

The Position of Yttrium within Lanthanides with Respect to Unit Cell Volumes of Isostructural Compounds as an Indication of Covalency in Lanthanide Compounds

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The position of yttrium in the lanthanide series with respect to unit cell volumes has been determined from literature data for 52 isostructural M_mX_n compounds of lanthanides and yttrium. A linear correlation between the position and the electronegativity of the X atom has been demonstrated. This result has been explained in terms of covalent shortening of the $M-X$ bonds in lanthanide compounds.

Introduction

The participation of $4f$ orbitals in bonding in lanthanide compounds has been discussed in several papers (1-8) from both experimental and theoretical points of view. It follows from these papers that although bonding in lanthanide compounds is predominantly ionic, there are also indications of a certain degree of covalency involving $4f$ orbitals. In spite of these and other studies the question of covalency in bonds formed by lanthanides and, in particular, the question of the degree of covalency in different compounds appears to be still open, so that further evidence for the presumed participation of $4f$ orbitals in bonding is needed. Such evidence may result from comparison of lanthanides with yttrium in respect to certain properties. It is well known that yttrium resembles lanthanides, however, its position within the lanthanide series is not constant, but depends on the property considered. The best

known example of the ability of yttrium to wander along the lanthanide series is the change of its position within lanthanides in respect to the free energy of complex formation. Although this particular behavior of yttrium seems to be correlated with covalency in lanthanide complexes (9), the correlation is not a simple one because of the complex character of the ΔG° function. On the other hand it can be expected from covalent shortening (10) that the position of yttrium within the lanthanides in respect to $M-X$ distances in M_mX_n lanthanide and yttrium compounds may be directly correlated with the participation of $4f$ orbitals in the bonding in the lanthanide compounds. Instead of comparing $M-X$ distances for lanthanides and yttrium, the respective unit cell volumes of isostructural M_mX_n compounds can be compared (10), since there exists a linear correlation between unit cell volume and the ionic volume of the cation in series of isostructural compounds (11). With the aid of unit cell volumes the atomic

number of yttrium relative to that of lanthanides, $Z_Y(V)$, can be calculated for each series of isostructural compounds of lanthanides and yttrium from the following relation based on linear interpolation:

$$Z_Y(V) = Z_{Ln'} + \frac{V_{Ln'} - V_Y}{V_{Ln'} - V_{Ln''}}, \quad (1)$$

where Ln' and Ln'' are two neighboring lanthanides encompassing yttrium ($V_{Ln'} > V_Y > V_{Ln''}$) and $V_{Ln'}$, $V_{Ln''}$, and V_Y are the respective unit cell volumes. The relative atomic number of yttrium defined in this way can serve as a quantitative measure of the position of yttrium in the series of lanthanides for each X atom, and because of covalent shortening expected for lanthanides, but not for yttrium, as a relative measure of covalency of the $Ln-X$ bond. In this respect, $Z_Y(V)$ plays a role similar to the "covalency contraction parameter," introduced by Shannon and Vincent (10), used in studying bonding in transition metal compounds.

Results and Discussion

The relative atomic number of yttrium, $Z_Y(V)$, defined by Eq. (1) has been calculated from literature data for 52 different series of isostructural compounds of lanthanides and yttrium and the results obtained are presented in Table I. With few exceptions, data for lanthanides and yttrium were taken from the same paper. As expected, $Z_Y(V)$ is not constant, but changes with the X atom from about 64 to over 67. The highest values of $Z_Y(V)$ are observed for compounds with fluorine and oxygen as ligand atoms. In the case of hydrogen, phosphorus, arsenic, antimony, sulfur, selenium, tellurium, and iodine, $Z_Y(V)$ is lower, generally between 65–66. Low values of $Z_Y(V)$ are also observed for borides, carbides, silicides, and in particular, for intermetallic compounds. The lowest value of Z_Y is observed for lanthanide

metals. The observed decrease in $Z_Y(V)$ corresponds to the general ideas of increasing tendency of covalent bonding with changing X atom. In order to obtain a quantitative correlation between $Z_Y(V)$ and covalency, $Z_Y(V)$ has been plotted in Fig. 1 as a function of the difference between the electronegativity of the X atom and the electronegativity of the lanthanide atoms, ΔE_{X-M} . For compounds with the same X atom but of different stoichiometry, mean value of $Z_Y(V)$ has been calculated and plotted. The value of $Z_Y(V)$ for the same X atom but in different compounds, differ in the mean by about 0.5. This difference may result from both changes in $M-X$ distances with the change in stoichiometry and structure, and from experimental error. It has been found that $Z_Y(V)$ calculated for the same X atom in the same series of M_mX_n compounds but from data of various authors differs sometimes also by about 0.5. The electronegativities used were taken from the paper of Batsanov (54). In his scale the electronegativity of yttrium is 1.2 and is equal to the electronegativities of heavy lanthanides.

It is seen from Fig. 1 that there is a good linear correlation between $Z_Y(V)$ and the electronegativity of the X atom. The straight-line equation is $Z_Y(V) = 1.10 \cdot \Delta E_{X-M} + 64.53$, with $\sigma = 0.17$ and $r = 0.93$. The correlation obtained can be accounted for in the following way. Let us assume at first that there is no contribution from covalency to both lanthanide- X and yttrium- X bonds. If so, then $Z_Y(V)$ would be practically independent of X and most probably near to 68. The inclusion of covalency in the case of lanthanides, but not yttrium, will shorten the $M-X$ distances, and decrease the unit cell volumes of lanthanide compounds, leaving the respective values for yttrium unchanged. According to Eq. (1) the decrease of V_{Ln} and the constancy of V_Y will result in the decrease of $Z_Y(V)$, provided the covalency is the same

TABLE I
 RELATIVE ATOMIC NUMBER OF YTTRIUM, $Z_Y(V)$

Compound	$Z_Y(V)$	Reference	Compound	$Z_Y(V)$	Reference
<i>Ln</i> -metals	64.0	(12)	<i>Ln</i> Si ₂ (hexagonal)	65.5	(28)
<i>Ln</i> Be ₁₃	65.0	(13)	<i>Ln</i> Si ₂ (orthorhombic)	65.2	(28)
<i>Ln</i> ₃ Al ₂	65.0	(14)	<i>Ln</i> Ge ₂	65.0	(30)
<i>Ln</i> Al ₂	64.7	(15, 16)	<i>Ln</i> N	66.5	(31, 32)
<i>Ln</i> In ₃	64.8	(17)	<i>Ln</i> P	65.8	(33, 34)
<i>Ln</i> Co ₂	64.6	(15, 18)	<i>Ln</i> As	65.8	(35)
<i>Ln</i> ₂ Co ₇	65.7	(19)	<i>Ln</i> Sb	65.0	(35)
<i>Ln</i> Co ₅	65.8	(20)	<i>Ln</i> ₂ O ₃ (monoclinic)	67.2	(36)
<i>Ln</i> ₂ Co ₁₇	65.2	(21)	<i>Ln</i> ₂ O ₃ (cubic)	67.1	(37)
<i>Ln</i> Ni ₃	65.1	(22)	<i>Ln</i> ₂ S ₃	66.0	(38)
<i>Ln</i> Ni ₅	65.2	(20)	<i>Ln</i> ₂ Te ₃	65.8	(39)
<i>Ln</i> ₂ Ni ₁₇	65.5	(21)	<i>Ln</i> S	65.8	(40)
<i>Ln</i> Cu	65.2	(23)	<i>Ln</i> Se	66.0	(41)
<i>Ln</i> Ag	65.5	(24)	<i>Ln</i> Te	65.7	(35)
<i>Ln</i> Au	65.8	(24)	<i>Ln</i> Te ₃	65.5	(42)
<i>Ln</i> Cu ₂	65.5	(25)	<i>Ln</i> F ₃	67.7	(43)
<i>Ln</i> Ag ₂	65.8	(26)	<i>Ln</i> Br ₃	67.0	(44)
<i>Ln</i> Au ₂	66.0	(26)	<i>Ln</i> I ₃	65.4	(45)
<i>Ln</i> Zn	65.0	(23)	<i>Ln</i> AO ₃ ^a	67.1	(46)
<i>Ln</i> H ₂	65.9	(27)	<i>Ln</i> AO ₄ ^b	67.1	(47)
<i>Ln</i> H ₃	65.7	(27)	<i>Ln</i> ₃ A ₅ O ₁₂ ^c	67.2	(48)
<i>Ln</i> B ₄	65.6	(28)	Li <i>Ln</i> F ₄	67.1	(49)
<i>Ln</i> B ₁₂	65.7	(28)	Na <i>Ln</i> F ₄	67.7	(50)
<i>Ln</i> ₃ C	65.2	(29)	K ₃ <i>Ln</i> F ₆	67.6	(51)
<i>Ln</i> ₂ C ₃	65.4	(29)	Cs ₂ Na <i>Ln</i> Cl ₆	66.6	(52)
<i>Ln</i> C ₂	66.2	(29)	Cs ₂ K <i>Ln</i> Cl ₆	66.7	(53)

^a A = Al, Ga, V, Cr, Fe, Co.

^b A = P, As, V.

^c A = Al, Fe, Ga.

for the two neighboring lanthanides *Ln'* and *Ln''*, i.e., the difference $V_{Ln'} - V_{Ln''}$ remains unchanged. If the difference in electronegativities is a proper measure of covalency then the decrease in ΔE_{X-M} should result in a proportional decrease of $Z_Y(V)$, as seen in Fig. 1. The scatter of points about the straight line in Fig. 1 is probably caused by three factors. The first factor is the experimental error in the determination of unit cell volumes, the second is due to the fact that the difference in electronegativities is only an approximate measure of covalency, the third and probably the most important factor results from comparing compounds of different structure type. In fact, a smooth

correlation between $Z_Y(V)$ and ΔE_{X-M} is expected only if all M_nX_n compounds were isostructural. This is because the *M-X* distance and the related degree of covalency depend also on the coordination number of the *M* atom.

The behavior of yttrium predicted from covalency due to the participation of 4*f* orbitals in bonding in lanthanide compounds is fully corroborated by the experimental results obtained. However, it should be noted that, according to some authors, covalency in lanthanide compounds is due to participation of 6*s* orbitals (55, 56). An explanation based on covalency involving 6*s* orbitals is also possible

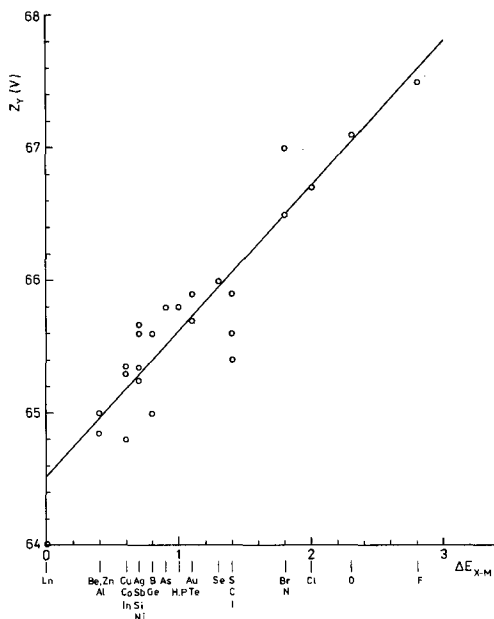


FIG. 1. The relative atomic number of yttrium as a function of the difference between the electronegativity of the X atom and the electronegativity of lanthanide atoms in M_mX_n compounds.

but needs the additional assumption that 6s orbitals in lanthanides are able to participate in bonding to a greater extent than 5s orbitals in yttrium.

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