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Comparison of the chemical and physical properties of f-element metals and oxides: their dependence on electronic properties

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Abstract

The chemical and physical properties of an element, its alloys and its compounds are determined largely by the electronic nature (electronic configurations energy levels, etc.) of the materials. Therefore, comparing systematically selected properties of these materials can often provide insight into their electronic structures. The actinide series displays more complex electronic structures than does the lanthanide series; this is reflected in the more complex and variable properties exhibited by the actinides. A limited comparison of the two f-electron series of elements can be made by comparing the behaviors of their metals and oxides. The most notable differences in electronic and material behaviors are found with the metallic state, while with the oxides of these elements, perhaps the most studied compounds, the electronic structures and properties are more consistent. The objective here is to establish trends and differences in selected physicochemical properties of these two materials for each series, which may reflect differences in electronic structures. In this exercise, plutonium appears to occupy a pivotal position in the actinide series with reference to such properties; there does not seem to be a complete counterpart to it in the lanthanide series.

Keywords: f-Elements; Metals; Oxides; Electronic nature; Lanthanides; Actinides

1. Introduction

Attempts to discover the first few transuranium elements proved to be difficult [1], as their chemistries were different from those expected as anticipated based on the behaviors of the 4-f elements. The subsequent chemical isolation of the transplutonium elements required the recognition that this group of elements would have properties different from those of the earlier actinides. Thus, it was established very early that plutonium occupied a pivotal position in the actinide series with regard to physicochemical properties across the series.

A major portion of the experimental data presently known for the second-half members of the actinide series has been acquired during the past two decades, after larger quantities of the elements became available. Even with larger quantities and this additional experimental information, data for the elements beyond californium remain very limited, and are almost nonexistent for the last three members of the series. Although information is limited for some elements, it is still possible to make extensive comparisons between the properties of the lanthanide and actinide series, and an effort is made here to compare important properties the metals and oxides of these f-elements.

Electronic structure controls the chemistry and much of the physics of an element. Therefore, understanding and classifying the two series of f-elements require a study of the changing role of the f-electrons across each series, as well as considering how particular parameters (e.g. temperature, pressure, alloying, environment, etc.) can alter the electronic nature of the unperturbed elements. Important differences between the two series can be highlighted by comparing both the basic properties of the pure metals, and their alloying behavior with other metals.

A fundamental aspect of these elements is what conditions, in any, must be imposed in order to have their f-electrons involved in the metallic bonding. With oxides, electronic structure plays a critical role in several of the physicochemical properties; this is especially obvious in regard to the number and value of displayed oxidation states, as well as whether or not intermediate oxides will form. But there are other systematic properties of the oxides, such as their vaporization behavior

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at high-temperature, which have an underlying dependence on the electronic nature of the f-element itself. In contrast, the phase behavior and the structure-type displayed by an oxide of a given oxidation state seems to be mainly a function of ionic radius. Thus, the properties are frequently the same for oxides of both series, when their ionic radius and oxidation state are the same.

2. Established properties and systematics for the metals

When examining the two series of f-elements, it is useful to consider the electronic configurations for the elements and for the ions representing different oxidation states. These data are provided in Tables 1 and 2 and should be useful in different contexts throughout the paper. It must be emphasized that the configurations listed for the atoms represent the ground state for gaseous atoms; not atoms in the condensed metal.

In comparing the metallic properties for the two f-series of elements, it must be decided how to consider lanthanum and actinium, as neither element is truly an f-element. Further, although lanthanum has been thoroughly studied and is well characterized, this is not the case for actinium. The situation with actinium will be touched on in a later section (in discussion on atomic volumes) of this paper, but at this point it will be assumed that both lanthanum and actinium represent comparable trivalent metals. The next actinide metal, thorium (d^2s^2 outer configuration), lacks an f-electron (which complicates a comparison of it with its homolog, Ce) but it is accepted that thorium metal has four electrons in its conduction band while Ce normally has only three. The attempt to compare the next four actinide metals (Pa–Pu) with the lanthanide metals becomes even more complicated, as these actinide have itinerant f-electrons, while the f-electrons of their lanthanide homologs are localized. These differences, and the differences in metallic valences, compose a significant portion of the difficulties encountered when comparing the two f-electron series of elements.

A comparison of the metals of these two series can be simplified to some degree by using a slightly different approach to viewing these elements. In comparing the two f-series of elements, it is frequently useful to compare the metals in terms of their metallic valence, defined simply as the number of bonding electrons in the metal's conduction band. With the lanthanide metals one then finds two groupings: the divalent metals, Eu and Yb, and the remaining twelve, which are generally considered trivalent metals. The actinide metals are far more complex but it is possible to provide a similar picture for them. In this approach, the first five members after Ac (e.g. Th–Pu) are considered as having metallic valences greater than three; the next four (Am–Cf) and the last member (Lr) are trivalent metals; while the other four members (Es–No) are divalent. This periodicity for the two series, in terms of metallic valence, is demonstrated in Fig. 1.

It is important to note that in comparing the two series there are obvious vertical mismatches (e.g. different valences for potential electronic homologs of each series) in Fig. 1. For example: Ce is trivalent (magnetic, one non-bonded, unpaired f-electron) while Th is tetravalent, non-magnetic and uses its four valence electrons in the metallic bonding; Eu is divalent while

Table 1
Electronic configurations for atoms, ions, and oxides of the lanthanides

Atomic number	Oxides formed [b]	Electronic configuration [a]				
		Element	Atom	M(II)	M(III)	M(IV)
57	La_2O_3	La	$5d6s^2$	5d	[Xe core]	–
58	Ce_2O_3; CeO_2	Ce	$4f5d6s^2$	4f5d	$4f^1$	[Xe core]
59	Pr_2O_3; PrO_2	Pr	$4f^36s^2$	$4f^3$	$4f^2$	$4f^1$
60	Nd_2O_3; NdO_2	Nd	$4f^46s^2$	$4f^4$	$4f^3$	$4f^2$
61	Pm_2O_3	Pm	$4f^56s^2$	$4f^5$	$4f^4$	$4f^3$
62	SmO; Sm_2O_3	Sm	$4f^66s^2$	$4f^6$	$4f^5$	$4f^4$
63	EuO; Eu_2O_3	Eu	$4f^76s^2$	$4f^7$	$4f^6$	$4f^5$
64	Gd_2O_3	Gd	$4f^76d6s^2$	$4f^76d$	$4f^7$	$4f^6$
65	Tb_2O_3; TbO_2	Tb	$4f^96s^2$	$4f^9$	$4f^8$	$4f^7$
66	Dy_2O_3	Dy	$4f^{10}6s^2$	$4f^{10}$	$4f^9$	$4f^8$
67	Ho_2O_3	Ho	$4f^{11}6s^2$	$4f^{11}$	$4f^{10}$	$4f^9$
68	Er_2O_3	Er	$4f^{12}6s^2$	$4f^{12}$	$4f^{11}$	$4f^{10}$
69	Tm_2O_3	Tm	$4f^{13}6s^2$	$4f^{13}$	$4f^{12}$	$4f^{11}$
70	YbO; Yb_2O_3	Yb	$4f^{14}6s^2$	$4f^{14}$	$4f^{13}$	$4f^{12}$
71	Lu_2O_3	Lu	$4f^{14}5d6d^2$	$4f^{14}5d$	$4f^{14}$	$4f^{13}$

[a] Configurations for electrons outside the [Xe] core: data are for ground-state gaseous neutral atoms and charged ions.
[b] Oxides having O/M ratios between 1.5 and 2.0 are not shown.

Table 2
Electronic configurations for atoms, ions and oxides of the actinides

Atomic number	Oxides formed	Electronic configuration [a]						
		Element	Atom	M(II)	M(III)	M(IV)	M(V)	M(VI)
89	Ac_2O_3	Ac	$5f^06d^17s^2$		$5f^0$			
90	ThO_2	Th	$5f^06d^27s^2$			$5f^0$		
91	PaO_2, Pa_2O_5	Pa	$5f^26d^17s^2$			$5f^1$	$5f^0$	
92	UO_2, U_4O_9, U_2O_5, U_3O_8, UO_3	U	$5f^36d^17s^2$			$5f^2$	$5f^1$	$5f^0$
93	NpO_2, Np_2O_5	Np	$5f^46d^17s^2$		$5f^4$	$5f^3$	$5f^2$	$5f^1$
94	Pu_2O_3, PuO_2	Pu	$5f^67s^2$		$5f^5$	$5f^4$	$5f^3$	$5f^2$
95	Am_2O_3, Am_7O_{12}, AmO_2	Am	$5f^77s^2$	$5f^7$	$5f^6$	$5f^5$	$5f^4$	$5f^3$
96	Cm_2O_3, Cm_7O_{12}, CmO_2	Cm	$5f^76d^17s^2$		$5f^7$	$5f^6$		
97	Bk_2O_3, BkO_2	Bk	$5f^97s^2$		$5f^8$	$5f^7$		
98	Cf_2O_3, Cf_7O_{12}, CfO_2	Cf	$5f^{10}7s^2$	$5f^{10}$	$5f^9$	$5f^8$		
99	Es_2O_3	Es	$5f^{11}7s^2$	$5f^{11}$	$5f^{10}$			
100	(Fm_2O_3)	Fm	$5f^{12}7s^2$	$5f^{12}$	$5f^{11}$			
101	(Md_2O_3)	Md	$5f^{13}7s^2$	$5f^{13}$	$5f^{12}$			
102	(NoO; No_2O_3)	No	$5f^{14}7s^2$	$5f^{14}$	$5f^{13}$			
103	(Lr_2O_3)	Lr [b]	$5f^{14}6d^17s^2$		$5f^{14}$			

[a] Only the electrons outside the [Rn] core are given: data are for ground-state gaseous neutral atoms and charged ions.
[b] Non-relativistic configuration.

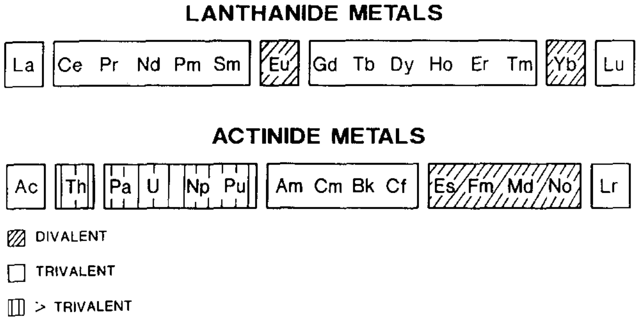

Fig. 1. Metallic valences for the 4f- and 5f-electron metals.

Am is trivalent; and so on. Major differences between the two series of f-elements are observed for: (a) the Pa–Pu group of metals, which normally have itinerant f-electrons involved in bonding; and (b) the group of four divalent Es–No metals, which are accepted as s-bonded metals having localized f-electrons. There is no counterpart to the Pa–Pu group in the lanthanide series, and only Yb in the second half of the lanthanide series compares to the divalent Es–No grouping in the second half of the actinide series.

Rather than looking at the electronic configurations for understanding the occurrence of divalent metals, it is clearer to realize that the divalency of these metals results from the larger promotion energies needed to promote a third electron to a metallic bonding state (e.g., f^ns^2 to $f^{n-1}ds^2$). If the energy outlay for promotion is not offset by the additional crystal energy acquired by forming a condensed trivalent metal [2], the result is the formation of a divalent metal. For the Pa–Pu group, it is the similarity in energy of the 5f and 6d electrons that in part leads to mixing or hybridizing of the orbitals of the early actinides. Thus, for the first half of each series, the 4f-orbitals stabilize more rapidly than the 5f-orbitals with increasing nuclear charge; for the second halves of each series, the situation is reversed. The f-electrons of the earlier members (Pa–Pu) are involved in bonding, as their f-electrons have not stabilized sufficiently to compete with the other orbitals [3]. The trend towards divalency in the higher actinide metals then cannot be deduced solely from position of the lanthanide homologs, except perhaps for case of nobelium, nor can the itinerant f-electrons for the Pa–Pu group be deduced from the lanthanide elements.

The transplutonium metals as a group tend to be more lanthanide-like than the earlier members of the actinide series, and they normally have localized, non-bonding f-electrons. Their properties are frequently similar to those of the lanthanide metals. With the Pa–Pu group of actinide metals, each element tends to have available a number of bonding configurations that involve different orbital types (s, p, d and f) that are nearly equivalent in energy. This allows multiple structure types to form with minimal changes in energy. Not only do these metals normally display different properties than the lanthanide metals but they also exhibit differences among themselves.

The different metallic valences, bonding arrangements, promotion energies, etc. for the two f-element series are responsible for the variable nature of their physicochemical properties, such as atomic volumes, structure, melting and boiling points, enthalpies of vaporization and solution, etc. Space does not permit discussions of all these properties and a number of other authors have already discussed many of these particular properties; some of these discussions appear in Refs. [2–9]. Although the most information is available for the Th to Cm members of the actinide series, limited experimental data do exist for the properties of elements through Md, and several extrapolations have been made for the elements through Lr. For example, an experimental value for the enthalpy of vaporization of Fm metal and extrapolations for the enthalpies of the last three members of the actinide series have been published [4].

Experimental evidence for delocalized f-electrons (5f-band behavior) in the lighter actinide metals is found in data for their atomic volumes (smaller volumes), melting behavior (lower melting), crystal structures (complex, multiple allotropic forms), cohesive properties (higher enthalpies of vaporization), bulk moduli (larger), magnetism (tend to be non-magnetic), and electron spectroscopy (observance of 5f-bands at the Fermi level). Only a brief discussion of selected properties for the two series of elements will be given here; the intent is to discuss those which are the most pertinent to considering metal-to-metal distances (both in the elements and in their compounds), and to basic issues involved in the alloying behavior of these elements.

The crystal structures, atomic volumes and melting points of the lanthanide metals all show a regular trend with atomic number, with the exception of the two divalent metals, Eu and Yb [8]. The structures for the trivalent metals can be summarized briefly as being hexagonal (dhcp or hcp, except for rhombohedral Sm) at lower temperatures (α-form) and in some cases, cubic (β-form) at higher temperatures. The atomic volumes (and metallic radii) of the α and β forms of the lanthanide metals are very similar and tend to change uniformly, decreasing only slightly with Z, while the melting points slowly increase with Z. The two divalent lanthanide metals are exceptions to the above generalizations, and have larger atomic volumes, lower melting points and display cubic, low temperature structures.

In contrast to the lanthanide metals, the actinides display far more complex behavior with regard to these above three properties. The unique and complex behaviors of Np and Pu metals are well known; they have exceptionally low melting points (even lower than those of the divalent metals, Eu, Yb, Es, Ba or Ra), complex, low-symmetry, room temperature crystal structures, and exhibit multiple phase changes structures with increasing temperature (for Pu metal, up to six crystalline modifications between room temperature and 640 °C). Only small energy changes are needed to change from one modification to another; this is due to the multiple, nearly equivalent energy levels that exist in these metals [3]. The structures of the transplutonium metals (α-dhcp and β-fcc for the trivalent metals; for Am and Cm, a γ-bcc form has also been postulated but X-ray data have not been obtained to confirm this form) and an expanded cubic α-form for divalent Es metal [5] resemble more closely the high-symmetry structures known for the trivalent and divalent lanthanides. It should be noted that a fcc form is the most likely high-temperature form to be encountered with the transplutonium metals, while with many of the lanthanide metals, it is a bcc structure (γ-form for La and Ce; β form for the Pr–Dy metals, except Eu, where it is the α-form).

Although it was believed initially that the β-forms of the trivalent transplutonium metals, Cm, Bk and Cf, had slightly larger atomic volumes than their α-forms, studies with pressure quenched samples of these metals [10] have shown that the atomic volumes for these two forms of each metal are essentially identical. This is in accord with the volume behavior known for the lanthanide metals. The two different volumes reported previously for the α and β forms of the Cm–Bk metals led to a suggestion that a slightly different metallic valence existed for each form of these metals [11]; the larger volume of the β form was assigned a somewhat smaller valence. As the atomic volumes for the two forms of each of these actinides have now been shown to be the same [10], the metallic valence of each form is accepted as being identical (presumably trivalent). Although the structural behavior and crystal forms of the transplutonium metals are more similar to those of the lanthanide metals, than to those of the early actinide metals, the fact remains that the volumes of the Am–Cf metals are still smaller than those of their lanthanide homologs. For example, the atomic volume of Cm (middle of the series; the largest of the transplutonium metals) is about the same as that of Lu metal (end of the series; the smallest of the lanthanide metals), and smaller than that of curium's electronic homolog, gadolinium. In contrast one finds that the volume of divalent Es metal is close to that expected based on the volumes of Eu and Yb metals, especially if some small allowance is made for radiation swelling in the Es metal, due to its intense self-irradiation. This suggests that additional bonding over that presence in the lanthanides (e.g. ds^2 bonding; trivalent metals) may be present in these Am–Cf metals, especially since the volume for Es metal [5] seems to be in accord with the atomic volumes for Eu and Yb (all three s^2 bonding).

Comparisons of the atomic volumes and radii of these supposedly trivalent lanthanide and actinide metals previously led Zachariasen [11] to suggest that the valence of the Am–Bk transplutonium metals (dhcp form) might be assigned a metallic valence of nominally four (see comment above about the two crystal forms of Cm metal) but magnetic measurements [12] and other data seem to support that they are essentially trivalent metals. Zachariasen [11] generated individual assignments for metallic valence and the number of non-bonding f-electrons for the metals based on their metallic radii. For example, valences for the different temperature forms of Pu metals ranged from 4.7 to 6.2; the alpha form of Cm was assigned a valence of 3.8, while its beta form had a valence of 3.5, etc. [11]. A major factor in making these assessments was the radius of Ac metal, which Zachariasen believed to be too small compared to that of La metal. He suggested a larger radius for Ac, concerned about the correctness of the single experimental value reported for Ac metal [13,14], but later accepted the originally published lattice parameter for Ac metal, after it had been duplicated in subsequent experiments by other workers [15]. In addressing this apparent problem with the radius of Ac metal, Hill [16] attempted to explain the smaller-than-expected parameter for Ac metal by suggesting that it represented a relativistic effect that became prominent with the appearance of 7s electrons. It is apparent that some caution must be applied in arriving at conclusions when based only on experimental parameters, such as radii, volumes, etc. Not only may new information change/correct the situation (e.g. the radii initially proposed for the α and β forms of the Cm–Cf metals) but interpretations based on other data may also change. However, it remains that the atomic volumes of the trivalent transplutonium metals are indeed smaller than expected based on their lanthanide counterparts, which are often considered/accepted as being trivalent metals.

In view of the above, it is worthwhile to contrast these volume relationships for the trivalent actinide and lanthanide metals with those for materials containing these elements; specifically their sesquioxides and monopnictides [9]. The volumes of the sesquioxides of the actinides are found to be slightly larger than their lanthanide homologs, which is the reverse of the trend observed with the metals. An interesting comparison can be made with the monopnictides of these elements. With the mononitrides, the earlier actinide nitrides have volumes smaller than their lanthanide nitrides homologs, which suggests additional bonding is present (perhaps f–f overlap between the actinide atoms) in these lighter actinide nitrides. With the monobismuthides, the volumes for the elements of each series are essentially identical, which suggests similar or identical bonding is present in these lanthanide and the actinide bismuth compounds.

A simple hypothesis for the above is that the smaller nitrogen atoms provides shorter An–An (An = actinide) distances, which offers a greater potential for f–f overlap of the actinide's orbitals, while the larger bismuth atoms necessitates larger An–An distances, which inhibit such overlap. This explanation touches on the Hill [16] concept, where it is proposed that there are critical An–An separations above which f-bonding or f–f overlap is lost. This concept will be addressed again in a later section where the assignment of pseudo Hill-type limits for the transplutonium elements is discussed.

Melting points are another important systematic property and worth considering from the standpoint of the bonding present in these elements. Some of the concepts derived from melting behavior will be useful when considering alloying behavior, which is discussed in a subsequent section.

The highest melting points for the actinide metals are found with the Th (d-bonded metal; transition metal character) and Pa (onset of f-bonding but some retention of d-character) metals. The effect of f-orbitals on the melting point is maximized with Np and Pu; both have very low melting points, which are believed to be a reflection of f-orbital repulsion [2,6]. Melting is believed to relieve this repulsion in Np and Pu, but a large liquid range (melting to boiling) and a significant liquid viscosity suggests some f-bonding remains even in their liquid state.

The melting points of the actinide metals begin to rise in the series after Pu (following the onset of f-electron localization) and they then again decreases. For the transplutonium metals whose melting points are known (Am–Es) [5], the maximum melting point is found at Cm; this probably reflects both its half-filled 5f-shell and the presence of a d-type valence electron (ds^2). The decrease in melting points observed for the transcurium metals reflects the onset of divalency (onset of s-type bonding; and loss of d-bonding). Presumably, the melting point would rise again at Lr (expected to be a d-bonded metal). Thus, the f-bonded actinide metals (Pa–Pu) are non-lanthanide like in many of their properties; as the f-electrons become more localized, the bonding involves s-and/or d-electrons, and the properties of these metals become more similar to those of the lanthanides, or may even acquire some transition metal (d-electron) character.

Some of the concepts, facts and observations of bonding discussed above for the melting behaviors of these f-series of elements can be transferred to their alloying behaviors. Specifically, in comparisons of the properties of the alloys themselves, and whether or not alloys will even form for: (1) members of the same series; (2) between members of the two series; or (3) between members of one f-series and another metal (e.g. transition metal). The important point is what effect alloying would have on bonding. For example, if alloying with another metal removed, or reduced significantly, the participation of f-electrons in the bonding in a light actinide metal (as Pu), the melting point of the resulting alloy may rise (f-orbital repulsion reduced; bonding in the alloy becomes more like that found in the trivalent transplutonium and lanthanide metals, or the d-bonded metals). Alloying an f-electron bonded actinide metal with a metal not having f-bonding may not occur until the f-bonding is diminished or depleted (which may not be thermodynamically favorable for the metal). For example, increasing the temperature of the metal to form a phase that either is no longer f-bonded, or that has a minimum or reduced amount of f-bonding, so that alloying may proceed. Upon cooling, the resulting alloy may retain a structure of higher symmetry then did the initial f-electron bonded, pure metal. The melting point of the alloy may also be higher than that of the f-electron bonded parent. An actinide with only s-bonding (e.g. Es) would not be expected to alloy with a f- or dsp- electron bonded actinide metal, until the bonding of one or the other of the metals was altered (e.g. Eu and Yb are not fully miscible with the trivalent lanthanide metals). Instead, Es would be more likely to alloy with divalent Eu or Yb metals. Metals with similar electronic configurations (e.g. Am–Cf metals and the trivalent lanthanide metals) would be expected to form alloys, although they may or may form ideal alloys. Alloying behavior in the context of electronic behavior will be considered further in a subsequent section.

3. Critical actinide-actinide distances

The existence of a localized versus itinerant f-electron state is important for defining the chemical and/or physical properties of the actinide elements. It is therefore important to be able to identify the actual and/or potential status of the f-electrons' involvement in the bonding of actinide and lanthanide metals and compounds. With respect to the atomic volume behavior of actinide metals and compounds, it is evident that the radii and the An–An distances reflect the presence or non-presence of f-bonding. The concept of having critical An–An distances for f-bonding was first applied systematically for U, Np and Pu for magnetic ordering and critical An–An distances; in graphical form these relationships were referred to as Hill plots [17]. Basically, Hill's approach related the broadening of 5f-bands with their overlapping, and identified the latter as a function of the interatomic spacing in the materials. If the band is too broad, there is a low density of states and the criterion for band magnetism is not met [18]; or stated differently, that magnetism requires localized f-electrons, which is a function of some critical An–An separation. This approach is not exact and exceptions are known, some of which may be explained. The most significant weakness, noted by Hill [17] himself, is the assumption that direct overlap (rather than hybridization) is the only parameter affecting the bandwidth. Yet, these Hill plots have proven to be very useful and have been used in understanding the behavior of many U, Np and Pu compounds.

Hill plots were not established for the transplutonium elements and their compounds because the metallic bonding is different from that in the three itinerant f-electron metals, U, Np and Pu; the f-electrons of the transplutonium metals are normally localized and critical actinide–actinide distances for the onset of f-electron bonding were not known. However, one can conceive generating pseudo Hill-type plots, if results from high-pressure studies of the transplutonium metals are considered. Under high-pressure the f-electrons of the Am–Cf metals are delocalized, and the metals form a low-symmetry, α-uranium structure [19]. The interatomic distances (An–An separations) that exist at the inception of this condition then suggest the distances required in transplutonium compounds to encounter potential f–f overlap. Fig. 2 represents this situation for the first four transplutonium metals, and the An–An distances for the potential overlap of f-orbitals (delocalization of f-electrons) for the Am–Cf metals are shown as a vertical bar to the left. The Es–Es distance in divalent Es metal is also given in Fig. 2, along with a suggested An–An distance expected for a hypothetical, trivalent (localized f-electron) Es metal. At the top of this figure is the range of An–An distances (Hill limits) exhibited for the U–Pu metals at normal pressure which have itinerant f-electrons. The final aspect of Fig. 2 shows the distances that have been found in Am and Cm dioxides [20], and in Cm and Cf monobismuthides [21] under both normal and high pressure. The range of distances shown for these compounds arises from the different phases observed under pressure; the existence of two different metal–metal distances are present in the tetragonal structures encountered.

The distances shown for the delocalized states of Am–Cf metals suggest that a considerable reduction in the An–An distances would be required in order to suggest the occurrence of f–f overlap in these compounds. It is noteworthy that the An–An distances in U, Np and Pu metals, which have itinerant f-electrons at normal pressure, are of similar magnitude to the distances that exist in the ambient pressure Am–Cf metals, which have localized f-electrons. This indicates

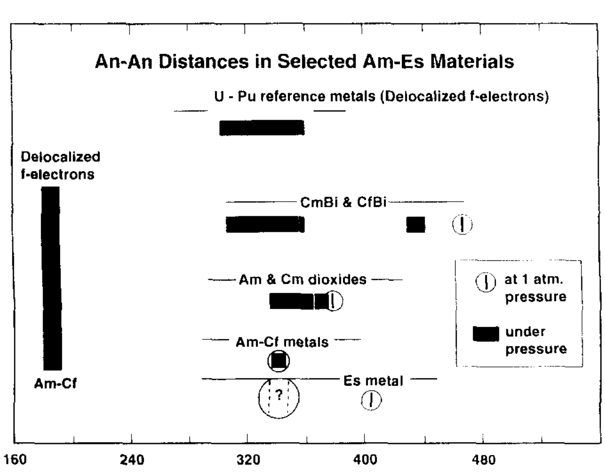

Fig. 2. Metal–metal distances for delocalized f-electrons in U, Np and Pu metals and in selected transplutonium materials.

that the f-electrons in the transplutonium metals are pulled-in considerably (well below the Fermi level and not involved in bonding), due in part due to an increased nuclear charge. The f-electrons of the latter metals only become involved in bonding when pressure decreases significantly these normal distances. Even greater An–An distances are shown to exist in divalent Es metal at normal pressure, which indicates an even smaller probability for f-electron involvement in its metallic bonding (an even greater reduction in its volume would be required to enhance f-bonding).

The above approach of using metal–metal distances from pressure experiments can be expanded to include the lanthanide metals (and even Th metal) for cases where f-delocalization is known, or suspected to have occurred, under pressure [22,23]. This would include the Ce, Pr, Nd, Sm metals and requires even greater latitude in the assumptions that are made. For example, in some cases the researchers reporting high-pressure data have not directly claimed the occurrence of delocalization with the specific phase changes, while in other cases, the exact parameters obtained under pressure were not reported for the specific pressures of interest. This necessitated the use of a range of metal–metal distances for representing the onset of delocalization in the metals. Finally, there is the special case of Th metal [24], where mixing of its unfilled f-band with the occupied d-band under pressure to yield a tetragonal structure was taken for estimating the Th–Th distances where f-electron delocalization occurred. The results of these approximations and assumptions are summarized in Fig. 3. If accepted, then these plots suggest: (1) that the metal–metal distances found in conjunction with the delocalization of f-electrons in the two series become smaller (delocalization more difficult) as the number of f-electrons increases; and (2) that for a given number of f-electrons (excluding Th, which normally has zero f-electrons), the 5f-electrons will delocalize at lower pressures (delocalization becomes easier) than will the 4f-electrons. The latter reflects the greater spatial extension of the 5f-electrons which would favor overlapping. Thus, the 5f-electrons in Pa, U, Np, and Pu are delocalized at normal pressures; the delocaliztion of the 4f-electron of Ce occurs as low as 1 GPa (if the first structure/volume change is accepted as representing delocalization) but requires more pressure for Pr (20 GPa), Nd (40 GPa), and Sm (95 GPa) which have two, three and five 4f-electrons). Delocalization occurs at 23–43 GPa for the Am–Cf metals, which have six to nine 5f-electrons. Delocalization of the f-electrons of the divalent metals should, of course, be more difficult; also, pressure may first bring about a metallic valence change to a form trivalent metal in these cases. Experiments with Eu and Yb metals have indicated a partial conversion to a trivalent metallic state [22,23].

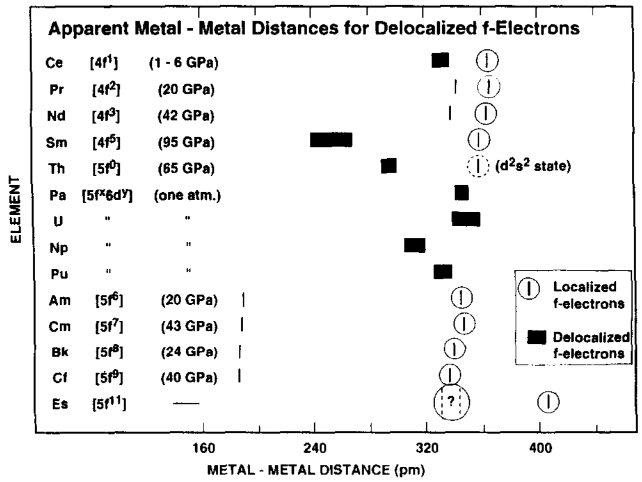

Fig. 3. Apparent metal–metal distances for delocalized f-electrons in selected lanthanide and actinide metals.

The bar graphs shown in Figs. 2 and 3 must be taken with some care, realizing the assumptions that have been made. Overall, the figures indicate: (1) that it takes less pressure to reduce the metal–metal distances in the transplutonium metals than in the transpraseodymium metals; and (2) that the f–f overlap in the transplutonium metals requires smaller An–An distances than Ln–Ln distances in the transpraseodymium metals. However, these distances are significant only for interactions between the metal atoms; they have little relevance for potential interactions between f-electrons and the orbitals of other atoms present in compounds.

4. Alloying behavior

The alloying behaviors of metals are important to both basic science and technology. Theoretical and empirical approaches have been used to predict and understand the formation and the properties of alloys. Estimates for the number of binary alloys and compounds for the elements of the periodic table range in the many thousands and may represent many types of structures. The crystal structure is one of the important properties of these materials, and its formation is undoubtedly dependent on bonding and the electronic structures of the alloy's components. To aid in the classification of these materials, structural stability maps (two dimensional matrices) that are in some regards similar to the periodic table of the elements, have been generated for many of the elements. However, little has been done in this regard with the lanthanides and actinides.

Only a superficial look at alloying behavior will be attempted here but still some interesting comparisons can be drawn regarding the two f-electron series of metals. An examination of the lanthanide series [8] has shown that there is mutual solubility and alloying between most of the trivalent metals, but that the trivalent and divalent metals (Eu and Yb) do not alloy with one another and are not mutually soluble. A more careful examination shows that even when mutually soluble, these lanthanide metals may not form ideal solutions. Thus, the solubility and alloying behaviors of these metals are clearly a function of electronic properties.

The behavior of the lanthanide trivalent metals in this regard can be seen by selecting the Pr–Nd and the Sm–Gd systems as two examples. The Pr–Nd metals are mutually soluble and essentially form ideal solutions, while although the Sm–Gd system are soluble in one another, their solutions show negative deviations in the activities of the components as a function of composition [8]. An explanation for this non-ideal behavior in this system has been attributed to the partial tendency of Sm to be divalent [8]. Even in the case of the two cubic, divalent (s-electron bonded; expected to comparable electronically) metals, Eu (bcc) and Yb (fcc), total mutual solubility is not achieved.

Given the more complex and variable electronic makeup of the actinide metals, it should be expected that their alloying behavior should also be more complex. Very simple predictions for alloying behaviors of the actinides would suggest the following: (1) that the itinerant f-electron metals (Pa–Pu) may be mutually soluble; (2) that the trivalent metals should also be mutually soluble in one another (ideal solutions?); and (3) that the divalent metals (Es, Fm, etc.) would have mutual solubility (form fcc phases?) but that they would probably not alloy with the trivalent metals or with the itinerant f-electron actinide metals (e.g. Pa–Pu). In the cases where the metals were not mutually soluble, it would be reasonable to expect some limited solubility of one metal in the other.

Experimental studies of actinide alloys have been carried out but are less extensive than work on the lanthanide systems, except for the cases of uranium and plutonium. Alloys of Am [25], Cm [26], Es [27] and Fm [4] have been studied and used in high-temperature studies, while alloys of Am and Bk [19] have been used in high-pressure work. Far more extensive studies have been, and continue to be, carried out with U and Pu metals [28] due to the strong interest in their technologies and their greater abundance. The potential for the alteration of one or both of the components' electronic structure as a result of alloying also provides an interesting and important means for probing electronic structures and their stabilities, either between members of the same series or between metals from each series. One interesting case for alloying concerns the Np–Am system [29], both for technological applications (e.g. for potential transmutation processes) or for understanding the resulting interactions between the two electronic structures/natures of these two elements. Specifically, the 5f-electrons of Np are itinerant whereas those of Am are localized, and the electronegativities and metallic radii of Np and Am are similar enough that intermetallic compound formation between them would not be anticipated [29]. Their mutual solubility should then be dominated by the differences in their metallic valences, which are reflected by their cohesive energies as defined by Brewer [30]. However, difficulties in predicting solubilities may arise if only differences between cohesive energies are emphasized [29]. This is exemplified by the observations that while similar differences in cohesive energy are noted for the U–Th, Np–Pu and the Np–Am pairs, the U–Th phase diagram [31] exhibits only limited solubility, the Np–Pu system [28] is characterized by complete solubility. In the study of the Np–Am system [29] it was determined that these two metals were not mutually soluble, and that the Np–La, Np–Nd and Np–Lu pairs likewise were not fully miscible. The phase behavior for these localized/itinerant f-electron metal pairs suggested the formation of a Np-rich and a trivalent metal-rich phase; that is, each metal phase having a limited solubility in the other metal. This implies that Np, with its greater cohesive energy, is resistant to alloy formation that would disrupt its f-bonding. This provides a simple picture for the alloying behavior that may be expected with these f-election bonded metals but it collapses when the Pu–Am system is considered. Itinerant f-electrons are present in the different structural phases of Pu metal (although the extent of hybridiziation decreases with temperature) and Am metal has localized f-electrons, yet these two metals are completely miscibility and form cubic alloy structures [28,32]. In contrast, several Pu–Ln (Ln = lanthanide; Pr, Nd and Sm) systems [33–35] are characterized by a very limited solubility ($<2\%$) of the lanthanides in the Pu but a greater solubility (~ 30 atom%) of Pu in the lanthanides, which depresses the lanthanide's liquidus and phase transition temperatures. This suggests that the Pu–Am system may be a special case; however, in general it appears that Pu metal is trying to become a lanthanide-like metal. The solubility of other non-f-bonded metals in Np and Pu, which have a high degree of f-bonding, should then very dependent depend on differences in electronic configuration, as well as on size and internal pressure [3].

The alloying behavior of the f-elements with non-f electron elements (e.g. d-electron, transition metals) provides another aspect of alloy formation, but is beyond the scope of the discussion here, although it is appropriate to provide some brief comments about these systems. It is clear that the 5f-electron bonded metals, Np and Pu, show multiple phases which differ only slightly in energy [3], and that phases with increased symmetry and different electronic configurations of these metals are formed with increasing temperature. These latter phases are expected to have more d-character, which should then alter their alloying behaviors. Brewer [3] suggested that their high-temperature bcc structural forms have at least two bonding d-electrons per atom, and these forms should overlap more effectively with d-electron (transition) metals having two d-electrons.Thus, since the Ti–Zr–Hf through the Cu–Ag–Au groups of elements use at least two d-electrons, these should then alloy with Np and Pu and stabilize the bcc structure. Recent work with Np alloys [29,36,37] has indicated that there may be differences between the behaviors of U, Np and Pu metals with regard to their alloying with Zr metal. Although there is considerable information about f-element alloys, much more effort will be required to fully define and understand differences in behavior and to be able to better relate these to electronic configuration and bonding in the metals.

5. Lanthanide and actinide oxides

The electronic configurations of the lanthanide and actinide elements also provide insights into the properties and chemistries of their oxides. It is the stability of these electronic states which determines the stoichiometries that are displayed in an element's oxides, but these electronic states can also play roles in other properties of the oxides.

Up to five oxidation states (II–VI) are observed in binary actinide oxides, while only three states (II, III and IV) are found in binary lanthanide oxides. The highest oxygen stoichiometry (e.g. the largest O/M ratio) for an f-element binary oxide is achieved in UO_3, although the highest attainable oxidation state for an actinide may not occur in its binary oxide. The larger variation in oxidation states for the actinides result from the close proximity and similar energies of their different electronic orbitals (7s, 6d and 5f), which give rise to variable electronic stabilities and oxide stoichiometries across the series.

With actinide metals, the largest number of electrons involved in bonding occurs with the Pa–Pu group, where there is a significant overlap of the f-orbitals with other valence electrons. This electronic complexity carries over to the oxides of Pa, U and Np, which display greater oxygen stoichiometries than do other members of the 5f series. In the lanthanide series, such complexity in electronic structure is not found and their oxides are centered around a sesquioxides stoichiometry.

In contrast to the metallic state, where the electronic orbitals are often linked with a specific phase and/or structural behavior, the phase behavior of the binary f-element oxides of a given oxidation state are not normally associated with a specific electronic structure. Instead, given the more ionic nature of these oxides, the ionic radii of the metallic ions are frequently the guiding factor in anticipating their phase behavior, as well as other physical properties of the oxides. However, it is apparent that the vaporization behavior of the f-element oxides is dependent indirectly on the electronic nature of these elements, principally because of the bonding nature of their gaseous monoxides.

A large variation in oxygen stoichiometry is found in the actinides series. After Np in the series, the highest solid binary actinide oxide formed is the dioxide and this stoichiometry is known for the elements, Th through Cf. Binary oxides with higher stoichiometries have been confirmed only for the elements, Pa, U and Np. The sesquioxide becomes the predominate oxide for the transplutonium elements, especially at the higher temperatures where vaporization of the oxide is encountered (Bk dioxide is an exception). Excluding actinium sesquioxide, the first solid sesquioxide in the series is encountered at Pu. This oxide is known for all the actinides from Pu through Es and is probably the highest binary oxide that will form for the elements beyond Cf in the series (No, which has not been studied; may only form a solid monoxide). A summary of the known binary oxides and the electronic relationships for the gaseous metal atoms and ions expected in the oxides are given in Tables 1 and 2.

The sesquioxide is the predominant binary oxide for the lanthanide series, although Ce, Pr and Tb dioxides are well established. Higher binary oxide stoichiometries are not known for this series. Of these three dioxides, only Ce dioxide is stable at temperatures (> 1200 °C) where vaporization can occur [38]. Both Eu and Yb form solid monoxides (monoxides may not exist as a separate, solid phase for the actinides), although the monoxide of Eu is better defined of the two. Monoxides of other lanthanides can be prepared from high pressure reactions between their metals and oxides [38] but frequently small amounts of metal are retained in the products attained by the route.

For the f-elements that form both a dioxide and a sesquioxide, there is a potential for forming complex intermediate oxides, which have O/M ratios between 1.5 and 2.0. A major difference between the two series is that such intermediate oxides appear to be far more structured and complex for the lanthanide series, which may be real difference or may merely reflect the greater amount of work that has been done with the lanthanide elements. At least six Tb oxides have been established (Tb_7O_{12}, $Tb_{11}O_{20}$, $Tb_{62}O_{112}$, etc.) [38]. In contrast, a material with the general formula, M_7O_{12}, is the main intermediate oxide formed with Am, Cm, and Cf, but this oxide is not known for Bk or Pu. The absence of the particular oxide for Bk and Pu may be due to a problem of preparation, which arises from the high stability of their dioxides.

Regarding the correlation of oxide formation from the standpoint of electronic structure, the formation of Cm dioxide would not be expected, as it requires the loss of an f-electron from a half-filled orbital (e.g. formation of a $5f^6$ rather than $5f^7$ state). Thus, it would be expected that only a sesquioxide would form with Cm, as is observed with its lanthanide homolog, Gd. Special consideration has been given to the electronic nature of Cm dioxide [39] to address the non-zero magnetic moment measured for Cm dioxide; a $5f^6$ state should have a zero moment. From the standpoint of electronic structure, the formation and high stability of Bk dioxide can be attributed to Bk attaining a half-filled 5f orbital, as can the existence of Tb dioxide in the lanthanide series.

The high-temperature and thermodynamic properties of the lanthanide oxides are also far better established than those of the actinides, except for elements as U and Pu, which have been studied extensively for military and commercial applications. This is especially true with regard to the vaporization behavior of the oxides. As lower oxidation states if the oxides are favored at higher temperatures [38], the vaporization of these oxides is limited to dioxides and sesquioxides as the vaporizing materials. For the lanthanides, it is the sesquioxide that is encountered in vaporization processes, except for Ce dioxide. With the actinides, the vaporization can concern the dioxides of Th, Pa, U, Np, Pu and possibly Bk (which has not been studied to date) plus the sesquioxides of the other actinide elements through Es. Most of the reported studies of the actinides have been with the Th–Pu oxides and only limited data exist for the transplutonium oxides. The vaporization behavior of the dioxides of Th through Np [40], the dioxide and lower oxides of Pu [41] (e.g. $PuO_{1.5}$, $PuO_{1.61}$, and $PuO_{1.92}$), and oxides of Pa [42] have been studied. Vaporization of these dioxides generates metal, monoxide and some dioxide vapors with the monoxides frequently being the major products; some dioxide vapor is also found during the vaporization of the dioxides of Ce, Th, Pa, U and Pu. With the lanthanide and actinide sesquioxides, the most probable vapor species are the monoxide and/or atomic vapor, although other species such as M_2O, M_2O2, M_2, etc. have also been observed with the more extensively studied lanthanide oxides [43].

As many of the lanthanide and actinide sesquioxides have physicochemical similarities, it is both useful and informative to compare their high-temperature vaporization/decomposition processes. The last segment of this paper will therefore focus on the vaporization processes for the sesquioxides and provide the basic concepts of a correlation that exists between the vaporization behavior of the oxides and the electronic structure of the parent elements.

Two major vaporization processes have been reported for the lanthanide sesquioxides [44,45]; in one case the main vapor products are the lanthanide monoxide and oxygen, while in the second the main products are atomic lanthanide and oxygen. A lanthanide monoxide is characteristically formed for the oxides of the lighter lanthanides (La–Gd), while atomic lanthanide is the product obtained when progressing to oxides of the heavier lanthanides and with oxides of the divalent lanthanides (Eu and Yb). It is significant that both Eu and Yb are divalent metals, and that they can exhibit divalent states in compounds. However, obtaining atomic vapor rather than a monoxide during vaporization of the sesquioxides of these two elements is not due directly to the availability of a divalent state. Rather, it is due to the lower stability (smaller dissociation energies) of their monoxides [44,45]. These dissociation energies for the monoxides rely on ds-type bonding in the monoxide, which requires that a d-state be available (e.g. ds^2 rather than a s^2 outer configuration for the metal atoms) for bonding. This required configuration already exists in both the solid and vapor states of the metals: La, Gd, Lu, Ac, Cm and Lr. For other lanthanide and transplutonium metals, it is necessary to promote an f-electron to a higher energy d-state and this energy must come at the expense of the monoxide bond that is formed. The correlation of promotion energies with monoxide bond stability was first developed [44] for the lanthanides and has been adapted by us for the transplutonium elements. The correlation requires establishing a base energy using the six above mentioned d-bonded metals and the f-electron promotion energies (f^ns^2--$f^{n-1}ds^2$) [2] for the two series of f-elements. Thus, the higher the promotion energy, the smaller the dissociation energy of the monoxide, and therefore the more likely will be the generation of atomic versus monoxide vapor. The product(s) generated during vaporization then become(s) a function of the electron configuration of the element itself (its f-electron promotion energy) rather than being a property of the oxide. This correlation has two important applications for the transplutonium oxides; (1) it establishes a means to predict the vaporization behavior for scarce actinides (those not amenable to experimental measurements); and (2) it provides systematics for interpreting experimentally data. To determine monoxide dissociation energies from experimental data for the transplutonium elements is difficult due to the scarcity of these materials.

Values that have been calculated for the dissociation energies of transplutonium monoxides are given in Table 3, along with values for the lanthanide monoxides. An approximate guideline for predicting which vaporization products will be obtained is as follows: as the dissociation energy becomes greater than 600 kJ mol^{-1}, the production of monoxide becomes more probable, while with lower energies atomic vapor is expected. A more

Table 3
Dissociation energies for the monoxides

Oxide	D_o (kJ mol^{-1})[a]	Oxide	D_o (kJ mol^{-1})[a]
LaO	794	AcO	(794)
CeO	786	ThO	891
PrO	736	PaO	788
NdO	699	UO	774
PmO	(711)	NpO	736
SmO	569	PuO	703
EuO	469	AmO	(550)
GdO	711	CmO	728
TbO	690	BkO	(598)
DyO	611	CfO	(498)
HoO	602	EsO	(460)
ErO	602	FmO	(443)
TmO	510	MdO	(418)
YbO	397	NoO	(268)
LuO	665	LrO	(665)

[a] Refs. [38,39,40,42 and 43]; ( ) = this work.

specific estimate can be obtained by comparing specific lanthanide and transplutonium monoxide dissociation energies and then adopt the lanthanide products that have been reported for the different lanthanide oxides [46]. Thus, for Am and the transberkelium oxides through No, elemental atomic vapor would be the expected oxide vaporization product. This prediction is in accord with our experimental data collected to date for Am, Cf and Es sesquioxides. With Bk sesquioxide, a mixture of monoxide and atomic vapor would be expected, which is what we have observed experimentally, whereas only a monoxide would be expected from Ac, Cm and Lr sesquioxides. It is not expected that experimental data can be obtained for oxides of elements above Fm oxide. Thus, their vaporization behaviors can only be estimated by using monoxide dissociation energies derived from the correlation with promotion energies.

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