ON THE INTERATOMIC DISTANCES OF LANTHANOIDS IN METALLIC CRYSTALS

1965

SovietRxiv

Abstract

Full Text

CHEMISTRY

E. S. SARKISOV

ON THE INTERATOMIC DISTANCES OF LANTHANOIDS IN METALLIC CRYSTALS

(Presented by Academician I. V. Tananaev, October 22, 1964)

As is known, the interatomic distances for most rare-earth elements in metallic crystals decrease as a result of lanthanoid contraction with increasing atomic number. The dependence of the magnitude of the contraction in the interatomic distances of the lanthanoids on the ordinal number was previously quantitatively related by us to the reduction of the effect of electronic repulsion as a consequence of the placement of electrons deeper in the $4f$ states [1–4].

However, some lanthanoids, especially europium and ytterbium, have a noticeable tendency toward an increase in their interatomic distances. In the opinion of a number of authors ([5],[6]), for cerium, praseodymium, and terbium, on the contrary, a greater decrease in the interatomic distance is observed than corresponds to the general tendency toward a decrease in atomic size due to lanthanoid contraction. The authors try to relate the magnitude of the interatomic distance of cerium, praseodymium, and terbium to the state of a tetravalent metal, since these elements, in addition to trivalent derivatives, also give compounds in which they are tetravalent.

The anomalous increase in the interatomic distances of europium and ytterbium is usually connected with the ability of these elements to form stable divalent chemical compounds (([5],[7] ,[8]) and others). In other words, the presence in them of abnormally large interatomic distances can be understood if they are regarded as divalent metals with two bonding electrons $6s^2$, respectively outside the subgroups $4f^{7}5s^{2}5p^{6}$ and $4f^{14}5s^{2}5p^{6}$. Like europium and ytterbium, divalent derivatives are also known for samarium. However, the investigation by the authors ([9]) showed that the observed value of the interatomic distance of samarium cannot be connected with the presence of the state of a divalent metal with two bonding electrons $6s^2$ outside the subgroup $4f^{6}5s^{2}5p^{6}$. Thus, the question of anomalous increase or decrease of interatomic distances for a number of rare-earth elements in the presence of the effect of lanthanoid contraction is undoubtedly of substantial interest. Unfortunately, for not a single case has anyone yet succeeded in giving an exact function permitting a quantitative description of the character of the change in the interatomic distances of rare-earth elements as a function of the effect of lanthanoid contraction and the number of bonding (valence) electrons.

In the preceding work (^{4}), in studying the dependence of interatomic distance on the coordination number of the lattice and the electronic structure of the atoms forming the crystal, we, in particular, substantiated also the course of the curve of the change in interatomic distances caused by lanthanoid contraction. However, in that work we ignored the anomalous behavior of a number of rare-earth elements. Our equation for calculating interatomic distances in crystals of metallic alloys of composition $A_{xB}y$ had the following form:

$$d = d_{\mathrm{H-H,met}\,(k=1)} \times \frac{p^{1/3}\left[(Z_1 - f_1)^{2/3} - z_\lambda^{2/3}\right]^{1/3} + (1-p)^{1/3}\left[(Z_2 - f_2)^{2/3} - z_\lambda^{2/3}\right]^{1/3} + k^{1/9}\left[pf_1 + (1-p)f_2\right]^{2/9}}{\left[pf_1 + (1-p)f_2\right]^{1/8}} \quad (1)$$

where Z is the total number of electrons in the atom (the atomic number of the element); f is the number of bonding electrons (or the metallic valence); $(Z-f)$ is the number of core electrons of the atom; z_λ is the number of deep-lying $4f$-electrons participating in the contraction effect; k is the coordination number of the lattice; p is the atomic fraction; $d_{\mathrm{H-H\,met}(k=1)}$ is the proportionality coefficient, numerically equal to the "metallic" interatomic distance of hydrogen with coordination number $k = 1$ ($d_{\mathrm{H-H\,met}(k=1)} = 0.965$ Å). For pure metals, since $Z_1 = Z_2 = Z$, $f_1 = f_2 = f$ and $p = (1-p) = 1/2$, equation (1) is transformed into

$$d = d_{\mathrm{H-H\,met}(k=1)} \frac{2\sqrt[3]{1/2}\left[(Z-f)^{2/3} - z_\lambda^{2/3}\right]^{1/3} + k^{1/3} f^{2/9}}{f^{1/3}}. \quad (2)$$

In equation (2) the quantity $z_\lambda^{2/3}$ expresses the effect of lanthanoid contraction as a result of completion of the inner $4f$ electron shell. Using

Table 1

Interatomic distances of rare-earth elements with coordination number $k = 12$

Element	Number of bonding electrons f	z_λ	d_{expt}, Å	d_{calc}, Å	Δ, Å	Δ, %
La	$3\,(5d\,6s^2)$	–	3.74	3.703	−0.037	−1
Ce	$3\,(4f\,6s^2)$	$4f$	3.64	3.653	+0.013	0
Pr	$3\,(4f\,6s^2)$	$4f^2$	3.65	3.627	−0.023	−1
Nd	$3\,(4f\,6s^2)$	$4f^3$	3.62	3.606	−0.014	0

Element	Number of bonding electrons f	z_λ	d_{expt}, Å	d_{calc}, Å	Δ, Å	Δ, %
Pm	$3\,(4f\,6s^2)$	$4f^4$	–	3.589	–	–
Sm *	$3\,(4f\,6s^2)$	$4f^5$	3.604	3.573	−0.031	−1
Eu **	$2\,(6s^2)$	$4f^7$	3.960	3.898	−0.062	−2
Gd	$3\,(5d\,6s^2)$	$4f^7$	3.56	3.547	−0.013	0
Tb	$3\,(5d\,6s^2)$	$4f^8$	3.54	3.535	−0.005	0
Dy	$3\,(4f\,6s^2)$	$4f^9$	3.50	3.524	+0.024	+1
Ho	$3\,(4f\,6s^2)$	$4f^{10}$	3.52	3.514	−0.006	0
Er	$3\,(4f\,6s^2)$	$4f^{11}$	3.47	3.504	+0.034	+1
Tm	$3\,(4f\,6s^2)$	$4f^{12}$	3.48	3.495	+0.015	+1
Yb ***	$2\,(6s^2)$	$4f^{14}$	3.866	3.870	+0.004	0
Lu	$3\,(5d\,6s^2)$	$4f^{14}$	3.47	3.478	+0.008	0

* The value d_{expt} for samarium with coordination number 12 is taken from (9). It was obtained from the parameters of the hexagonal lattice ($a = 3.621$ Å; $c = 26.25$ Å), calculated from the lattice period of rhombohedral samarium ($a = 8.996$ Å, $\alpha = 23°13'$).

** The experimental interatomic distance of europium is given for the body-centered cubic lattice. Therefore its interatomic distance was calculated by formula (2) for coordination number $k = 8$.

*** For Yb the experimental interatomic distance of the face-centered cubic lattice is given ($k = 12$).

our equation (2), we calculated the interatomic distances for all rare-earth metals with coordination number $k = 12$. The calculated interatomic distances of the lanthanoids (with the constant $d_{\mathrm{H-H\,met}(k=1)} = 0.965$) are given in the table and compared with Goldschmidt' s atomic diameters for coordination number 12 (8). As can be seen from Table 1, for all rare-earth metals there is very good agreement between the calculated and experimental values of the interatomic distances; the discrepancy does not exceed ±1%. The only exception is europium, for which the calculated interatomic distance is somewhat lower than the experimental value, although even this deviation does not exceed 2%.

Our calculations show, therefore, that the interatomic distances of the lanthanoids in the metallic state are determined by three bonding electrons ($5d6s^2$ or $4f6s^2$). The only exceptions are europium and ytterbium,

for which the interatomic distances, with an accuracy very close to that of the experimental determinations, as with the other lanthanoids, are in functional dependence not on three, but on two bonding electrons ($6s^2$). Moreover, the

Fig. 1. Dependence of the interatomic distances of lanthanoids on the atomic number of the element. a —experimental, b —calculated values

Figure 1: Fig. 1. Dependence of the interatomic distances of lanthanoids on the atomic number of the element. a —experimental, b —calculated values

effect of lanthanoid contraction for europium and ytterbium, irrespective of the anomalous increase in the interatomic distance caused by the divalent-metal state, also occurs, as for the other rare-earth elements.

From the graphical representation of the dependence of the interatomic distances of the lanthanoids on the atomic number (see Fig. 1), it is evident that samarium, like europium and ytterbium, does not behave as a divalent metal (Sm^{2+}). In this case the interatomic distance calculated precisely for the Sm^{3+} state agrees very satisfactorily with the experimental value. Likewise, in the case of cerium, the interatomic distance calculated for the Ce^{3+} state agrees well with the experimental value. A similar picture is also observed for praseodymium and terbium. Indeed, if the metallic valence of cerium were four (Ce^{4+}), the anomalous decrease would considerably exceed its experimental value of the interatomic distance (see Fig. 1). Calculations based on data on magnetic properties and metallic radii also show that the metallic valence of cerium is less than four ([10]).

Fig. 1. Dependence of the interatomic distances of lanthanoids on the atomic number of the element. *a* —experimental, *b* —calculated values.

The data given above show that equation (2), clearly expressing the dependence of the lanthanoid-contraction effect in interatomic distances on the atomic number, makes it possible to correctly establish the number of valence electrons in the metallic state for all lanthanoids. Equation (2) also made it possible to calculate the previously unknown value of the interatomic distance of promethium, taking the number of bonding electrons for it to be equal to three ($4f6s^2$).

Institute of Fine Chemical Technology
named after M. V. Lomonosov

Received
12 X 1964

CITED LITERATURE

1. É. S. Sarkisov, DAN, **60**, No. 3, 371 (1948).
2. É. S. Sarkisov, ZhFKh, **24**, 487 (1950).
3. É. S. Sarkisov, ZhFKh, **34**, 433 (1960).

4. É. S. Sarkisov, ZhFKh, **37**, 396 (1963).

5. H. Remy, *Lehrbuch der anorganischen Chemie*, **2**, Leipzig, 1959, p. 581.

6. D. Iost, G. Russell, K. Garner. *Rare-Earth Elements and Their Compounds*, IL, 1949, p. 85.

7. W. Klemm, H. Bommer, *Zs. anorg. u. allgem. Chem.*, **242**, 277 (1939).

8. V. Yu-Rozeberg, V. V. Reinder, *Structure of Metals and Alloys*, Moscow, 1959.

9. A. H. Daane, R. E. Rundle et al., *Acta crystallogr.*, **7**, 532 (1954).

10. K. A. Schneider, *Problems of Modern Metallurgy*, **2**, 53 (1960).

Note: Figure translations are in progress. See original paper for figures.