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Compressibilities of Copper–Bismuth Liquid Alloys

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A simple macroscopic model proposed by Varotsos and Alexopoulos is successfully applied in the copper–bismuth liquid alloy. The isothermal compressibility for any concentration can be evaluated provided that the isothermal compressibilities for two compositions (or, for a single concentration and for one of the constituents) are known. The results are compared with those recently computed by Rao and Satpathy.

Ein einfaches, von Varotsos und Alexopoulos vorgeschlagenes makroskopisches Modell wird erfolgreich für die flüssige Kupfer–Wismuthlegierung genutzt. Die isotherme Kompressibilität für jede Konzentration läßt sich berechnen, vorausgesetzt, daß die isothermen Kompressibilitäten für zwei Zusammensetzungen (oder für eine einzige Konzentration und für eine der Konstituenten) bekannt sind. Die Ergebnisse werden mit den kürzlich von Rao und Satpathy berechneten verglichen.

1. Introduction

Varotsos and Alexopoulos have previously formulated a macroscopic model that considers an alloy as a defect crystal [1]. If experimental data on the density and the compressibilities for two concentrations (or, equivalently, of one constituent and one concentration of the alloy) are available, then it allows the evaluation of the compressibility for any composition. This model has already successfully been applied in a large variety of solid alloys, such as mixed ionic crystals [2 to 8] and metal alloys [9 to 13]. We have recently shown that it also works well for alkali metal liquid alloys [14].

According to the Varotsos and Alexopoulos model [1], the introduction of an impurity atom into a pure material with mean atomic volume Ω_0, results in an increase of the initial volume by $\Omega_0 + u^d$. So, when n foreign atoms get into a host material containing N atoms, then an alloy is produced having $n + N$ atoms. Its volume will be

$$V_{N+n} = N\Omega_0 + n(\Omega_0 + u^d) .$$

This can be written as

$$V_{n+N} = V_0 + (n/N)(V_0 + Nu^d) , \tag{1}$$

where V_{n+N}, V_0 are the volumes of the alloy and the host material, respectively. N can be set equal to Avogadro's number. For reasons of simplicity we identify V_{n+N} with V. We stress that u^d is not necessarily constant (i.e. independent of the composition) or equal to the difference between the mean atomic volumes of the two components, and is derived from the molar volume obtained from density measurements.

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Differentiating (1) with respect to pressure we get

$$\varkappa V = \varkappa_0 V_0 + (n/N)\,(\varkappa^{\mathrm{d}} N u^{\mathrm{d}} + \varkappa_0 V_0)\,, \tag{2}$$

where $\varkappa_0$ is the compressibility of the host material, $\varkappa$ the compressibility of the mixed system, and $\varkappa^{\mathrm{d}}$ the compressibility of the defect volume defined as follows:

$$\varkappa^{\mathrm{d}} = -\frac{1}{u^{\mathrm{d}}}\frac{\mathrm{d}u^{\mathrm{d}}}{\mathrm{d}P}\,. \tag{3}$$

We note that (2) holds either for isothermal or adiabatic compressibility.

The volume V of the mixture is readily extracted from density measurements, since

$$V = \frac{m_0 + (n/N)\,m_1}{\varrho}\,, \tag{4}$$

where m_0, m_1 is the mass (in g-atom) of the host and the impurity material, respectively, while ϱ is the density of the alloy. We notice that the molar fraction χ is connected to the ratio n/N by

$$n/N = \chi/(1 - \chi)\,. \tag{5}$$

If $V = V(n/N)$ is a straight line, we conclude that the defect volume u^{d} is constant and independent of the concentration. In this case (u^{d} = const), if $\varkappa^{\mathrm{d}}$ is also constant, the relation $\varkappa V = \varkappa V(n/N)$ is linear.

The interest is focused on the following point: If u^{d} and $\varkappa^{\mathrm{d}}$ are constant and $\varkappa$ is known just for a couple of concentrations (or, for a single concentration and for the host material), then $\varkappa$ may be calculated for any desired concentration.

2. Application of the Varotsos-Alexopoulos Model on Liquid Copper–Bismuth Alloys

Gomez et al. [15] have measured the density of liquid copper at various temperatures as well as the densities of liquid copper–bismuth alloys for different atomic concentrations of

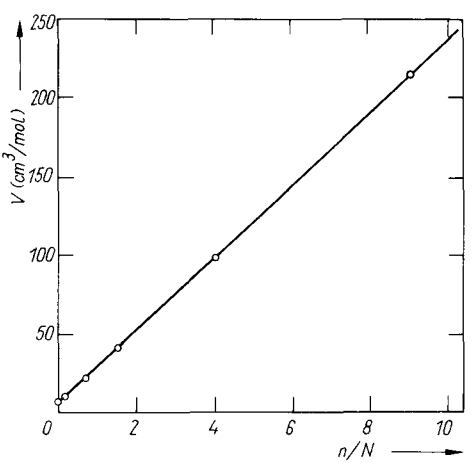

Fig. 1. The volume V vs. n/N at 1373 K for the Cu–Bi alloy. Its linearity defines a constant defect volume u^{d} that is independent of the composition

Table 1
The volume V, the isothermal compressibility $\varkappa$, and the product $\varkappa V$ for various atomic fractions of bismuth at 1373 K

χ (at% Bi)	n/N	V (cm^3/mol)	$\varkappa$ (10^{-11} m^2/N)	$\varkappa V$ (10^{-17} m^5/N)
0	0	8.021	1.51	12.112
10	0.11	10.168	1.85	18.811
40	0.67	22.253	3.18	70.765
60	1.50	40.900	4.66	190.594
80	4.00	98.153	6.15	603.641
90	9.00	212.755	6.88	1463.754

Cu versus temperature. Using (4) we plot V versus n/N at $T = 1373$ K that is obviously a straight line with unit correlation factor (Table 1, Fig. 1). Therefore, the defect volume u^d is constant and independent of the concentration. A least-squares fit gives $Nu^d = 14.77$ cm^3.

Ebert et al. [16] have evaluated the isothermal compressibilities of copper, bismuth, and Cu–Bi alloys in the melt for various concentrations versus temperature. Combining these data with those extracted for the volume V, we plot $\varkappa V = \varkappa V(n/N)$ for $T = 1373$ K which is a straight line with correlation factor 0.999 (Table 1). This line leads to the evaluation of the defect compressibility $\varkappa^d = 1.0221 \times 10^{-10}$ m^2/N and the ratio $\varkappa^d/\varkappa_0 = 6.77$. In Fig. 2 we have drawn $\varkappa = \varkappa(n/N)$ together with $\varkappa V = \varkappa V(n/N)$. It is worth noticing that the compressibility $\varkappa$ versus n/N is definitely nonlinear in contrast with the product $\varkappa V$ versus n/N that is a straight line with correlation factor 0.999.

We have repeated the above procedure at 1398, 1423, and 1448 K and got also excellent results.

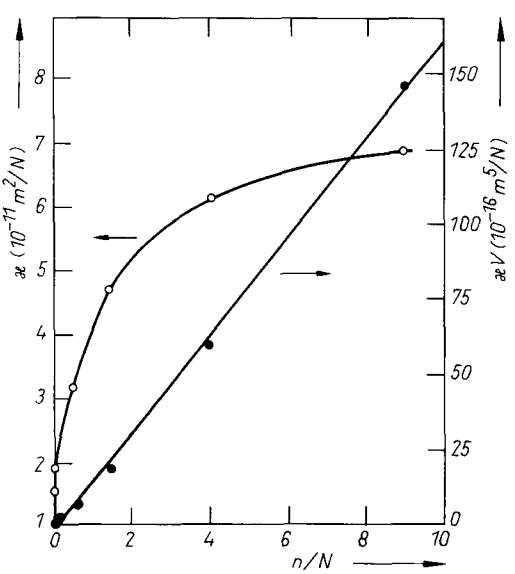

Fig. 2. The isothermal compressibility $\varkappa$ (circles) and the product $\varkappa V$ (points) vs. n/N at 1373 K. Notice the non-linear increase of $\varkappa$ and the linear dependence of $\varkappa V$ on n/N

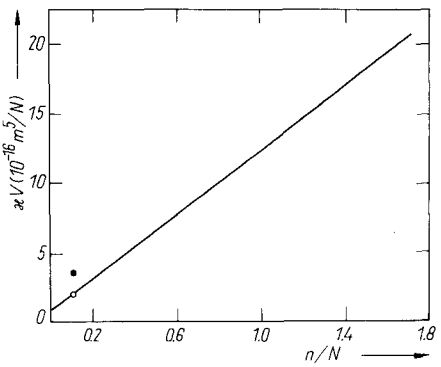

Fig. 3. $\varkappa V$ vs. n/N at the arbitrarily chosen temperature $T = 1275$ K. ——— according to the Varotsos and Alexopoulos model, ○ experimentally determined value, ● computed by Gopala Rao and Satpathy [17]

3. Prediction of the Compressibility for any Composition

In a recent paper Gopala Rao and Satpathy [17] have computed the partial structure factors and the Bhatia-Thornton structure factors for copper–bismuth liquid mixtures of various concentrations. The isothermal compressibilities versus the concentration have been evaluated from the Kirkwood-Buff equation. At 1275 K and $x = 10\%$ Bi a value $\varkappa = 3.52 \times 10^{-11}$ m^2/N is computed.

We apply the Varotsos and Alexopoulos model to the above system; i.e. $T = 1275$ K. The compressibilities of the alloy are known for $\chi = 40\%$ and 60%, where χ is the atomic fraction of bismuth. As already mentioned the defect volume u^d in the above system is constant, therefore, a linear relation of $\varkappa V$ versus n/N must be valid (Fig. 3). The above line for $\chi = 10\%$ Bi gives $\varkappa V(\chi = 10\%) = 18.149 \times 10^{-17}$ m^5/N. From density measurements [15] by using (4) we evaluate the volume $V(\chi = 10\%) = 10.075$ cm^3/mol. Consequently the compressibility $\varkappa$ of the alloy for $\chi = 10\%$ Bi must be equal to 1.80×10^{-11} m^2/N. Our value coincides with the experimental one found by Ebert et al. [16]. The value computed by Gopala Rao and Satpathy [17] is two times larger than the experimental one ($\varkappa_{exp} = 1.8 \times 10^{-11}$ m^2/N) [16].

4. Conclusion

The Varotsos and Alexopoulos model is proved to be a simple tool for accurately predicting the compressibility of copper–bismuth liquid alloys for any concentration if we know the compressibilities for two compositions.

References

[1] P. VAROTSOS and K. ALEXOPOULOS, Thermodynamics of Point Defects and their Relation with Bulk Properties, Ed. S. AMELINCKX, R. GEVERS, and J. NIHOUL, North-Holland Publ. Co., Amsterdam 1986 (pp. 325 to 347).
[2] P. VAROTSOS, phys. stat. sol. (b) **99**, K93 (1980).
[3] P. VAROTSOS and K. ALEXOPOULOS, J. Phys. Chem. Solids **41**, 1291 (1980).
[4] P. VAROTSOS, J. Phys. Chem. Solids **42**, 405 (1981).
[5] J. GRAMMATIKAKIS, M. LAZARIDOU, and K. EFTAXIAS, J. Phys. Chem Solids **46**, 1243 (1985).
[6] M. LAZARIDOU and C. VAROTSOS, J. Phys. Chem. Solids **46**, 643 (1985).
[7] C. VAROTSOS and M. LAZARIDOU, phys. stat. sol. (b) **129**, K95 (1985).
[8] P. MANORAVI and K. SHAHI, Solid State Ionics **45**, 83 (1991).

[9] P. VAROTSOS and K. ALEXOPOULOS, phys. stat. sol. (b) **102**, K67 (1980).
[10] J. GRAMMATIKAKIS, K. EFTAXIAS, S. PATAPIS, and V. HADJICONTIS, J. Phys. Chem. Solids **49**, 965 (1988).
[11] J. GRAMMATIKAKIS and C. LONDOS, J. Phys. Chem. Solids **49**, 1465 (1988).
[12] V. HADJICONTIS, C. VAROTSOS, and K. EFTAXIAS, J. Phys. F **18**, 1133 (1988).
[13] J. GRAMMATIKAKIS and V. KATSIKA, J. Phys. Condensed Matter **2**, 3903 (1990).
[14] A. N. PAPATHANASSIOU, J. GRAMMATIKAKIS, and N. BOGRIS, phys. stat. sol. (a) **125**, 529 (1991).
[15] M. GOMEZ, L. MARTIN-GARIN, H. EBERT, P. BEDON, and P. DESRE, Z. Metallkd. **67**, 131 (1967).
[16] H. EBERT, J. HOHLER, and S. STEEB, Z. Naturf. **29a**, 1890 (1974).
[17] R. V. GOPALA RAO and ALOK SATPATHY, Phys. Rev. B **41**, 995 (1990).

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