Journal of Solid State Chemistry 184 (2011) 959–964

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

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.

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:

(a) the choice of the suitable compositions of the binary phases;
(b) the calculation of the "observed" volume for the chosen compositions, even when they do not correspond to existing phases; and
(c) 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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doi:10.1016/j.jssc.2011.01.036

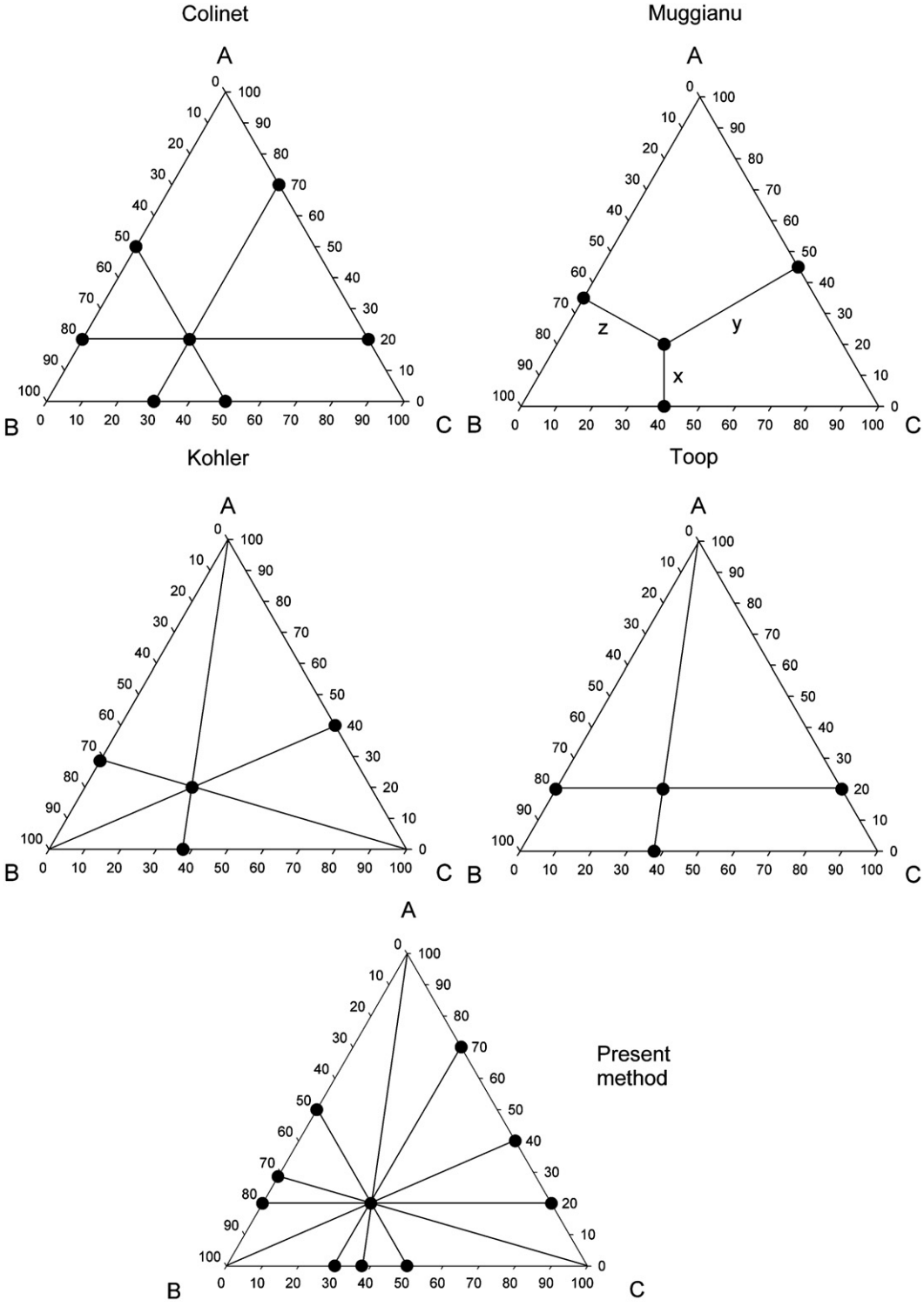

Fig. 1. Methods of selecting compositions of the binary phases to extrapolate a physical property of a ternary phase.

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 $\mathbf{V}_{at}$ within an $\mathbf{A_{1-x}B_x}$ system

$$\mathbf{V_{at}} = (\mathbf{1}-\mathbf{x})\mathbf{V_A^\circ} + \mathbf{x}\mathbf{V_B^\circ} - \mathbf{K}\mathbf{x^n}(\mathbf{1}-\mathbf{x}) \quad (1)$$

$$\mathbf{V_{at}} = (\mathbf{1}-\mathbf{x})\mathbf{V_A^\circ} + \mathbf{x}\mathbf{V_B^\circ} - \mathbf{K}\mathbf{x^n}(\mathbf{1}-\mathbf{x})^\mathbf{2} \quad (2)$$

where $\mathbf{V_A^\circ}$ and $\mathbf{V_B^\circ}$ 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].