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Structure and Phase Transitions of the Lanthanide Metals

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The structures and phase transitions of the lanthanide metals can be related to *f* orbital contributions to the bonding. With increasing availability of the *f* orbitals the structure sequence hexagonal closest packed, double hexagonal closest packed, δ-samarium, cubic closest packed, and body-centered cubic is observed. Increases in temperature and/or pressure result in an increased availability of the *f* orbitals resulting in predictable phase transitions.

Introduction

Many attempts have been made to explain the structures of metals. In the case of the lanthanide metals, four methods have been utilized to explain their structures and the observed phase transitions.

The first of these methods is based on pseudopotential theory (*1, 2*) which can, to a degree, make predictions as to which structure a particular metal will adopt. While this theory has had many successes, it has not been as successful as it had been hoped. Johansson and Rosengren (*3*) applied pseudopotential theory to the lanthanides using a characterizing parameter *f*, which is related to the pseudopotential, to explain the observed phase transitions. The second method was proposed by Hodges (*4*). In this case the interactions between close-packed planes was used to predict the stability of a structure. A similar method was also proposed by Havinga *et al.* (*5*). In the third method, correlations with the atomic number either directly (*6*) or indirectly (from the size of the metal atom) (*7*) were used. The final method considers the influence of the 4*f* electrons (*8–11*). It has been argued, however, that participation of the 4*f* electrons in bonding should be neglected (*4, 5*). The basis for this argument is that the radial distribution of the 4*f* electrons is such that they are kept within the ion core of the metal atom, and therefore are not available to influence the bonding. However, it does appear that the influence of the 4*f* electrons is important and it is useful in explaining observations (*12*). We will show that, from a valence bond approach, the participation of the 4*f* electrons is necessary to explain the observed structures.

Pauling (*13*) first proposed the application of valence bond theory to metals. The approach was later modified by Altmann, Coulson, and Hume-Rothery (*14*) and Brewer (*15*). Altmann *et al.* used hybrids of *s*, *p*, and *d* orbitals to explain the structures of metals. However, they did not include the *f* orbitals in their hybrids. Hybridization of *f* orbitals is important to the understanding of the lanthanide metal structures. This

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hybridization will be considered in a future paper (*16*). The use of hybrids containing *f* orbitals (from *17*) indicated that the greater the 4*f* contribution to the hybrid the more favored would be the ccp structure (*ABCABC*), while the lack of *f* orbitals for hybridization would favor the hcp structure (*ABAB*). These two structures along with the two intermediate structures also observed for the lanthanide metals, dhcp (*ABACABAC*—50% hcp) and δ-samarium (*ABABCBCACABABCBCAC*—67% hcp) complete a series ccp → dhcp → δ-Sm → hcp in which the percentage of hcp character increases indicating that the degree of participation of the 4*f* orbitals in hybridization is decreasing (*10*). There has not been a complete explanation of this, nor has there been an explanation of how the bcc structure fits into this scheme. However, Duthie and Pettifor (*18*)were able to use *d*-orbital filling to account for this sequence. This paper will discuss the correlation between the availability of 4*f* orbitals and this sequence, along with fitting the bcc structure into this sequence.

Observations

Table I lists the structures of the lanthanide metals along with the temperatures at which they undergo solid–solid phase transitions or melt (at 1 atm pressure). The data for the transition to the bcc structure along with the melting points are plotted in Fig. 1.

From the melting point curve it can be seen that the values for Eu and Yb are well below their extrapolated values, and Pm, Sm, and Tm are slightly below their extrapolated values. The values for La are higher than expected. The line for the bcc phase transition is similar to the melting point curve up to Ho, where it extrapolates to above the melting point line (except for Yb). Ho does have a bcc form at moderately high pressures (*19*), thus indicating that the extrapolation is reasonable.

The orthorhombic modifications of Tb and Dy are basically distortions of the hcp structure (*20*). At its transition temperature, Tb becomes ferromagnetically ordered (*21*), while Dy undergoes an antiferromagnetic–ferromagnetic transition (*22–24*). These are apparently the only lanthanides which change structure and magnetic properties simultaneously.

Table II lists the pressure-induced phase transitions (at room temperature) for the lanthanides. Only those transitions for which the structures of both are high- and low-pressure forms are known or at least inferred are included.

The structure of the high-pressure phase of Eu is uncertain (*29*); however, it is near the pressure calculated for the transition of divalent europium to the trivalent state (*3*, *26*). This high-pressure phase may be hcp (*19*). A similar valence change is expected for Yb at about 140 kbar (*3*, *26*).

Discussion

For the lanthanide metals the 6*s*, 5*d*, and 4*f* electrons are all of similar energies, therefore, it should not be too difficult to form hybrid orbitals from among this set. However, these orbitals, especially the 4*f*, change in energy when proceeding from one lanthanide to another. The change in the energy of the 4*f* orbitals is very important because they are nearly withdrawn into the ion cores, especially for the heavier lanthanides (*10*), and so even a small change can drastically affect their availability for hybridization.

Figure 2 plots, in arbitrary units, the relative stabilization energies (according to the method of Slater (*30*)) for the 4*f* electrons versus the atomic number. The lower the energy of the 4*f* orbital the greater the degree of withdrawal into the ion core. The

TABLE I

TEMPERATURE-INDUCED PHASE TRANSITIONS OF THE LANTHANIDE METALS (12)

Metal	Low-temperature Phase	High-temperature Phase	Transition temperature (°C)
La	dhcp	ccp	310 (heating) 260 (cooling)
	ccp	bcc	865
	bcc	liquid	918
Ce	ccp(α)	dhcp	−158
	dhcp	ccp(γ)	−23
	ccp(γ)	bcc	726
	bcc	liquid	798
Pr	dhcp	bcc	795
	bcc	liquid	931
Nd	dhcp	bcc	863
	bcc	liquid	1021
Pm	dhcp	bcc	890
	bcc	liquid	1042
Sm	δ	bcc	922
	bcc	liquid	1074
Eu	bcc	liquid	822
Gd	hcp	bcc	1235
	bcc	liquid	1313
Tb	orthorhombic	hcp	−53
	hcp	bcc	1289
	bcc	liquid	1365
Dy	orthorhombic	hcp	−187
	hcp	bcc	1381
	bcc	liquid	1412
Ho	hcp	liquid	1474
Er	hcp	liquid	1529
Tm	hcp	liquid	1545
Yb	hcp	ccp	−3
	ccp	bcc	795
	bcc	liquid	819
Lu	hcp	liquid	1663

two heavy diagonal lines are for the divalent (M^{2+}) and the trivalent (M^{3+}) ions. Nonintegral valencies will fall between these lines.

The divalent line falls above the trivalent line because there is a lower effective nuclear change for the divalent metals and so the $4f$ electrons are not drawn into the cores as much as they are for the trivalent metals. The slopes of the lines are due to the increasing effective nuclear charge. Recall that the f orbitals are more strongly affected by screening than are the s, p, or d orbitals. The metals are all assumed to have

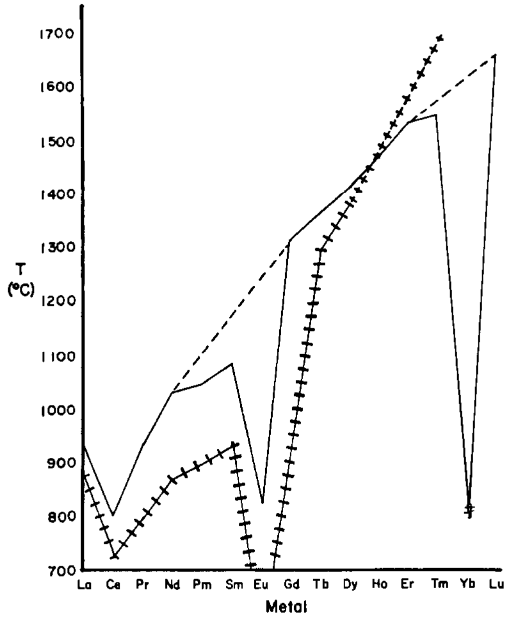

FIG. 1. Transition temperatures for the lanthanide metals. The melting points (——) and the transition temperatures for transformations from various structures to the body-centered cubic structure (┼┼┼) are plotted along with extrapolated values (--- and + + +, respectively).

integer valence values and are plotted as such; this is not necessarily true, but it is not an unreasonable simplification.

The only two lanthanides which may be considered even close to divalent in the metallic state are Eu and Yb. As divalent elements they have stable half-filled and completely filled *f* orbitals, respectively. This tendency towards divalency is exhibited, in general, in their chemistry. The chemistry of two other lanthanides show a slight tendency towards divalency. These two metals are Sm and Tm. This tendency towards divalency can be seen in Fig. 1 from the slightly low values at Sm and Tm. Since the stabilizations of divalent Sm and Tm are much less than for Eu and Yb the deviations from the extrapolated values are much less. The graph also indicates that Pm may have a tendency towards divalency which is greater than expected.

The horizontal lines in Fig. 2 indicate the stability ranges for the different structure types. Note that, on proceeding vertically

TABLE II

OBSERVED HIGH-PRESSURE PHASE TRANSITIONS FOR THE LANTHANIDES[a]

Metal	Low-pressure phase	High-pressure phase	Pressure (kbar)	Reference
La	hcp	ccp	23	(*20*)
Ce	ccp	ccp	7	(*19*, *25*)
	ccp	$\alpha' + \alpha''$	51	(*26*)
Pr	dhcp	ccp	39	(*9*)
Nd	dhcp	ccp	65	(*9*)
Pm				
Sm	δ	dhcp	30	(*19*)
Eu	bcc	(hcp?)	150	(*19*, *27*)
Gd	hcp	δ	32	(*3*)
Tb	hcp	δ	38	(*3*)
Dy	hcp	δ	52	(*3*)
Ho	hcp	δ	72	(*3*)
Er	hcp	δ	99	(*3*, *28*)
Tm	hcp	δ	119	(*3*, *28*)
Yb	ccp	bcc	39.5	(*20*)
Lu	hcp	δ	≈200	(*19*)

[a] The high-pressure phases for Er, Ho, and Tm may be α-samarium instead of dhcp (*19*).

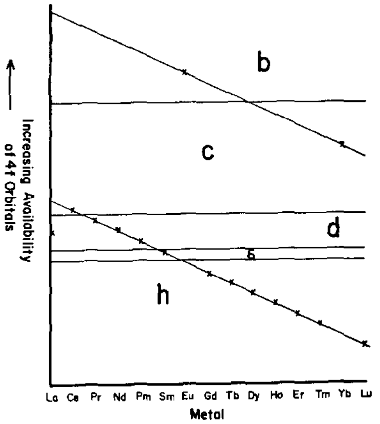

FIG. 2. Relative availability of the 4*f* orbitals for the lanthanide metals, showing regions where different structures are stable. b = body-centered cubic, h = hexagonal closest packed, d = double hexagonal closest packed, c = cubic closest packed, δ = δ-samarium.

on the graph, one sees the structure sequence of Gschneidner and Pearson (*10*) plus the bcc structure. Thus if the theory that the structure sequence is due to increased participation of the 4*f* orbitals in bonding then the bcc structure should require the greatest degree of *f* character. The validity of this is a consequence of the fact that it is impossible to have a set of equivalent bonding orbitals directed at the corners of a cube (nearest neighbors in bcc) without some contribution from the *f* orbitals.

It may be seen from Fig. 2 that the availability of the 4*f* orbitals may be correlated with the observed structures. This correlation is emphasized by the phase transitions of the lanthanides. However, the transitions of some lanthanides may skip over one or more of these phases.

First we will consider the effect of temperature on the phase transitions. Since the screening of the nuclear charge increases with temperature the 4*f* orbitals should increase the availability. There are two reasons for the increased screening (*5*): first, the mean free path is decreased and second, the Fermi level becomes more diffuse. The increased availability of the 4*f* orbitals results in their upward movement in Fig. 2. In general, this is what is observed. The only real exception is the α-Ce to β-Ce transition at −158°C. This may be in part due to the fact that the valence of Ce in α-Ce is not 3 but 3.77 (*31*). This high valence for Ce may result in an empty 4*f* subshell as in La (see below). There is evidence that the 4*f* orbitals of α-Ce are not withdrawn as far as expected and are therefore still available for bonding.

The orthorhombic distortions of the hcp lattices of Tb and Dy are probably the result of magnetic ordering in addition to the valence bond effect.

The La point below the M^{3+} line does not, in this case, indicate a valency greater than 3^+, however, it does indicate that the *f* orbitals are not as readily available as would be expected. This may be due to the fact that the *f* orbitals on La are empty and therefore are not drawn to the core (not drawn down to a favorable energy). A similar situation arises in α-Ce as the tetravalent Ce also has vacant *f* orbitals. Again the vacant orbitals are not drawn towards the core like orbitals with electrons in them, so the 4*f* orbitals are not drawn so far down as to be down to the +4 line (not indicated in Fig. 2) but only to a position slightly below the +3 line and so the α to dhcp transition observed for Ce would plot higher than expected and thus appear just below the +3 line and not near the +4 line. An alternative explanation is that being empty the 4*f* orbitals do not contribute any electrons to bonding and thus do not contribute to the stability of the structure.

Phase transitions to the bcc structure are often assumed to be due to the increase in entropy that should accompany a closest packed to body centered phase transition. However, the validity of this statement may be questionable for some of the lanthanide metals. Pearson (*32*) has shown that an hcp structure with a *c*/*a* ratio of 0.05

less than ideal is more "open" than a bcc structure. In addition, he points out that there is some question as to the constraints imposed by the eight near neighbors. Thus it may not be entirely valid to attribute the transitions to the bcc structure as being solely due to entropy effects.

Because the 4*f* electrons sink lower in energy as the atomic number increases it becomes more difficult to raise them to the level needed to utilize them in producing the bcc structure. As they sink lower a higher temperature is needed to bring them up, through increased screening, so the transition temperatures increase with the atomic number.

Since the maximum in the radial distribution of the 4*f* orbitals is less than that of the 6*s* or 5*d* orbitals they are not greatly affected by increases in pressure (*10*). Therefore an increase in pressure leaves the 4*f* orbitals relatively unaffected and pushes the 6*s* and 5*d* orbitals in. This results in an increased availability of the 4*f* orbitals. Thus an increase in pressure should simulate an upward movement in Fig. 2. This is what is observed. The only exceptions, Ce and Eu, apparently are due to valency changes, +3 to +4 for Ce and +2 to +3 for Eu (*3*, *26*). This, of course, assumes that there is a +2 to +3 valence change for Eu which has not been confirmed. This increase in valence should result in a downward movement in Fig. 2. This is just what is observed. Eu is transformed from bcc to hcp (?), while Ce transforms from ccp to α'-Ce (α'-Ce is isostructural with α-U (*31*), a distorted hcp structure (*20*). Note that metastable α''-Ce also forms with α'-Ce; α''-Ce is a distorted ccp structure (*31*)). It should be noted that Yb transforms from a ccp to a bcc structure at 39.5 kbar (*20*). Such a transition, from a closest packed to a more "open" structure, is the reverse of what is expected, and should not be pressure induced. However, if the increased availability of the 4*f* orbitals is taken into account then such a transition is predictable.

The variations in the pressures required for the phase transitions may be explained by an argument similar to that used for the variation with temperature.

It is important to remember that a large amount of *f* character is not needed for the resulting hybrid orbitals to drastically affect the bonding. Pauling (*33*) showed that by adding 4% *d* character and 2% *f* character to the sp^3 hybrids of two carbon atoms results in a 38% increase in the bond strength. Therefore arguments based upon the assumption that the 4*f* orbitals are too low lying are valid only if a significant amount of *f* character is required; but since the bonding argument in this paper does not require considerable *f* orbital contribution such reservations are not applicable here. In addition Pauling's argument implies that there may be a contribution from the *f* orbitals for all metals, not just the lanthanides and actinides.

It is apparent that the availability of the *f* orbitals is related to the crystal structures of the lanthanide metals. This trend can be extrapolated to barium, cesium, and hafnium, resulting in further correct structure predictions, but beyond these elements other factors seem to predominate. Due to the similarities between the lanthanides the influence of the *f* orbitals which is normally masked by other factors may be seen. This similarity is greater than for any other group of metals including the actinides. It is very likely that the *f* orbitals contribute to the structures of most metals and so their contribution, even though small, must always be taken into account.

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