic configurations

The electronic configurations of many isolated actinides in the vapor state have been reported [1] for their ground states and several excited states. The configurations for the condensed state are more complicated and are altered by different influences and total energy considerations. The physical state, temperature, specific phases, magnetic and electronic spin interactions all may be critical parameters for the electronic configurations and bonding behaviors displayed by these 5f elements. Correlations of behavior with these specific structural parameters can often provide unique insights and understanding of the elements' bonding behaviors under different conditions (Table 1).

Table 1
Outer electronic configurations

An	Gas	Solid[a,b,c]	An	Gas	Solid[a,b,c]
Ac	$6d7s^2$	Same	Bk	$5f^97s^2$	$5f^86d^17s^2$
Th	$6d^27s^2$	"Same"	Cf	$5f^{10}7s^2$	$5f^96d^17s^2$
Pa	$5f^x6d^y7s^2$	$5f^x6d^y7s^2$	Es	$5f^{11}7s^2$	Same
U	$5f^36d7s^2$	$5f^x6d^y7s^2$	Fm	$5f^{12}7s^2$	Same
Np	$5f^46d7s^2$	$5f^x6d^y7s^2$	Md	$(5f^{13}7s^2)$	Same
Pu	$5f^67s^2$	$5f^x6d^y7s^2$	No	$(5f^{14}7s2)$	Same
Am	$5f^77s^2$	$5f^66d^17s^2$	Lr	(5f146d7s2)	"Same"
Cm	$5f^76d7s^2$	Same	[Lr	$(5f^{14}7s^2p_{1/2})$?]	

[a] $f^xd^ys^2$ signifies an overlapping band.
[b] "Same" signifies a similar configuration to that in the gas phase.
[c] ds^2 or dsp bonding.

At the risk of oversimplification, some feeling for the differences between the configurations of gaseous atoms and those in the solid state can be seen in the listing shown in Table 1. Here, only the outer orbitals are indicated for the ground states and the "$f^xd^ys^2$" notation shown indicates an overlapping electronic band formulation. The term, "same" for the condensed state of thorium in the figure ignores the potential for some 5f-electron character being present. The latter situation is accepted to occur for thorium under pressures of a megabar [30] where experimentally a change in structure is observed to occur.

In Table 1 it is of interest to note that plutonium is divalent in its atomic state but in the solid state it is one of the most complex metals in the periodic table, and several of its six different phases are expected to have some degree of overlapping of electronic bands with the 5f-electrons in the bonding. With americium, berkelium and californium, they are divalent in their atomic vapor states, but in the condensed states are trivalent metals. Einsteinium and fermium are divalent in both their atomic and condensed states. Experimental data do not exist for mendelevium and nobelium but one may assume they behave like einsteinium and fermium, as indicated by the larger volumes shown for them in Fig. 1. Finally, experimental structural data are not known for lawrencium but it is expected to behave like curium; trivalent in both the vapor and condensed states. It has been suggested that lawrencium could be unique due to relativistic effects and assume a configuration having a single $p_{1/2}$ state as indicated in Table 1. This would offer the potential for a monovalent state, but apparently this does not occur as the difference in energy is too small. Some evidence from adsorption enthalpies (see later section) supports the trivalent state for lawrencium [11].

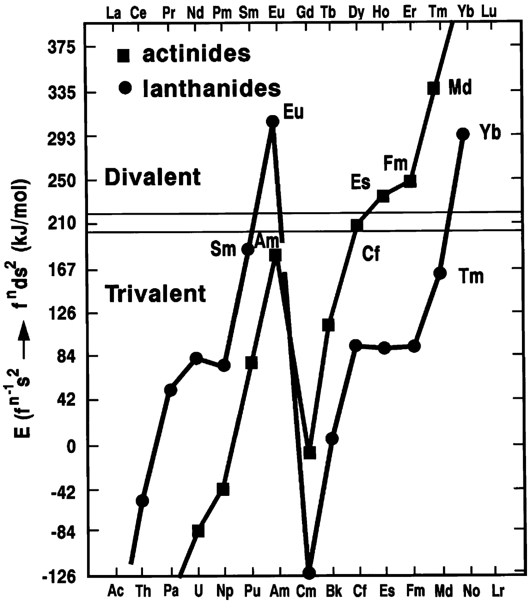

Fig. 2. Plot of promotion energies for f → d conversion in the two f-electron series of elements.

The simplified outline in Fig. 2 and Table 1 indicates the complexity of the actinides and their electronic behaviors. The smaller atomic volumes and more complex crystal structures of the protactinium through plutonium metals then are attributed to the greater degree of metallic bonding due to involvement of the 5f-electrons in their bonding. In contrast, the volume and crystal structure of the divalent and trivalent actinides also reflect the different bonding present in them.

5. Promotion energy

An important concept for these actinides and nature of their bonding is promotion energy, the energy needed to promote an f-electron to a d electron state. These promotion energies for the two f-electron series are shown in Fig. 2. Some implications and/or applications for these promotion energies are listed in Table 2. The specific bonding and metallic divalency observed for these 4f- and 5f-electron divalent metals and why americium is not divalent like europium are explained on the basis of these promotion energies. For the divalent metals, they are divalent due to their higher f → d electron promotion energies, which prevent promotion of an 5f-electron to a 6d orbital for bonding. The latter promotion occurs to enable the formation of the trivalent transplutonium elements. Thus, the bonding in these divalent metals is similar to that in the elements' vapor states rather than acquiring additional bonding from a promoted f-electron for the trivalent localized f-electron metals.

For these divalent metals, the promotion energy required is larger than the crystal energy attained by gaining an additional bonding electron, and the element remains divalent. For americium, the crystal energy required from the additional bonding of a third electron is larger than needed for promoting a 5f-electron to a 6d-state, and promotion occurs. This is not the case for europium and it remains divalent. Thus, the concept of f → d promotion, specifically the f^n to $f^{n-1}d$ promotion energies, are

Table 2
Applications of promotion energies correlations

- The f → d energies explain the divalency of the Es through No elements
- The nature/trends of vaporization enthalpies
- Potential for understanding pressure behavior
- The reactivity of gas An + ions ("d–s states")
- The stability of monoxides ("d–s states")
- Use to "track" solution oxidation potentials
- More!

a useful and important concept, which has been discussed and some applications for them applied [3,31,32].

In addition, there are also $f^n d \rightarrow f^{n-1}d^2$ promotion energies [3], which in principle would provide four bonding electrons when including available “s” orbitals, but this concept is not appropriate in the case of the protactinium through plutonium elements; rather than involving promotion of f-electrons to d-states, the bonding of these lighter actinide elements involves overlapping bands with the f-electrons (e.g., generating itinerant 5f-electron behavior).

These promotion energies are also useful for discussing the reactivities of gaseous actinide and lanthanide ions (e.g., reactions with M+) and the thermal stability of monoxides [31,32]. One can also “track” and explain the oxidation potentials ($E^0(M^{3+}/M^{2+})$ and $E^0(M^{4+}/M^{3+})$ of the f-electron elements using these promotion energies [1]. Another important application for these promotion energies is their correlation with the variation of the enthalpies of vaporization or adsorption, and what role they may play in high-pressure behaviors. These questions are addressed in subsequent sections.

6. Enthalpies of vaporization and adsorption

Enthalpies of vaporization and/or adsorption for the actinides are thermodynamic quantities. A systematic review and discussion of these and others properties appear in reviews, two being one by Ward et al. [4] and a more recent compilation by Konings et al. [6]. Vapor pressure measurements together with other thermodynamic parameters can be used to derive enthalpies or heats of sublimation, and such experimental measurements have been made for the actinides through fermium. Data for einsteinium [33] and fermium [10] were acquired through a special technique with alloys because of the limited materials available. A complimentary technique permits the determination of the enthalpies of adsorption, which allows studies of very small quantities of material. This approach has been discussed [7–9]. In essence, the sublimation enthalpy reflects energy to vaporize while the adsorption enthalpy looks at the energy for deposition of the vapor. This latter technique is very useful for the transfermium actinides and the transactinide elements, where the number of atoms is scarce and may involve as little as a few atoms.

These two approaches are represented in Fig. 3. Drawbacks in the adsorption approach are the less direct thermodynamic basis and variability of results with the material being used for the adsorption surface. Adsorption enthalpy studies have been reported and discussed for the actinides from curium through lawrencium elements [11].

These enthalpies can be related to the electronic configurations and metallic valences of the f-electron elements, and reflect the promotion energies that have been discussed above. The trends or variations for both of these enthalpies are understood in terms of the electronic states of the condensed and vapor states of the atoms; for the elements with a divalent atomic state and a trivalent condensed phase, the variations are essentially the differences between the electronic levels of $f^n s^2$ and the $f^{n-1}ds^2$ states. The lower values and the similarities for the divalent lanthanide and actinide elements reflect their similar bonding states in the gas and condensed states. The higher enthalpies for the thorium through neptunium elements then reflect the greater number of “effective” bonding electrons.

The variation of the enthalpies of sublimation for the two f-series is shown if Fig. 4, where estimations for mendelevium, nobelium and lawrencium are necessary due to an inability to obtain experimental data. The two values indicated for lawrencium in Fig. 4 depend on which electron configuration is accepted for it (see Table 1); very likely, its enthalpy of sublimation is in line with that for curium. The trends and values obtained for the two different enthalpies are displayed in Fig. 5. Included in this figure are also the values estimated for the first two transactinide elements (elements 104 and 105), which presumably have “effective” metal valances above three. Preliminary data for the enthalpy of adsorption for lawrencium [11] supports the contention that this element is trivalent and not monovalent.

Several in depth attempts [7–9] to interrelate these adsorption and vaporization enthalpies; such a correlation would provides a more uniform concept for evaluating electronic behavior via

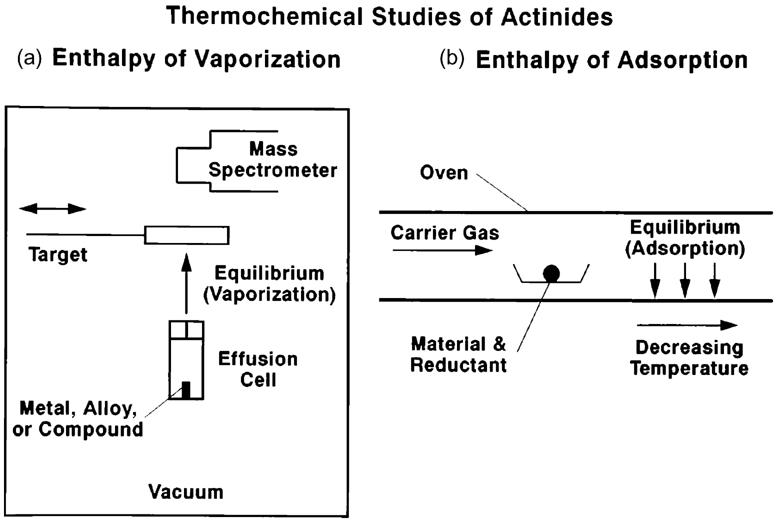

Fig. 3. Schematic for the experimental techniques used to determine the enthalpies of sublimation and adsorption.

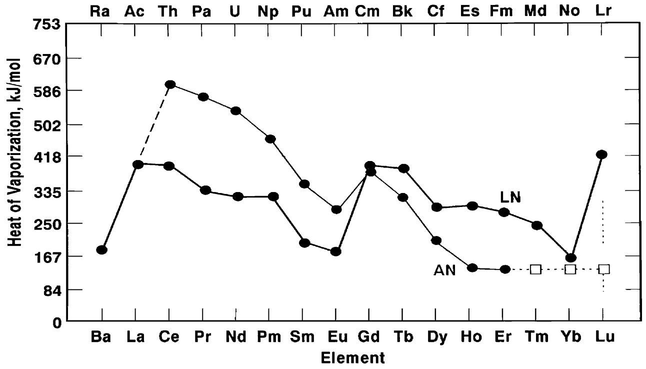

Fig. 4. Variation of the enthalpies of sublimation for the two f-electron series of elements.

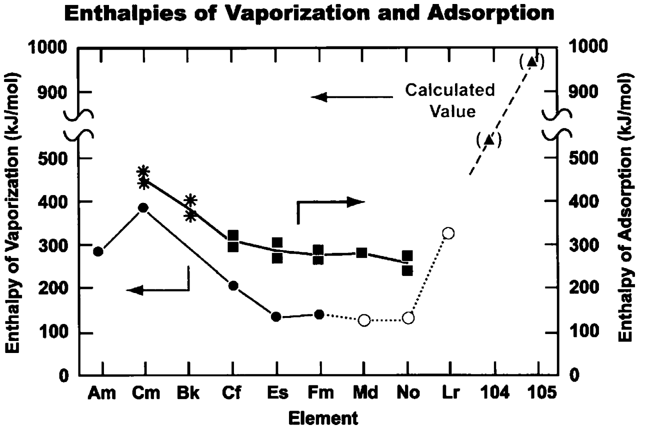

Fig. 5. Comparison of the enthalpies of vaporization and adsorption for selected actinides and the first two transactinide elements.

these different enhalpies. This would allow extending the comparisons of the f-elements with the transactinide elements, as suggested from the data in Fig. 5.

7. The effect of pressure on bonding

The change in interatomic distances and atomic volumes plays a significant role in total energy of the system and the particular bonding and structures that are acquired. In conjunction with Fig. 1, it was mentioned that changing the atomic volumes should perturb the bonding, electronic configurations and total energies of the f element materials. For example, the question becomes when the volumes of the actinide trivalent metals are reduced to the atomic volumes displayed by the protactinium through plutonium elements, what would happen with their bonding? Further, if the volume of a divalent metal is reduced to that of a trivalent metal, what changes in bonding would be expected?

It has been found that when the volumes of the trivalent elements, americium and curium with localized 5f-electrons, are reduced significantly they acquire 5f-electron character in their bonding and adopt lower-symmetry structures characteristic of the protactinium through plutonium metals at atmospheric pressure [13–16]. Thus, the 5f-electrons of several actinide metals, their alloys and compounds are affected greatly by pressure, due to the very large decreases in interatomic distances encountered under pressure. The latter can bring about significant changes in the energy levels and the potential for overlap or hybridization of electronic orbitals. In contrast to the behaviors of the elements, changes observed with compounds are often not be linked directly to the involvement of 5f-electrons, due in part to the presence and bonding role of non-actinide atoms. The latter effect both interatomic distances and the type of electronic orbitals that are interacting. The changes in bonding and the electronic behavior of metals and alloys from the application of pressure provide different insights into the materials than examined by other techniques and under different conditions. The decreasing interatomic distances occurring under pressure alter energy levels and certainly provide an increased potential for overlap or hybridization of electronic orbitals.

In contrast, changes observed in compounds under pressure may or may not reflect the involvement or participation of the f-electrons. This difference with compounds reflects the presence of the non-f element atoms and their bonding roles, which affect not only the interatomic f-element distances but also the type of electronic orbitals that can interact.

8. Americium and curium under pressure

Studies with americium under pressure have probed electronic interactions and bonding as a function of decreasing interatomic distances. In essence, to determine if decreasing its atomic volume would force this element to adopt the bonding similar to that which exists in the protactinium through plutonium elements. It was determined that under pressure americium underwent: (a) dynamic compression and (b) structural transformations, which in some instances were accompanied by “volume collapses”. The two changes in (b) have been interpreted as reflecting the onset or changes in the 5f-electron bonding in the element. By applying pressure both the structural and bonding nature of materials can be altered. Using pressure, one can “tune” the electronic band structure and the density of states at the Fermi level, and the results can be used to correlate the different behaviors with the electronic configurations and nature of the elements.

The most recent experimental studies of americium [13–16] have shown that it undergoes three structural transformations up to 100 GPa. The four structures associated with its pressure behavior have been designated as Am(I), Am(II), Am(III) and Am(IV), and this terminology has carried over to the behavior of curium under pressure. Although curium may be expected to behave like americium under pressure, it has been determined that a unique intermediate structure and bonding behavior is encountered in it under pressure due to spin polarization effects [18]. The structural behaviors of americium and curium under pressure are compared in Fig. 6.

The structural behavior of americium as a function of pressure, displayed shows the first two structures Am(I), a double hexagonal close packed (dhcp) structure, space group $P6_3/mmc$; Am(II), a face centered (fcc) structure, space group $Fm3m$). Both represent situations where the f-electrons are believed to be fully localized from an experimental perspective. Both structures

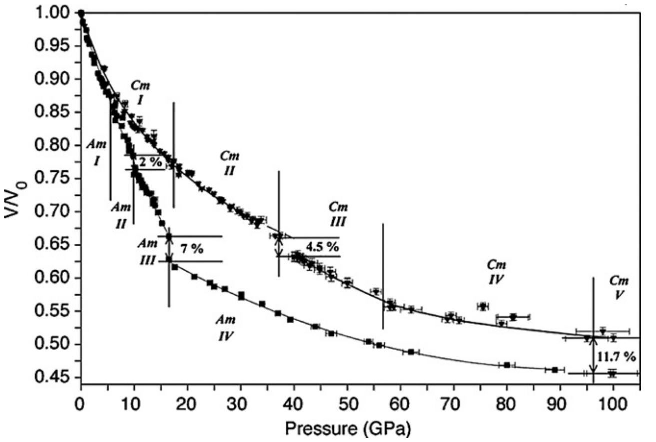

Fig. 6. The high-pressure structural behavior of Am and Cm metals up to 100 GPa.

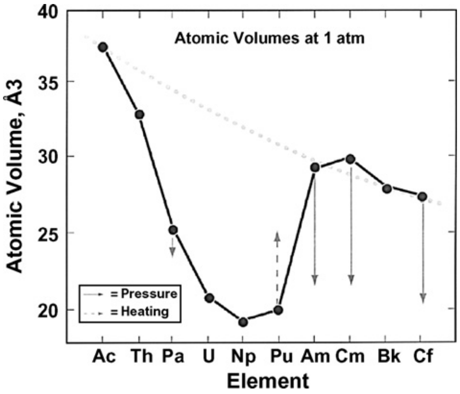

Fig. 7. The atomic volumes of selected actinides showing the effects of temperature and pressure. [The solid arrows point to pseudo volumes expected if the high-pressure phases were retained at one atmosphere. The broken arrow for plutonium indicates the volume change resulting from phase and bonding changes by heating at one atmosphere].

are known to exist at atmospheric pressure and room temperature. While the fcc phase is often considered a high-temperature phase, it is also a high-pressure phase. It can be retained at atmospheric pressure and 25 °C, by quenching from elevated temperatures at one atmosphere or higher pressures at 25 °C. The fcc phase exhibits an identical atomic volume as the dhcp phase at atmospheric pressure and 25 °C [38]. To a first approximation, this implies similar bonding may exist in the two phases, perhaps differing only in small differences in the d-band content and in the total energy of the system.

With additional pressure, two other structures of americium were found: (a) an orthorhombic Am(III) structure, space group *Fddd*; at higher pressures a second orthorhombic Am(IV) structure, space group *Pnma*) [13–16]. Both of the phase transitions were accompanied by "volume collapses" (changes in V/V) of 2% and 7%, respectively). The Am(III) structure is isostructural with the γ-Pu structure, where plutonium is believed to have partial itinerant (bonding) 5f-electrons. This supports that the Am(III) phase may also have acquired 5f-electron participation in its bonding.

The Am(IV) structure is very similar to that for the *α*-U structure, but has a slightly distorted arrangement of a few atoms. It is accepted that there are itinerant 5f-electrons in this structural form of uranium, which thus suggests that this is also the case for americium in the Am(IV) phase The compression behavior (their "stiffness", which reflects the degree of bonding present in materials) of the Am(IV) phase was found to be very similar to that in α-uranium. This would be expected if the bonding in both metals had similarities (e.g., some 5f-electron involvement in their bonding).

Thus, the picture emerging from the experimental studies on americium is that pressure forced the delocalization of americium's 5f-electrons in two steps: first, partial delocalization in Am(III); then full delocalization in Am(IV) [13–16]. The 'volume collapses and their magnitudes in the volume-pressure behaviors are also taken as reflecting and supporting these conclusions.

Extrapolation of the atomic volume of Am(IV) back to atmospheric pressure to (e.g., estimating the atomic volume at one atmosphere for this structural form of Am) produced an atomic volume compatible to those for the uranium through plutonium metals at atmospheric pressure. This "adjusted" atomic volume for americium, if it existed at atmospheric pressure, would eliminate the large jump in volume in going from plutonium to americium that is seen in Fig. 7. That is, the large difference in volume normally encountered in going from plutonium to americium is clearly seen as being due to differences of 5f bonding normally found in these elements.

8.1. Experimental results—curium

Curium lies at the middle of the actinide series and has a half-filled, 5f shell with seven electrons residing inside of a radon core, as opposed to the six f-electrons found with americium. While americium is non-magnetic given its $5f^6$ configuration (see later section, *Bonding in Americium*), curium is magnetic and has an experimental moment of about $8\mu_B$ for its dhcp structure at atmospheric pressure. These actinides are near neighbors in the series and both have localized 5f-electrons at atmospheric, pressure. One may then expect that comparable phase transformations in Cm should occur at higher pressures, as its 5f-electron core is "pulled in" due to a greater nuclear change (increased atomic number). It would be expected that this would require higher pressures to force involvement of curium's 5f-electrons into bonding. The stabilizing effect of a half-filled 5f state (seven localized 5f-electrons) is another consideration for the stabilization of its structure and with regard to delocalization of its 5f-electrons. Another major difference – the effect of magnetism [18] – was an unexpected event in its pressure behavior.

Under pressures up to 100 GPa, curium displays all four of the structures found for americium except there is one additional, unique phase observed at intermediate pressures [18]. This results in Cm exhibiting five different crystallographic phases (four transitions) under pressure to 100 GPa, versus four phases and three transitions for americium. The unique phase observed for Cm has been designated as Cm(III), a monoclinic structure, space group *C*2/*c* [18] The behavior of Cm under pressure is displayed in Fig. 6 for comparison with that of americium. The “volume collapse” observed between the Cm(II) and Cm(III) transition is 4.5%, and between the Cm(IV) and Cm(V) transition it is 11.7%. This gives a total change of 16.2% for curium as compared to 9% for the two changes with americium.

Thus, the picture emerging from the experimental studies with Cm is that pressure forced the delocalization of Cm metal’s 5f-electrons in steps: first, partial delocalization occurring in Cm(III) which carries over to the Cm(IV) phase; then full delocalization is acquired in the Cm(V) phase. The volume collapses, their magnitudes and structures formed in the Cm III, Cm IV and Cm V phases were all taken as reflecting these electronic changes. Further, extrapolation of the atomic volume of the Cm(V) phase back to one atmospheric also provided a pseudo-atomic volume comparable to situation with the Am(IV) phase and to volumes normally observed for uranium, neptunium and plutonium at one atmosphere of pressure. Again, the volume-element plot using these pseudo volumes extracted for americium and for curium (Fig. 7) reduces or eliminates the large jump in volume seen in Fig. 1 in going from plutonium to curium. Arrows show the volumes found by the extrapolations of the Am(IV) and Cm(V) phases back to atmospheric pressure, which suggests volumes more similar to the protactinium through plutonium volumes. This assumes the itinerant 5f-electron structures for americium and curium attained at high pressures would be retained at one atmosphere. These extrapolations provide perspectives to the importance and effects of 5f bonding in the actinides—that is, to demonstrate the significance of 5f character in the bonding.

9. Theoretical results—americium and curium under pressure

Earlier theoretical concepts for americium under pressure published were not in accord with experimental findings, however, more recent theoretical assessments of americium under pressure [20–25] present a different perspective. These more recent theoretical results with regard to structural changes are now in good accord with the experimental findings, even in regard to the magnitude of the accompanying “volume collapses”. However, there are still differences between experimental and theoretical outlooks concerning the interpretations of the bonding changes that occur in americium under pressure. These differences are addressed in subsequent sections.

The most recent experimental and theoretical results for Cm appeared in the same publication [18], so there is full agreement between them in this report. Calculations (FPLMTO method [18]) on the total energy of Cm(II), Cm(III), Cm(IV) and Cm(V) phases as a function of atomic volume are shown in Fig. 6. The energy of the fcc Cm(II) phase is shown as “zero” for a reference. The dhcp Cm(I) and fcc Cm(II) phases are nearly identical in energy [18], and the Cm(I) phase is not included in Fig. 1 The figure therefore depicts the sequence observed, starting with the Cm(II) phase. The Cm(III) phase (line denoted by open circles) becomes lower in energy just below a volume of 18 Å^3 (dashed vertical line); then the Cm(IV) phase (denoted by solid circles) become stable until just below 15 Å^3 (second dashed vertical line). The Cm(V) phase has the lowest energy after a volume of 14 Å^3. The calculations discussed in reference [18] suggest the Cm(III) phase should be stable between 17 and 15 Å^3 – experimentally it is found between 20 and 17 Å^3. Considering several factors in such calculations, these values are in good agreement. The important point is that the calculations for total energy show the correct experimental sequence only when all of the structures are considered with respect to magnetic factors and the system is treated as being in an antiferromagnetic (AFM) configuration. Thus, the concept of the role of magnetism in high-pressure energy levels is encountered in this work on curium [18].

10. Bonding in am and cm under pressure: experiment versus theory

The theoretical examination of americium’s behavior under pressure has been discussed [20–26] and the structural behavior is in good agreement with experiment. Both density-functional type of electronic calculations (DFC) have been used to investigate the high-pressure behavior of americium, and both of these theoretical results now agreed fully with the structures and pressure–volume behaviors found experimentally [13–16]. The role of magnetism in the Cm III phase is a part of these computational approaches, but this concept also raises some important interpretative aspects. It is important to note that in the case of americium, its ground state ($J = 0$), either by Russell–Saunders coupling ($L = -S = 3$) or a *jj* coupling scheme (six 5f-electrons in a full $j = 5/2$ shell), and therefore it should not have a magnetic moment. Nor, has a magnetic moment been observed for americium experimentally. This would suggest that the 5f-electrons are de-coupled from the spd bonding electrons to give a “trivalent” lanthanide-like metal with three bonding electrons.

From experimental data, it is known that Am(I) and Am(II) phases have localized 5f-electrons and americium is non-magnetic in these phases. The formation of the fcc phase can be attributed to some change in the “d” character of the bonding. Pressure can alter the relative energies of the “s” and “d” electronic states and therefore the degree of their involvement in the bonding. As mentioned above, both the Am(I) and Am(II) phases (where the Am(II) phase is either a high-temperature phase or a high-pressure phase), can exist and be maintained at 25 °C and one atmosphere of pressure [34]. In contrast, the Am(III) and the Am(IV) phases revert to Am(I) orAm(II) upon the release of pressure. Thus, from an experimental perspective: (1) the Am(III) phase acquires 5f character (with a volume collapse; it is isostructural with γ-Pu, known to have f-bonding); (2) the Am(IV) phase acquires additional or full 5f-electron contributions to its bonding (a larger volume collapse is observed; this phase has a structural similarity to that of α-uranium.

Pènicaud [23–25] determined that in order to obtain the experimentally observed pressure behavior for americium it was necessary to invoke magnetism and relaxed structures. In this way, excellent agreement could be obtained with the experimental structures for americium and their appearance with specific pressures. The important conclusions of this theoretical effort are that the 5f-electrons in Am(I), Am(II) and Am(III) are localized, and that it is only in the Am(IV) phase that the 5f-electrons are fully delocalized. This conclusion conflicts with the position arrived at from experimental considerations.

In the work by Söderlind [20] and by Söderlind and Landa [21,22], calculations were undertaken for the pressure behavior of americium. In this recent work site magnetism for americium was also employed and excellent agreement of structural behavior was obtained with the experimental findings. The important conclusions reached from these theoretical efforts were: (1) that the 5f-electrons are partly delocalized in the Am(III) phase; (2) they are fully delocalized in the Am(IV) phase.

Thus, some differences are found in the computational results and experimental conclusions regarding the Am(II) and Am(III) pressure phases. Conclusions from Söderlind and Landa [21,22] for the Am(III) phase is thus in conflict with Pènicaud's [23–25]. But, the conclusions based on theoretical and experimental efforts are in accord concerning the occurrence of full delocalization of the 5f-electrons in the Am(IV) phase. Söderlind and Landa [21,22] concluded that at even higher pressures, beyond those obtainable presently in experimental work, that a body centered cubic (bcc) structure of americium should form at higher pressures.

Experimentally, the Am(I) and Am(II) phases do not display magnetic moments while theoretical treatments suggest they exist in these phases and decrease when advancing to the Am(III) and Am(IV) structures. It is important to note that the magnetic behavior of the Am(III) and Am(IV) phases have not been measured experimentally and as the bonding situation changes from a localized f^6 state, the magnetic state may change until all of the 5f-electrons are itinerant (e.g., as in the Am(IV).

Many of the same considerations discussed above for americium under pressure can be applied to curium's pressure behavior. The appearance of the additional Cm(III) phase requires an additional consideration. The experimental findings for Am(I) and Am(II) and these two forms of curium (which also can be retained at one atmosphere and at 25 °C) are the same for both metals. That is, Am(II) and Cm(II) phases both can be quenched (temperature and/or pressure quenching) and retained at 25 °C and atmospheric pressure [35]. Therefore, it is reasonable that bonding in both the Cm(I) and Cm(II) phases may involve the same bonding or at least very similar (as in the case of Am(I) and Am(II) forms) and that from experimental perspectives, there may not be 5f-electron involvement in the bonding of these structures. Structurally and thermodynamically, there is very little difference in the energies of the dhcp and fcc phases for these two elements.

However, in contrast to the situation with the Am(I) and Am(II) phases, both Cm(I) and Cm(II) are magnetic and have experimental moments in the range of 7–8μ_B, as expected for a half-filled 5f shell with full polarization and R-S coupling. But, the Cm(III) phase is both unique and interesting, as its unique structure is stabilized by the spin polarization of its 5f-electrons [18]. Curium is one of only a few elements (iron and cobalt being two others) that has this property. Calculations [18] for the behavior of curium under pressure indicate that the moment decreases and reaches a value of $\sim 4\mu_B$ at the Cm(III) to Cm(IV) transition. This finding supports the initialization of 5f-electron involvement in the bonding together with the formation of the Cm(III) phase, and is in accord with the volume collapse (4.5%) observed in the transition from Cm(II) to Cm(III). For the Cm(IV) to Cm(V) transition, the calculated magnetic moment disappears, suggesting full delocalization of its 5f-electrons. Experimentally, a greater (11.7%) volume collapse is observed at this Cm(IV) to Cm(V) transition, also supporting that a major change in bonding. The same conclusion concerning 5f-electron delocalization in americium was reached theoretically for the comparable Am(III) to Am(IV) transition found experimentally. These additional volume collapses further suggest that the 5f-electrons of the Fddd phase for both metals (Am(III) and Cm(IV)) are not yet fully delocalized.

11. Other aspects of americium under pressure

The resistivity behavior of americium under pressure has also been measured [35,36] but given the nature of the experimental system, pressures were limited to less than 30 GPa in these studies. The earlier efforts [35] did not examine the behavior of Am under pressure in magnetic fields, as done in the second study [36], which also considered theoretical aspects of the experimental resistivity changes observed. In this latter work it was suggested that at ~16 GPa (prior to the Am(III) to Am(IV) transition), the 5f-electrons of Am were still not fully delocalized, in accord with both the experimental from structural considerations and theoretical results based on magnetic moments on specific sites. The resistivity results were also discussed in terms of the superconductivity of Am, which was first found and reported many years ago at low temperatures at one atmosphere [37]. Experimental studies of the resistivity of curium under pressure remains to be performed.

12. Summarizing comments

Modern experimental and theoretical approaches have explored the changing roles of f-electrons in materials, advancing the knowledge and understanding of these systems. Understanding their pressure behavior has contributed greatly to the advancement of their science. While some differences between theory and experiment remain, there is increasing compatibility, not only for americium and curium but also other actinide elements as well. Hopefully, there will be further advances in this regard in the future.

Computational capabilities have become improved overall, and in the arena of high-pressure, it is possible to calculate behaviors at much higher pressures than presently attainable experimentally by static diamond anvil cell technology. But, there still exist some computational limitations [27]. Thus, experimentalists are now challenged to advance studies to higher pressures, to explore the reality of the predictions and acquire the details of the predicted changes under extremely high pressures as proposed by theory.

Overall, multiple experimental studies of the f elements have offered multiple insights into the electronic configurations, bonding and energy levels of f-electron metals, alloys and compounds. Theoretical computations have been an important aid and offer guidance in understanding these complex elements.

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