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The Itinerant Character of 4f Orbitals in Lanthanide Metals by a Comparison of Lanthanide Contraction in Metals and Ionic Compounds

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Abstract

Changes in the atomic number of the metallic and ionic radii of lanthanides, and in the unit cell volumes of intermetallics, monopnictides, monochalcogenides and typically ionic compounds of lanthanides have been compared. It was found that ionic radii and unit cell volumes of ionic compounds decrease almost monotonically with increasing atomic number. However, in the case of metallic radii contraction in the Pm–Gd interval is much smaller than in any other interval consisting of four lanthanides. The difference between the contraction of metals and ionic compounds was explained by delocalization of 4f orbitals in lanthanide metals due to direct f–f overlap.

Introduction

It is generally assumed that 4f orbitals, contrary to 5f orbitals, are localized in lanthanide metals and intermetallics [1]. However, the change from the dhcp structure for light lanthanide metals to the hcp structure for heavy ones, and the low melting points of light lanthanides have been explained by hybridization of some of the 4f electrons and s and d valence electrons [2, 3]. Theoretical arguments have also been presented for 4f electron delocalization in lanthanide metals due to direct 4f–4f overlap [4]. Moreover, changes in the position of yttrium in the lanthanide series with respect to unit cell volumes of isostructural compounds and the magnitude of the double–double effect in unit cell volumes of lanthanide compounds have been explained in terms of a contribution from covalency to bonding due to the participation of 4f orbitals [5, 6].

The aim of this paper is to present evidence for the itinerant character of 4f orbitals in lanthanide metals from the shape of contraction. For that purpose contraction in consecutive intervals of the lanthanide series has been compared for metals, intermetallics and some lanthanide compounds including, in particular, typically ionic compounds such as oxides and fluorides. As a measure of contraction either changes in radii (metallic and ionic) with the atomic number or changes in unit cell volumes of isostructural compounds have been used.

Results and Discussion

Table I shows changes in the radii and unit cell volumes in the La–Nd, Pm–Gd, Gd–Ho and Er–Lu intervals (tetrads) as a percentage of the total change from lanthanum to lutetium. Table I also shows the ratio of the change in the second to that in the third tetrad, Δ(Pm–Gd)/Δ(Gd–Ho). Unit cell volumes were taken from published data referred to in the last column of Table I. Unit cell volumes of promethium compounds were calculated by linear interpolation of the corresponding values of neodymium and samarium compounds. Except for the metals, Ln_2S_3 and LnF_3 all compounds listed in Table I are isostructural from La to Lu. In the case of the sesquisulfides unit cell volumes in the Ho–Lu interval have been recalculated from monoclinic to orthorhombic values on the basis of Dy_2S_3 which exists in both modifications. In the case of the trifluorides contraction refers to the hexagonal unit cell calculated for heavy lanthanides by comparison of the orthorhombic and hexagonal unit cells of GdF_3. Figure 1 represents plots of the metallic radii of lanthanides [7] and actinides [17, 18] and ionic radii of lanthanides [8] *vs.* the atomic number. The metallic radius of cerium is that calculated by Gschneider and Smoluchowski [19] for hypothetical trivalent cerium metal.

From data presented in Table I and Fig. 1 the following conclusions can be drawn:

(a) For metals, ions and all compounds listed in Table I contraction is greatest in the La–Nd tetrad and, except for metals, is smallest in the last tetrad.

(b) In the case of the lanthanide metals contraction in the Pm–Gd tetrad is considerably smaller than in the consecutive tetrads.

TABLE I. Percent Contraction in the Tetrads.

	Δ(La–Nd)	Δ(Pm–Gd)	Δ(Gd–Ho)	Δ(Er–Lu)	$\frac{\Delta(\text{Pm–Gd})}{\Delta(\text{Gd–Ho})}$	Reference
Metallic radius, CN = 12	40.4	6.7	24.4	15.0	0.27	[7]
Ionic radius, CN = 6	31.0	19.3	20.7	14.5	0.93	[8]
Ionic radius, CN = 8	27.9	21.9	20.8	12.0	1.05	[9]
LnAg	33.4	18.1	21.7	13.2	0.83	[10]
LnZn	36.3	16.8	19.8	14.6	0.85	[10]
LnCd	37.1	16.2	19.5	13.1	0.83	[10]
LnHg	34.2	16.8	22.4	13.9	0.75	[10]
$LnAl_2$	36.8	17.2	20.4	12.7	0.84	[11]
Ln_2In	36.9	15.6	21.5	13.7	0.73	[12]
LnP	40.0	15.4	18.9	13.9	0.81	[13]
LnAs	38.3	18.2	19.3	13.3	0.94	[13]
LnSb	40.2	18.4	19.6	10.7	0.94	[13]
LnBi	38.0	18.2	20.2	10.3	0.90	[13]
Ln_2S_3	34.6	18.3	19.9	14.5	0.92	[14]
Ln_2O_3	33.0	19.6	19.9	14.5	0.98	[15]
LnF_3	33.4	21.1	20.3	10.6	1.04	[9]
$Cs_2NaLnCl_6$	31.2	21.1	20.0	14.2	1.06	[16]

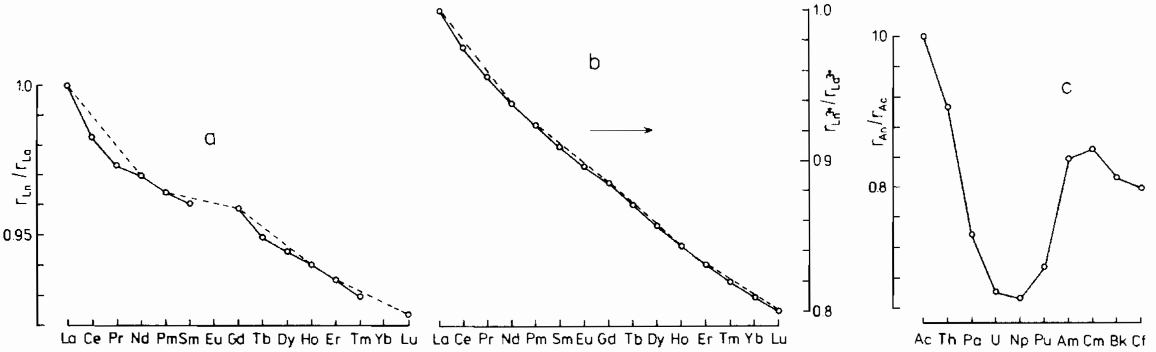

Fig. 1. Contraction of : (a) lanthanide metallic radii, (b) lanthanide ionic radii and (c) actinide metallic radii.

(c) With increasing ionic character of bonding, contraction tends to decrease monotonically across the series. For the metals contraction is much smaller in the Pm–Gd than in the Gd–Ho interval. For intermetallics contraction is still perceptibly smaller in the second than in the third interval; it is practically the same in the two intervals for oxides, whereas for fluorides and complex chlorides the decrease in the unit cell volume appears to be slightly greater in the Pm–Gd than in the Gd–Ho interval.

(d) Contraction in the La–Nd tetrad is greater for metals than for ionic compounds, at least partially at the cost of the contraction in the second tetrad.

(e) There is a striking analogy between changes in the lanthanide and actinide metallic radii. The very small decrease in the lanthanide metallic radii in the Pm–Gd interval corresponds to the increase in the metallic radii of actinides, observed in the analogous Np–Cm interval.

(f) The double–double effect observed in the singular position of the f^3, f^4, f^{10} and f^{11} configurations, in addition to the f^0, f^7 and f^{14} configurations, is much more pronounced in the case of metallic than ionic radii [6].

Changes in the metallic radii of actinides as a function of the atomic number and similar changes in the lattice parameters of the actinide monopnictides and monochalcogenides have been explained as due to varying contribution from the tetravalent state or to 5f orbitals delocalization [17, 20]. In the case of the lanthanides only metallic cerium is partially tetravalent, whereas it is generally accepted that the remaining lanthanide metals, except for divalent europium and ytterbium, are trivalent. Therefore, the difference between changes in the lanthanide metallic and ionic raddi across the series can be explained only by delocalization of 4f orbitals, which should be much greater in metals than in ionic compounds.

In highly ionic compounds of lanthanides such as fluorides or oxides the spatial extension of 4f orbitals in the La–Nd interval is probably similar to that in free ions. The outer 5p orbitals are not sufficiently shielded from the nuclear charge and contract considerably in this interval. In the Pm–Gd tetrad the radial extent of 4f orbitals in free ions and ionic compounds appears to decrease abruptly, which results in an increased screening effect towards the 5p orbitals and a comparatively small contraction, equal to that in the consecutive Gd–Ho tetrad. From gadolinium on the spatial extension of 4f orbitals continues to decrease but in a more gradual way, so that contraction also shows a gradual decrease.

In the case of the lanthanide metals and to a lesser extent of the intermetallics there appears to be at the beginning of the group additional delocalization of 4f orbitals due to direct f–f overlap or hybridization with more itinerant orbitals. The increased delocalization results in a slightly greater contraction of the metallic than ionic radii in the La–Nd tetrad. In the Pm–Gd tetrad the increase in the intrinsic (free ion) localization of 4f orbitals also diminishes the f–f overlap and hybridization, so that for metals the screening effect towards the outer orbitals decreases in this tetrad to a much greater extent than in the case of ionic compounds. The result is the very small contraction of lanthanide metallic radii observed in the Pm–Gd interval. For actinide metals the additional delocalization due to direct f–f overlap or hybridization is considerable [1], and is certainly much greater than for lanthanide metals. Therefore, contraction is much greater in the Ac–U than in the La–Nd interval, see Fig. 1. On the other hand the combined effect of intrinsic localization of f orbitals and of decreased f–f overlap is much greater in the Np–Cm than in the Pm–Gd interval, so that shielding increases to a much greater extent for actinide than for lanthanide metals. As a result the metallic radii of actinides increase between Np and Cm, instead of decreasing slightly as is the case with lanthanide metals in the respective Pm–Gd interval.

The effect of decreased contraction in the Pm–Gd interval is much greater for metals than for intermetallics. Since on the other hand the Ln–Ln spacing is smaller in metals than in intermetallics, it follows that the delocalization of 4f orbitals in metals is mainly due to direct 4f–4f overlap, which decreases with increasing Ln–Ln spacing.

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