The Itinerant Behavior of Actinides. Comparison of Unit Cell Volumes of Isostructural Actinide and Lanthanide Compounds

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Abstract

The positions of Ac, U, Np, Pu, Cm, Bk and Cf in the lanthanide series with respect to unit cell volumes of a number of isostructural lanthanide and actinide $M_m X_n$ compounds were determined from published data. It was found that with increasing electronegativity of the X atom actinides shift across the lanthanide series from heavy to light lanthanides. The itinerant properties of actinides, which increase from Ac to U and decrease from U to Cm, have been explained by delocalization of the 5f orbitals. The delocalization increases with decreasing electronegativity of the X atom and is high in the U–Pu interval and low for Cm and beyond.

Introduction

The 4f and 5 f groups of elements are very similar to each other with respect to many properties, but also show remarkable differences. These differences can be attributed to different spatial extention of the 4f and 5f orbitals and to their different contribution to bonding. A method of comparing 5f with 4f electron elements consists in locating a given actinide in the lanthanide series, *i.e.* in finding its closest analog among lanthanides with respect to the property studied. The place which an actinide occupies in the lanthanide series can be quantitatively specified by the actinide relative or apparent atomic number, Z_{An}. In the case where the property considered is the unit cell volume, V, of isostructural $M_m X_n$ compounds, this number can be calculated from the following formula based on linear interpolation [1, 2]

$$Z_{An}(V) = Z_{Ln'} + \frac{V_{Ln'} - V_{An}}{V_{Ln'} - V_{Ln''}} \qquad (1)$$

where Z_{Ln} is the lanthanide atomic number, and Ln' and Ln'' are two lanthanides encompassing the actinide ($Z_{Ln'} < Z_{Ln''}$).

It has been shown in previous papers [1, 2] that the positions which yttrium and americium occupy in the lanthanide series change with the electronegativity of the X atom in the yttrium, americium and lanthanide isostructural $M_m X_n$ compounds. Thus for fluorides, yttrium is a heavy and americium is a light pseudo-lanthanide, whereas for intermetallics both yttrium and americium are located in the middle of the lanthanide series. The opposite itinerant behavior of yttrium and americium with respect to unit cell volumes is similar to that observed for free energies of complex formation and has been explained by the contribution from covalency to bonding. This contribution increases in the order yttrium < lanthanides < americium and depends on the counteratom in the lattice [1, 2]. The inclusion of covalency to the initially purely ionic bonding results in covalency shortening of the M–X bond [3]; this is greater for americium (and generally for actinides) than for lanthanides and absent for yttrium. The inclusion of covalency produces the itinerant properties of americium and yttrium, as shown schematically in Fig. 1.
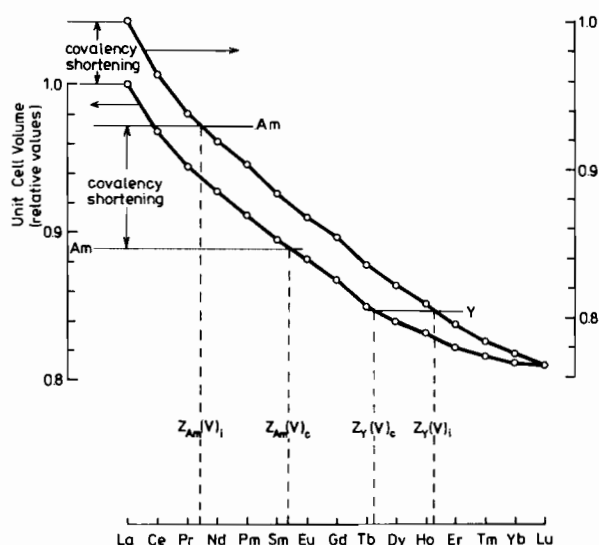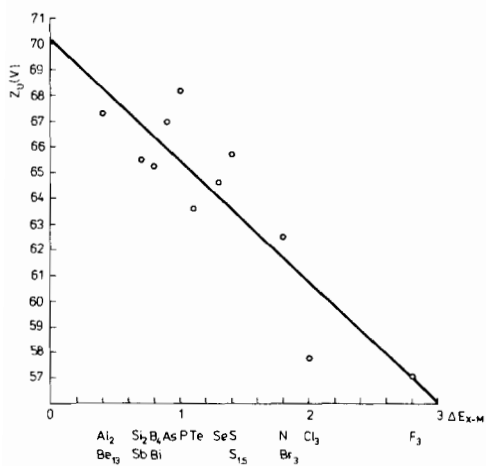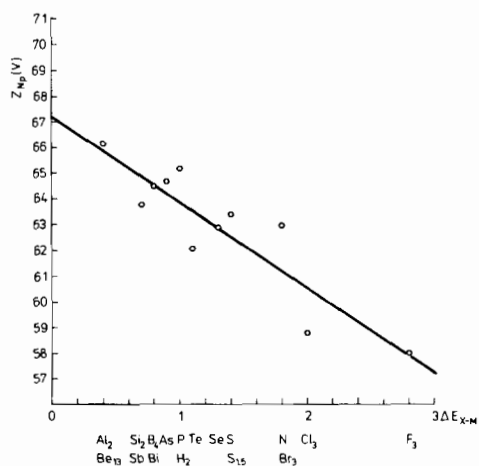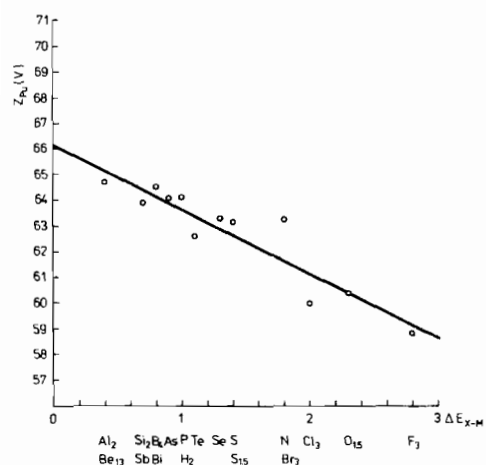

Fig. 1. The position of Y and Am in the lanthanide series with respect to unit cell volumes for ionic and covalent solids. Upper curve: purely ionic $Ln_m X_n$ compound; lower curve: the same compound but with delocalization of the 4f orbitals.
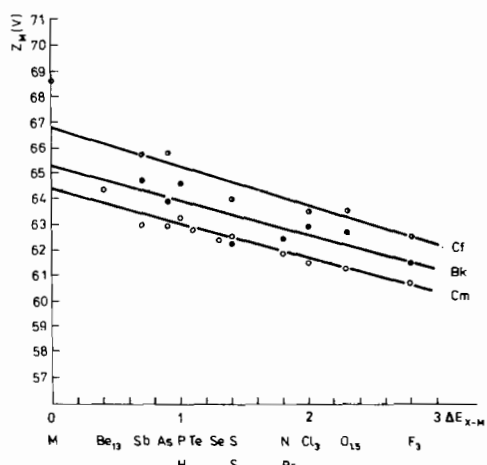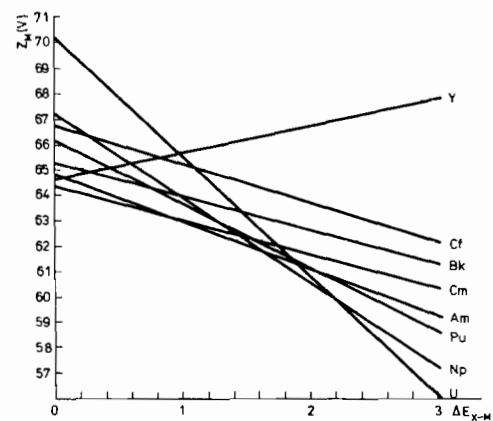
(a)

(b)

(c)

(d)

(e)

Fig. 2. The position of actinides in the lanthanide series as a function of the electronegativity of the X atom in $MX_{n/m}$ isostructural lanthanide and actinide compounds: (a) U; (b) Np; (c) Pu; (d) Cm, Bk and Cf; (e) comparison of results.

Within each lanthanide and actinide group of elements the delocalization of f orbitals is high at the beginning of each group and then decreases with increasing atomic number [4, 5]. Therefore, one can anticipate that, with respect to unit cell volumes, uranium, neptunium and plutonium should be more itinerant than americium, whereas curium and heavier actinides should be less itinerant. The aim of this work was to check this presumption on the basis of published crystallographic data.

Results and Discussion

Unit cell parameters of Ac, U, Np, Pu, Cm, Bk and Cf compounds were taken from refs. 6–11 and those of lanthanide compounds from references listed in refs. 1, 2. The apparent atomic numbers of actinides have then been computed from expression (1). In the case of actinium, only data for the following five compounds isostructural with lanthanide compounds were found: Ac_2S_3, $AcBr_3$, Ac_2O_3, $AcCl_3$ and AcF_3. For each of these compounds actinium falls out of the lanthanide series, so that $Z_{Ac}(V)$ could be only approximately estimated by extrapolating unit cell volumes of respective lanthanide compounds to atomic numbers smaller than 57. The apparent atomic numbers of actinium found for these compounds are: 53, 53, 52, 53.5 and 52.5, respectively.

The apparent atomic numbers of actinides determined in this work, together with the previously obtained results for Y and Am, were plotted against the difference between the electronegativities of the X and Ln (An) atoms (Fig. 2). Following the idea of Pauling [12], it was assumed that the difference in electronegativity, ΔE_{X-M}, may serve as an approximate measure of the tendency of the M and X atoms to form covalent bonding. In the case of two different X atoms having the same electronegativity value, the mean apparent atomic number has been calculated and plotted. It is seen from Fig. 2 that for all actinides from uranium to californium, $Z_{An}(V)$ increases with decreasing difference in electronegativity. The relationship between $Z_{An}(V)$ and ΔE_{X-M} can be approximated by straight lines with different slopes for different actinides. With reference to Fig. 1 and to the presumed relationship between electronegativity and bond covalency, it may be concluded from the itinerant behavior of actinides that 5f orbitals are, in general, more delocalized than 4f orbitals and that the difference in delocalization increases with the ability of the X atom to form covalent bonding. As far as individual actinides are concerned, there is apparently no difference in delocalization of 5f orbitals in actinium and 4f orbitals in the light members of the lanthanide series, because there is no change in $Z_{Ac}(V)$ with the change of the X atom.

Between actinium and uranium a dramatic increase in the itinerant behavior is observed. The covalency shortening of the M–X distance in uranium compounds is much greater than in the respective compounds of lanthanides, so that for intermetallics uranium resembles holmium, whereas for the ionic trifluorides uranium is pseudo-lanthanum.

The itinerant behavior of actinides and the delocalization of their 5f orbitals decrease from U to Cm and appear to be constant between Cm and Cf. There is a qualitative relationship between the slope of the $Z_{An}(V)$ *versus* ΔE_{X-M} plot and the actinide metallic radius. The increase in the absolute value of the slope between actinium and uranium corresponds to the decrease in the metallic radius, and the decrease of the slope between uranium and curium corresponds to the increase in the metallic radius. Since changes in actinide metallic radii are due to changes in delocalization of 5f orbitals [9], the observed correlation supports the view that the itinerant behavior of actinides with respect to unit cell volumes originates from and is evidence for considerable contribution of 5f orbitals to bonding in many actinide solids. It is seen from Fig. 2 that metallic Cm is a heavier pseudo-lanthanide than expected from the $Z_{An}(V)$ *versus* ΔE_{X-M} linear relationship. The same was found previously for americium [2]. Comparison of unit cell volumes shows that metallic Bk and Cf even fall out of the lanthanide series, *i.e.* are heavier pseudo-lanthanides than lutetium. Since in actinide metals the delocalization is probably caused by direct 5f–5f overlap [4], the mechanism of delocalization in actinide solid compounds should be different, and may consist in hybridization of 5f orbitals with more itinerant 7s, 6d orbitals and overlapping with the X atom orbitals.

Acknowledgement

References

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