



# A new method to estimate the atomic volume of ternary intermetallic compounds

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## ARTICLE INFO

### Article history:

Received 17 December 2010

Received in revised form

24 January 2011

Accepted 31 January 2011

Available online 3 February 2011

### Keywords:

Ternary intermetallics

Volume calculations

Rare earth compounds

Alkaline earth compounds

## ABSTRACT

The atomic volume of an  $A_xB_yC_z$  ternary intermetallic compound can be calculated starting from volumes of some proper  $A-B$ ,  $A-C$  and  $B-C$  binary phases. The three methods by Colinet, Muggianu and Kohler, originally used to estimate thermodynamic quantities, and a new method here proposed, were tested to derive volume data in eight systems containing 91 ternary phases with the known structure. The comparison between experimental and calculated volume values shows the best agreement both for the Kohler method and for the new proposed procedure.

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## 1. Introduction

The possibility to estimate the atomic volume of an intermetallic compound can be useful for several reasons. The estimated value can be a simple check to see if the structure and the composition of a newly discovered phase are reasonable. The volume can be previously estimated for not yet known phases, for unstable phases, for phases which are synthesized with difficulty in form of monophasic sample, owing to the complicated phase diagram. In some cases, the high difference between observed and estimated volumes may point out a particular bond situation, different from a typical metallic arrangement with good space filling: structures with directional features and low coordination numbers, or layer structures.

The simplest way to obtain the phase volume value is based on the proper combination of the elemental volumes [1]. However, it is known that this approach provides only a rough approximation, as strong deviations from the experimental value are often observed, usually volume contractions (up to 28%) [2].

A possible way to obtain a more precise volume estimate lies in a procedure similar to that used to derive thermodynamic quantities (like excess Gibbs energy) in polynary systems [3 and references therein]. Following this approach, to our knowledge not yet used for volume calculations, a property of a ternary phase can be obtained combining the known contributions of binary phases.

The present work is devoted to apply this method to evaluate the volume of ternary intermetallics on the basis of the structural

data of binary phases. Since different methods have been proposed in the literature for the choice of the binary phases, the main goal will be to select the best procedure. This is possible owing to the large number of known crystallographic data both of binary and ternary compounds. In the second place, as the data of the binary phases show the volume effects due to the binary interactions, the comparison between the so estimated volumes of the ternary phases and those observed gives an idea of the additional weight of the ternary interactions.

## 2. Extrapolation methods

The problems to be solved preliminarily are:

- the choice of the suitable compositions of the binary phases;
- the calculation of the “observed” volume for the chosen compositions, even when they do not correspond to existing phases; and
- the weighing system of the binary contributions.

For the first problem, four geometrical methods have been suggested by Colinet, Muggianu, Kohler and Toop [3]. As can be seen in Fig. 1, the first three methods are symmetrical, as they treat contributions from the binary systems in the same way, while Toop’s method should be applied when one element is considered different from the others. A fifth method, proposed in the present work, and based on a symmetric variant of the Toop method (see Section 3.2), is also shown in the figure.

The second problem can be solved by fitting empirical equations to the experimental average atomic volumes of the known

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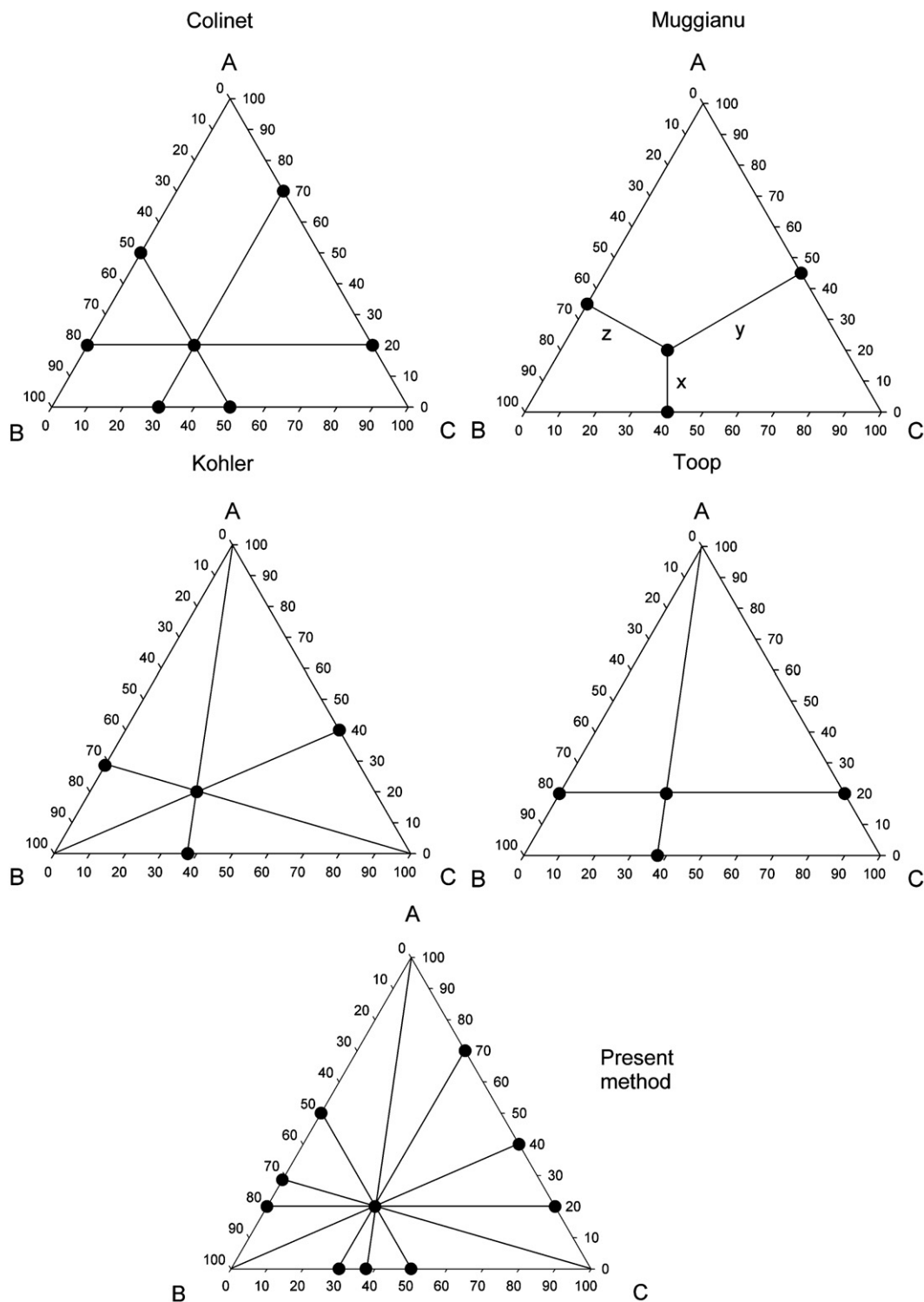


Fig. 1. Methods of selecting compositions of the binary phases to extrapolate a physical property of a ternary phase.

intermediate phases within each binary system, so it is possible to calculate the atomic volume for any composition. This method can give acceptable results only if the experimental points lie in a regular way within the system, as it really happens in most binary intermetallic systems. Two simple analytical expressions, already used [2,4], are here selected to represent the compositional dependence of the average atomic volume  $V_{at}$  within an  $A_{1-x}B_x$  system

$$V_{at} = (1-x)V_A^c + xV_B^c - Kx^n(1-x) \quad (1)$$

$$V_{at} = (1-x)V_A^c + xV_B^c - Kx^n(1-x)^2 \quad (2)$$

where  $V_A^c$  and  $V_B^c$  are the elemental volumes [5],  $K$  and  $n$  are adjustable parameters. As can be seen, the first two terms of both equations refer to the linear Vegard-like trend, while the last term is a measure of the observed deviations, usually volume contractions. For a given  $A-B$  system, the maximum value of the volume contraction is shown by the phase with the stoichiometry  $AB_n$  or  $AB_{n/2}$ , using Eqs. (1) and (2), respectively [2,4].

The third problem can be solved by applying the lever rule to the binary contributions. In particular, for a given ternary compound, each binary phase gives a contribution which is proportional to its reciprocal distance from the ternary point. For example, following Muggianu's method, for the ternary phase  $A_xB_yC_z$ , the weight of the volume of the binary phase  $B_{x+2y}C_{x+2z}$  is given by the ratio  $(1/x)/(1/x+1/y+1/z)$ , where  $x$ ,  $y$ ,  $z$  are the distances of the three binary phases from the ternary one (Fig. 1). The stoichiometries of the binary compositions necessary to calculate the atomic volume of a ternary compound are listed in Table 1 for the different applied methods.

A further question is the choice of some ternary  $A$ – $B$ – $C$  systems as check points to judge the reliability of the method. The selected conditions in the present work are: the occurrence of many intermediate phases both in binary and in ternary systems, and the availability of structural data for all compounds, if possible. The search in the databases for intermetallic compounds [6,7] shows that such conditions are often found when  $A$  is a 2 or 3 group element (alkaline earth or rare earth),  $B$  is a transition metal,  $C$  is a post-transition element, mostly belonging to the 13 and 14 groups.

The selected cases are three recently studied systems, namely Ca–Cu–Sn [8] (6 ternary phases with known crystal structure), Yb–Cu–Sn [9–12] (12 ternary phases), Eu–Cu–Sn [13–15] (6 ternary phases), and the following systems: Nd–Cu–Sn (9 ternary phases), Gd–Ni–Al (12 ternary phases), Ho–Ni–Ga (23 ternary phases), Y–Ni–Si (12 ternary phases) and Er–Ni–Ge (11 ternary phases) [6,7].

The distribution of the points of the ternary phases within the corresponding composition–volume plots was previously controlled, in order to check the occurrence of a regular trend analogous to that observed for the binary phases. Actually, a good geometrical regularity can be seen in the eight three dimensional plots, and this was quantitatively confirmed by fitting a simple quadratic equation to all volume data of each ternary system, namely volumes of the three elements, of the binary phases and of the ternary phases. By imposing the constraints that the paraboloid surface meets the three points of the elements, the following equation was used

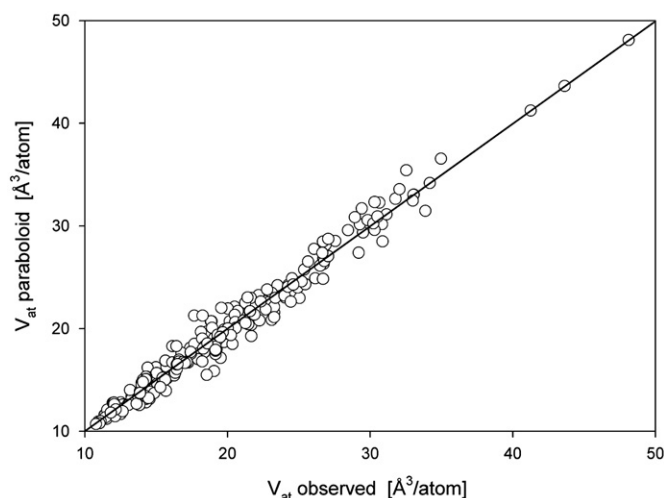
$$V = V_B + aX + bY + (V_C - V_B - a)X^2 + 4/3(V_A - 0.75V_B - 0.25V_C)Y^2 - 1/3aY^2 - 2/\sqrt{3}bY^2 \quad (3)$$

where  $V_A$ ,  $V_B$  and  $V_C$  are the volumes of the elements,  $a$  and  $b$  are refinable parameters,  $X$  and  $Y$  are the cartesian coordinates of the  $A_xB_yC_z$  phases. With respect to the triangular representation of the ternary system, the origin of the Cartesian coordinates is placed at the  $B$  corner, while the  $X$  axis coincides with the  $BC$  side. Fig. 2 reports, as a function of the observed values, the volumes calcu-

**Table 1**

Stoichiometries of the binary compositions selected in the five discussed methods to calculate the atomic volume of a ternary phase  $A_xB_yC_z$ .

Method	Binary compositions	
Colinet		
$A_xB_{y+z}$	$A_xC_{y+z}$	$B_yC_{x+z}$
$A_{x+z}B_y$	$A_{x+y}C_z$	$B_{x+y}C_z$
Muggianu		
$A_{2x+z}B_{2y+z}$	$A_{2x+y}C_{y+2z}$	$B_{x+2y}C_{x+2z}$
Kohler		
$A_xB_y$	$A_xC_z$	$B_yC_z$
Toop		
$A_xB_{y+z}$	$A_xC_{y+z}$	$B_yC_z$
Present method		
$A_xB_{y+z}$	$A_xC_{y+z}$	$B_yC_z$
$A_{x+z}B_y$	$A_xC_z$	$B_yC_{x+z}$
$A_xB_y$	$A_{x+y}C_z$	$B_{x+y}C_z$



**Fig. 2.** Average atomic volumes  $V_{at}$  of elements and of binary and ternary phases occurring in the eight considered systems, calculated by means of the paraboloid Eq. (3), versus the observed volume values. The solid line represents the equality conditions between experimental and calculated values.

**Table 2**

Fitting parameters values of the atomic volume vs. composition (Eqs. 1 and 2) for the considered binary systems.

A–B system	Number of phases	Equation	$K$	$n$
Ca–Cu	3	(1)	15.32	1.34
Ca–Sn	7	(1)	18.97	0.68
Cu–Sn	7	See text		
Eu–Cu	4	(1)	20.02	1.62
Eu–Sn	5	(1)	22.32	0.79
Yb–Cu	5	(1)	12.28	0.83
Yb–Sn	6	(1)	24.24	0.83
Nd–Cu	5	(1)	3.70	6 <sup>a</sup>
Nd–Sn	7	(1)	24.69	3 <sup>a</sup>
Gd–Ni	10	(2)	74.50	3.42
Gd–Al	10	(1)	5.68	1.29
Ni–Al	6	(2)	12.69	1.31
Ho–Ni	8	(2)	74.30	3.57
Ho–Ga	10	(1)	27.35	2.44
Ni–Ga	7	(1)	16.34	1.57
Y–Ni	9	(1)	11.24	1.55
Y–Si	5	(1)	45.08	2.11
Ni–Si	6	(1)	18.05	1.31
Er–Ni	10	(1)	10.71	1.85
Er–Ge	10	(1)	29.53	1.63
Ni–Ge	6	(1)	13.23	1.02

<sup>a</sup> Fixed value.

lated after Eq. (3) fitted by the least squares method to the eight considered ternary systems, which contain a total of 273 elements, binary and ternary compounds. As can be seen, this simple analytical representation provides a reasonable agreement with the experimental data, with a 3.9% average deviation from the ideal equality line, confirming the regular spatial distribution of the points of the ternary compounds within each system.

### 3. Results

#### 3.1. Volume calculation in the binary systems

Table 2 reports the fitting parameters of the atomic volume versus composition for the 21 considered binary systems. Eq. (1) was used in most cases, while the strong scatter of the experimental data of the  $Cu_{1-x}Sn_x$  phases suggested a simple quadratic dependence

$$V_{at} = 11.81 + 13.6x + 1.64x^2$$

Moreover in order to avoid unphysical trends, the point corresponding to the maximum volume contraction must lie within the composition range of the existing phases. So, in the Nd–Cu and Nd–Sn systems the  $n$  value was fixed corresponding to the maximum copper and tin content.

Fig. 3 reports the analytical representation of  $V_{at}$  as a function of composition for some binary systems, which correspond to the different observed trends (Ho–Ni, Nd–Cu, Gd–Al, Nd–Sn, Yb–Sn and Ni–Si). As can be seen, the points of the intermediate phases follow a regular trend and show small deviations from the

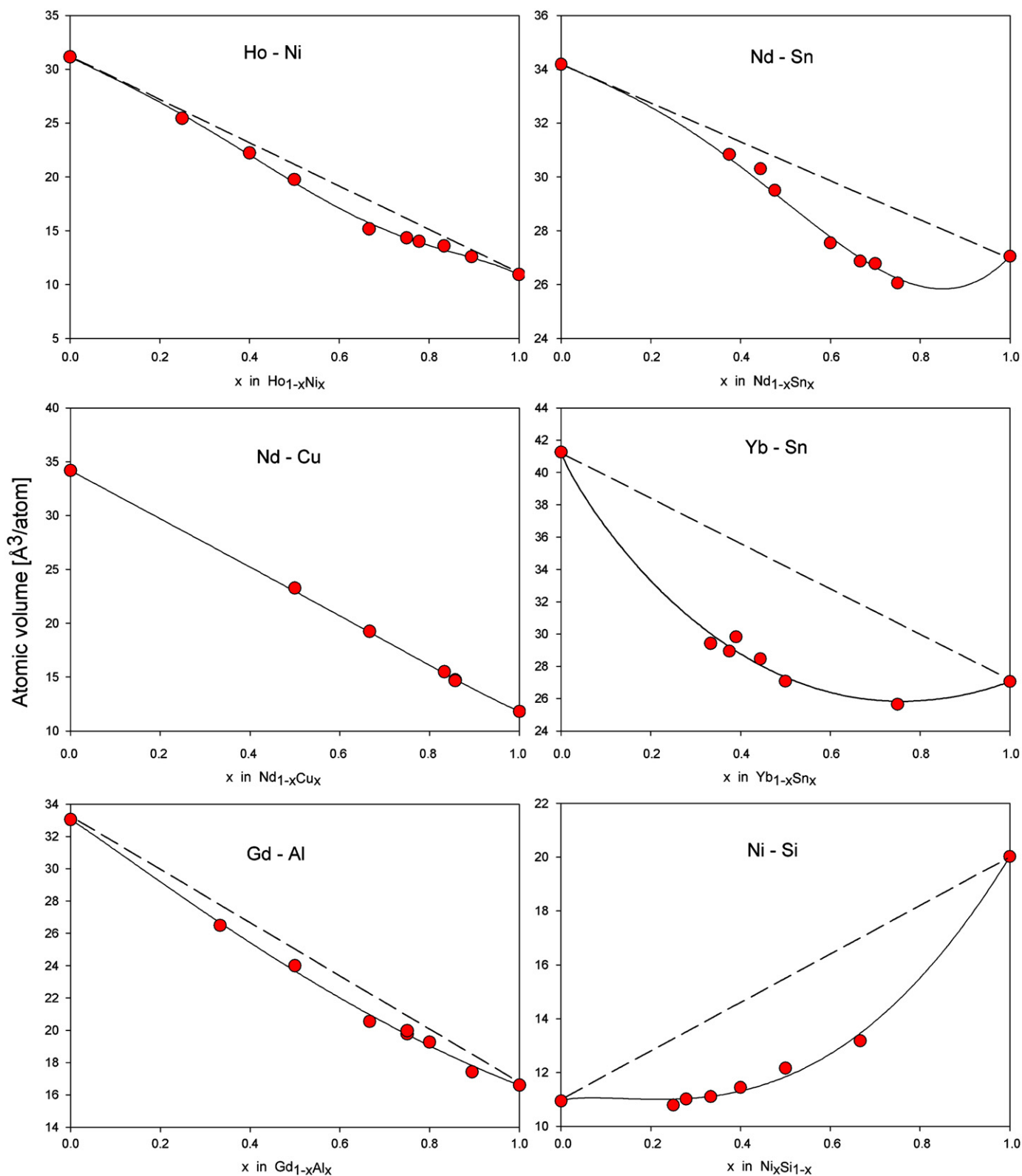


Fig. 3. Average atomic volumes vs. compositions in the binary systems Ho–Ni, Nd–Cu, Gd–Al, Nd–Sn, Yb–Sn, Ni–Si. Full circles: experimental points; solid line: calculated trend; and dashed line: Vegard-like behavior.

calculated curves. So, it is possible to calculate the atomic volume for any composition with an acceptable reliability.

### 3.2. Volume calculation of the ternary phases

The extrapolation methods by Colinet, Muggianu and Kohler were employed to calculate the average atomic volume  $V(A_xB_yC_z)$  of the  $A_xB_yC_z$  ternary phase, with  $x+y+z=1$ . The corresponding formulae are:

#### Colinet-like

$$V(A_xB_yC_z) = w_1[V(B_{x+y}C_z) + V(B_yC_{x+z})] \\ + w_2[V(A_{x+y}C_z) + V(A_xC_{y+z})] \\ + w_3[V(A_xB_{y+z}) + V(A_{x+z}B_y)]$$

$$w_1 = [2x(1/x + 1/y + 1/z)]^{-1} \\ w_2 = [2y(1/x + 1/y + 1/z)]^{-1} \\ w_3 = [2z(1/x + 1/y + 1/z)]^{-1}$$

#### Muggianu-like

$$V(A_xB_yC_z) = w_1V(B_{x+2y}C_{x+2z}) + w_2V(A_{2x+y}C_{y+2z}) \\ + w_3V(A_{2x+z}B_{2y+z})$$

$$w_1 = [x(1/x + 1/y + 1/z)]^{-1} \\ w_2 = [y(1/x + 1/y + 1/z)]^{-1} \\ w_3 = [z(1/x + 1/y + 1/z)]^{-1}$$

#### Kohler-like

$$V(A_xB_yC_z) = [w_1/\sum w_i]V(A_xB_y) + [w_2/\sum w_i]V(B_yC_z) \\ + [w_3/\sum w_i]V(A_xC_z)$$

$$w_1 = [3z^2/4 + (y+z/2 - y/(1-x))^2]^{-1/2} \\ w_2 = [3x^2/4 + (y+x/2 - y/(1-x))^2]^{-1/2} \\ w_3 = [3y^2/4 + (z+y/2 - z/(1-y))^2]^{-1/2}$$

where  $V(B_{x+y}C_z)$  and the like are the volumes of the corresponding binary compositions and  $w_i$  are the weights.

A new procedure is also proposed, which can be considered as a modified and symmetric variant of Toop's method. Referring

**Table 3**  
Observed and calculated volumes for the ternary phases in the Ho–Ni–Ga system. All values are in  $\text{\AA}^3/\text{at}$ .

Phase	$V_{\text{observed}}$	$V_{\text{Vegard}}$	$V_{\text{Colinet}}$	$V_{\text{Muggianu}}$	$V_{\text{Kohler}}$	$V_{\text{present formula}}$
Ho <sub>5</sub> Ni <sub>0.4</sub> Ga <sub>2.6</sub>	24.91	26.37	25.12	25.05	25.74	24.91
Ho <sub>6</sub> Ni <sub>2</sub> Ga <sub>1</sub>	24.04	25.37	24.76	24.71	25.38	24.65
Ho <sub>6</sub> Ni <sub>2</sub> Ga <sub>2</sub>	23.25	24.79	23.83	23.75	24.58	23.54
Ho <sub>6</sub> Ni <sub>2.3</sub> Ga <sub>1.7</sub>	22.67	24.53	23.61	23.54	24.32	23.36
HoNi <sub>0.3</sub> Ga <sub>1.7</sub>	19.77	22.57	19.87	19.73	20.44	19.06
HoNi <sub>0.4</sub> Ga <sub>1.6</sub>	18.72	22.28	19.71	19.54	20.20	18.78
HoNi <sub>0.5</sub> Ga <sub>1.5</sub>	19.05	21.99	19.54	19.34	19.88	18.53
Ho <sub>4</sub> NiGa <sub>12</sub>	18.13	21.79	18.86	18.76	19.34	18.18
Ho <sub>3</sub> Ni <sub>1.8</sub> Ga <sub>9.2</sub>	17.67	20.95	18.26	18.04	18.51	17.16
HoNi <sub>0.9</sub> Ga <sub>1.1</sub>	18.04	20.84	18.76	18.48	18.55	17.70
Ho <sub>2</sub> Ni <sub>2</sub> Ga	18.36	20.75	19.07	18.95	19.22	18.46
HoNiGa	17.75	20.55	18.54	18.27	18.27	17.53
HoNiGa <sub>2</sub>	16.93	20.31	17.86	17.52	17.45	16.58
HoNiGa <sub>4</sub>	16.76	20.07	17.50	17.23	17.41	16.29
Ho <sub>4</sub> Ni <sub>10</sub> Ga <sub>21</sub>	15.08	18.43	15.89	15.53	15.17	14.72
Ho <sub>2</sub> Ni <sub>6</sub> Ga <sub>2</sub>	15.75	18.02	16.24	16.07	15.94	15.55
Ho <sub>2</sub> Ni <sub>5</sub> Ga <sub>5</sub>	15.09	17.91	15.65	15.22	14.54	14.45
HoNi <sub>2.5</sub> Ga <sub>2.5</sub>	15.20	17.91	15.65	15.22	14.54	14.45
Ho <sub>2</sub> Ni <sub>7.5</sub> Ga <sub>9.5</sub>	14.24	17.39	14.93	14.54	13.99	13.88
HoNi <sub>2.9</sub> Ga <sub>2.1</sub>	14.88	17.33	15.26	14.87	14.19	14.19
HoNi <sub>3</sub> Ga <sub>2</sub>	14.85	17.19	15.17	14.79	14.12	14.14
Ho <sub>2</sub> Ni <sub>9.4</sub> Ga <sub>7.6</sub>	13.78	16.52	14.33	13.96	13.34	13.42
Ho <sub>2</sub> Ni <sub>7</sub> Ga <sub>3</sub>	14.44	16.47	14.72	14.43	13.91	13.92

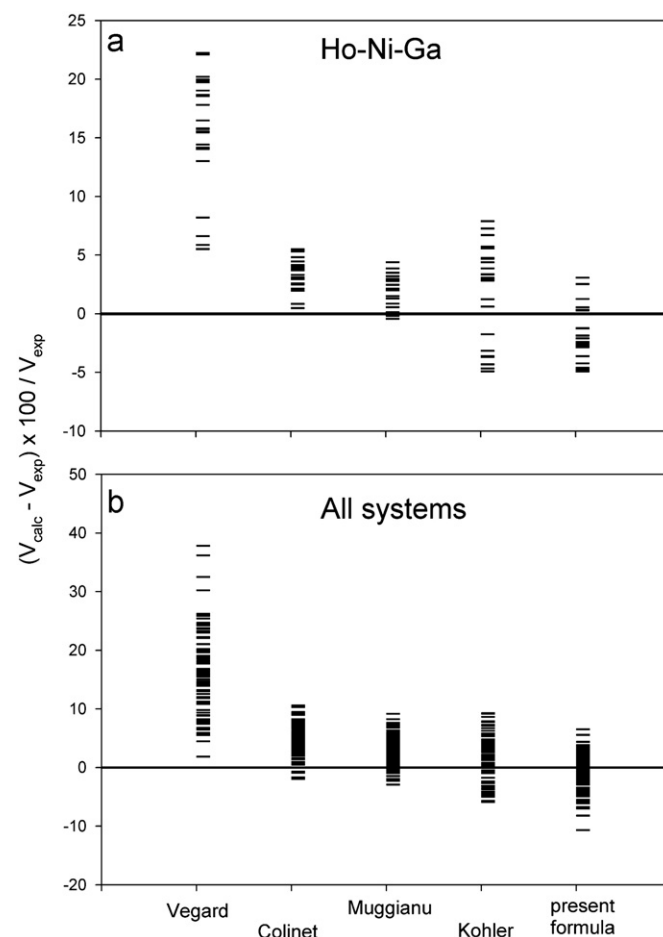
to symbols used in Fig. 1 (Toop's method), the simple linear contribution of the  $A_xB_{y+z}$  and  $A_xC_{y+z}$  binary compositions is lowered by a quantity equal to the volume contraction of the  $B_yC_z$  composition, namely the difference ( $V_{\text{Vegard}} - V_{\text{observed}}$ ). This negative contribution is weighed by the expression  $(y+z)^2$ , a parabolic dependence on the distance between the ternary point and the B–C side. This procedure is extended to all three sides of the system and the results averaged. The resulting expression is:

#### Present work

$$V(A_xB_yC_z) = 1/3\{[x/(x+y)]V(A_{x+y}C_z) + [y/(x+y)]V(B_{x+y}C_z) \\ - (x+y)^2[V_0(A_xB_y) - V(A_xB_y)]\} \\ + 1/3\{[y/(y+z)]V(A_xB_{y+z}) + [z/(y+z)]V(A_xC_{y+z}) \\ - (y+z)^2[V_0(B_yC_z) - V(B_yC_z)]\} \\ + 1/3\{[x/(x+z)]V(A_{x+z}B_y) + [z/(x+z)]V(B_yC_{x+z}) \\ - (x+z)^2[V_0(A_xC_z) - V(A_xC_z)]\}$$

where  $V_0(B_yC_z)$  and the like correspond to the ideal Vegard-like values.

As an example, the observed volumes and those calculated on the basis of the Vegard rule and of the above formulae are reported in Table 3 for the Ho–Ni–Ga system, which contains the highest number of ternary intermediate phases. For a better comparison, the percentage deviation of the five empirical predictions from the experimental data are also plotted (Fig. 4a). Finally, an overall graph is given in Fig. 4b, showing results of the 91 ternary compounds occurring in the eight studied systems.



**Fig. 4.** Percent deviation from the experimental data of the volumes calculated after Vegard, Colinet, Muggianu, Kohler methods and present formula for the Ho–Ni–Ga system (a), and for the eight examined ternary systems (b).

#### 4. Discussion

The obtained results allow to make the following comments:

- (a) As expected Vegard's criterion provides too high volume values, but it shows the volume effects occurring in the phase formation (ranging from 2% to 28% of volume contraction, with the maximum values for the Si and Ge systems).
- (b) Colinet- and Muggianu-like methods give similar results, usually higher than the experimental data.
- (c) The Kohler-like method and the here proposed formula show an acceptable agreement between observed and calculated values.
- (d) Since a good agreement can be obtained starting from a proper choice of the binary phases that means the minor role played by the additional ternary interactions.

In conclusion, the best estimate of the atomic volume of any ternary intermetallic compound can be obtained from the crystallographic data of the corresponding binary systems, applying both the Kohler method and the new procedure here proposed.

Moreover, according to the (d) observation, the volume effects occurring in the formation of a ternary phase can be mostly imputed to the process of formation of the binary compounds. This is in agreement with the principle that, going to systems of higher order, the additional interactions are less and less important.

Finally, the present results can be taken into account as a general check of the cited methods, not only for the here discussed volume calculations, but also for the validity of the predictions of thermodynamic quantities.

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