Volume effects in rare earth intermetallic compounds

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Abstract

In the binary intermetallic phases formed by rare earths with other elements the experimental values of the average atomic volume $\bar{V}$ are generally lower than the values calculated on the basis of the elemental atomic volumes. This follows from the analysis of crystallographic data of about 1800 compounds with known structure, occurring in 378 binary R–M systems, with R $\equiv$ Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu and M $\equiv$ Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Mg, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi. The volume contractions can be described by the equation

$$\bar{V}=(1-x)V_R^0 +xV_M^0 -0.5(n+1)(n+2)(n+3)x^n(1-x)^2|\chi_R-\chi_M|$$

where V_R^0 and V_M^0 are the elemental atomic volumes, x is the atomic fraction of the M element, n is a parameter related to the composition of the phase with the maximum volume contraction within a given system and χ is an empirical volume parameter. The χ quantity results correlated with the electronegativity for the transition elements, assuming mainly the role of a charge transfer parameter. For the non-transition elements χ resembles the periodic trend of the compressibility, indicating the greater influence of elastic effects.

1. Introduction

In the classical works by Vegard [1] and Biltz [2] the lattice parameters of solid solutions or intermediate phases are calculated by means of the sizes of the components (atomic radii or volumes). Deviations from the linear trend with composition have been attributed to geometric effects (different packing efficiencies in the elements and compounds), elastic effects (energy necessary to change the volume of the Wigner–Seitz cell up to the equilibrium density of the alloy) and electrochemical effects (charge transfer due to the electronegativity difference between the atoms).

In the present work the R–M binary systems formed by 14 trivalent rare earth elements (R $\equiv$ Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) with 27 M elements (M $\equiv$ Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Mg, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi) have been considered. For all intermediate phases a volume contraction is observed, save in some systems formed by the light rare earths with Mg, Al, Cu and Ag where almost no volume deviation occurs.

With the same approach used for the intermetallic compounds of the divalent rare earths (Eu, Yb) and alkaline earths (Ca, Sr, Ba) [3], a phenomenological description of the volume effects is carried out. The aim was both to obtain an equation for calculating the mean atomic volume of a large number of phases, including those with unknown structure, and to investigate the physical meaning of the parameters employed in the experimental data fitting.

2. The volume calculation

Preliminary inspection of the mean atomic volume values ($\bar{V}$) shows that in nearly all systems a regular trend *vs.* composition is observed. A first attempt to represent the volume–composition curves for the $R_{1-x}M_x$ phases was carried out using the same equation proposed [3] for the systems containing divalent elements, namely

$$\Delta V=\bar{V}_o-\bar{V}=Kx^n(1-x)$$

where

$$\bar{V}_o=(1-x)V_R^0 +xV_M^0$$

V_R^0 and V_M^0 are the elemental atomic volumes of the components, x is the M atomic fraction and K and n are adjustable parameters. The goodness of fit was unsatisfactory and a better representation was obtained with the relation

$$\Delta V=Kx^n(1-x)^2$$

Using the same approach previously proposed, an average measurement of the volume effects in a given system can be the integral quantity

$$\Delta V_{int} = \int_0^1 (\bar{V}_o - \bar{V})\, dx$$

If χ_R and χ_M are the values of a physical quantity for the R and M atoms, in the R–M systems the simplest hypothesis is to put

$$\Delta V_{int} = |\chi_R - \chi_M|$$

Combining all the expressions, one obtains

$$\bar{V} = \bar{V}_o - 0.5(n+1)(n+2)(n+3)x^n(1-x)^2|\chi_R - \chi_M| \quad (1)$$

The value of the n parameter is related to the composition of the phase with the highest volume contraction within a given system; the maximum ΔV value corresponds to the phase with formula $RM_{n/2}$.

Experimental data were taken from *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* [4]. A set of about 1800 compounds with known structure, occurring in 378 binary systems, provided $\bar{V}$ values (elementary cell volumes divided by the total number of atoms per cell). The examined phases belong to 130 structure types, distributed over 45 compositions, ranging from the R_3M to the RM_{13} formula. The atomic volumes of the elements were taken from ref. 5. For Si and Ge the volumes of the β-Sn-type form were selected, namely 14.19 and 16.05 Å^3 atom^{-1} respectively [4]. The n parameter shows a large range of values, from 0.7 to 26. This indicates the strong variation in the stoichiometry of the phases with the maximum value of volume contraction, which goes from $Sc_{11}Os_4$ to $LaZn_{13}$.

An iterative process of data fitting to eqn. (1) was carried out to obtain the best values of the χ parameter. The values of n were restricted to 12, assigning, for a given M element, three distinct values to the systems containing (a) light rare earths; (b) heavy rare earths and yttrium and (c) scandium. The final results are reported in Table 1, where the χ scale was adjusted to the value 1.00 for yttrium.

3. Discussion

The results for some R–M systems are reported in Fig. 1, where the points represent the mean atomic volume of the intermediate phases and the curve is the trend calculated by means of the proposed equation. The observed contractions range from zero to about 15% and the overall agreement between experimental and calculated volume data amounts to 1.5%.

TABLE 1. Parameters χ and n used in eqn. (1). The three n values refer in order to systems with (a) light rare earths (La, Ce, Pr, Nd, Sm), (b) heavy rare earths and yttrium (Gd, Tb, Dy, Ho, Er, Tm, Lu, Y) and (c) scandium

Element	χ	n	n	n	Element	χ	n	n	n
Sc	1.05				Ni	2.15	4	4	3
Y	1.00				Pd	2.25	6	3.5	2.5
La	1.55				Pt	2.40	6	3.5	3
Ce	1.7				Cu	1.65	3	3	2
Pr	1.55				Ag	1.65	3	3	4
Nd	1.50				Au	2.00	3	3	3
Sm	1.45				Mg	1.50	2	2	2
Gd	1.20				Zn	1.45	17	10	2
Tb	1.20				Cd	1.70	7	6	2
Dy	1.20				Hg	2.65	5	4	3
Ho	1.20				Al	1.70	4	4	5
Er	1.20				Ga	2.50	6	5	5
Tm	1.20				In	2.55	6	5	2
Lu	1.15				Tl	3.30	4	3.5	
					Si	2.05	4	3	2
Fe	2.15	3	3	3	Ge	2.15	4	3	1
Ru	2.50	3	2.5	1.5	Sn	2.75	5	3	1
Os	2.50	3	2.5	1	Pb	2.85	5	3	1
Co	2.45	2.5	2.5	2.5	As	3.25	2	2	1
Rh	2.60	3.5	2.5	2	Sb	3.35	2	2	1
Ir	2.60	2.5	2.5	1.5	Bi	3.60	1	1	2

A particular comment is devoted to the systems containing cerium. The χ value of 1.7 reported for Ce in Table 1 is only indicative. Unlike the other rare earths, the apparent values to be used for this element in the different systems range from 0.6 to 2.1. This can be imputed to valence instability phenomena, which are typical of cerium, especially in intermetallics with transition elements. Actually, the lowest χ values appear in the systems with Fe, Ru, Os, Co, Rh and Ni, where cerium shows in some compounds an anomalous valence state and smaller atomic dimensions.

Another observation regards the RM phases crystallizing with the NaCl type (RAs, RSb, RBi). Often the $\bar{V}$ value of these phases does not follow the regular trend shown by the other phases but is clearly higher. This deviation is imputed to the geometric effects caused by the low coordination number (six) occurring in NaCl.

The equation proposed in the present empirical approach is an oversimplified representation of a complex process controlled by more than one factor. Thus the χ quantity cannot have a unique physical meaning because it must incorporate the different factors which give rise to the elastic, geometrical and charge transfer effects.

Figure 2 reports, for the considered M elements, the χ values obtained in the present work, the electronegativity x_P (Pauling scale) and the compressibility μ [6]. From the iron group to the copper group a nearly
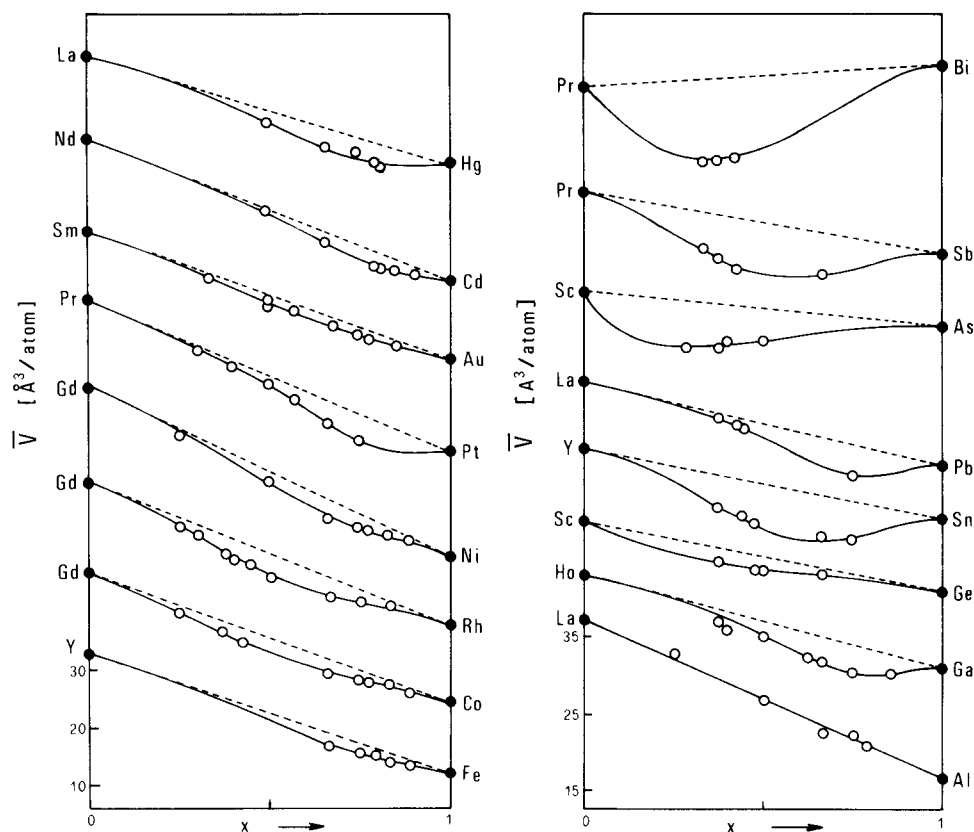
Fig. 1. Atomic volume $\bar{V}$ plotted against atomic fraction of M element in some R–M systems. Open circles indicate experimental values for intermediate phases with known structure occurring in each system. Broken lines refer to a linear trend; full curves are calculated by eqn. (1). For the sake of simplicity the $\bar{V}$ scale is indicated only for the Y–Fe and La–Al systems.
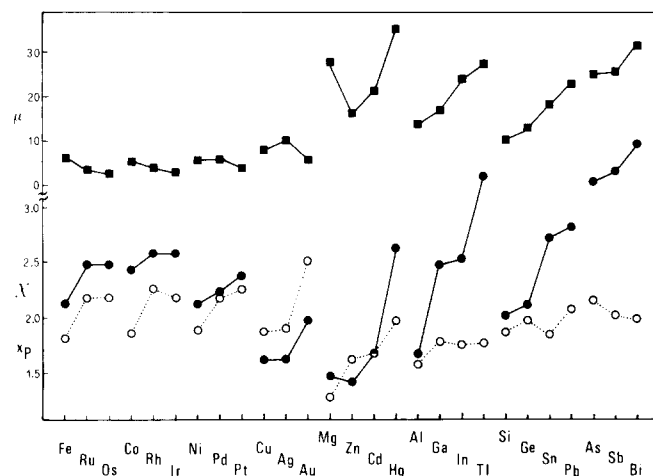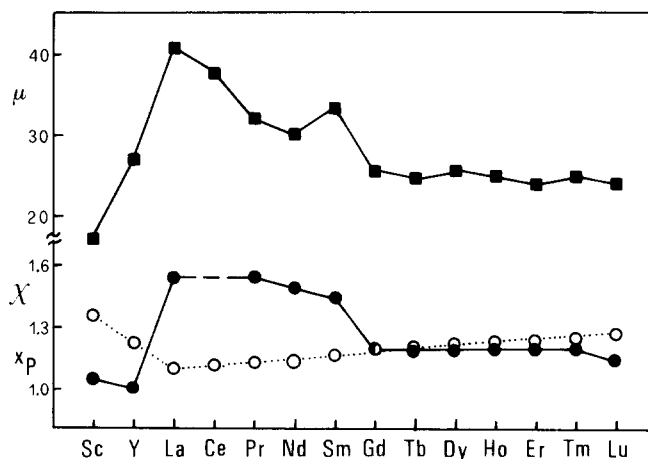

Fig. 2. Comparison of χ values (full circles), Pauling electronegativities x_P (open circles) and compressibilities μ (full squares, $\times 10^7$ cm^2 kg^{-1}) for M elements.

Fig. 3. Comparison of χ values (full circles), Pauling electronegativities x_P (open circles) and compressibilities μ (full squares, $\times 10^7$ cm^2 kg^{-1}) for R elements.

parallel trend between χ and x_P is observed, indicating the influence of the electrochemical factor in the systems with transition elements. This confirms that volume effects in these systems are mainly due to charge transfer,

as stated by Miedema and Niessen [7] and Watson and Bennett [8]. From the zinc group to the arsenic group the plot shows an increasing difference between the χ and x_P values, especially for the elements of the fifth

and sixth periods. The sharp rise of the χ values reflects the contribution of the elastic effects, which should have a greater importance in systems with non-transition elements, as asserted by Hafner [9]. This is confirmed by comparing the trends of χ and μ: the two quantities map one another roughly across the post-transition elements.

The same three atomic quantities (χ, x_P, μ) are plotted in Fig. 3 for the 14 rare earth metals. One can recognize a combined influence of both electronegativity and compressibility on the observed trend of the χ volume parameter, which shows an inverted order as regards the usual electronegativity scales.

In conclusion, the proposed equation describes the volume effects for the rare earth binary intermetallics and can be used to estimate the volume of phases with unknown structure. Moreover, strong observed deviations from the regular trend can be an indication of particular properties (valence instabilities, glass-forming ability) or simply show incorrect data. The periodic trend of the empirical volume parameter χ shows the influence of both elastic and charge transfer effects in the compound formation.

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