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Compressibilities of Potassium–Rubidium and Sodium–Cesium Liquid Alloys

By

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The isothermal bulk moduli of Na–Cs and K–Rb liquid alloys for various compositions are calculated by applying a simple macroscopic model proposed by Varotsos and Alexopoulos. The results are in agreement with experimental data and are compared with the computed ones by Rao et al..

Die isothermen Elastizitätsmodule von flüssigen Na–Cs- und K–Rb-Legierungen verschiedener Zusammensetzung werden unter Anwendung eines einfachen von Varotsos und Alexopoulos vorgeschlagenen makroskopischen Modells berechnet. Die Ergebnisse befinden sich in Übereinstimmung mit experimentellen Werten und werden mit den von Rao et al. berechneten verglichen.

1. Introduction

Gopala Rao and his coworkers have recently computed the partial structure factors of K–Rb liquid alloys [1] and some years ago for Na–Cs liquid alloys [2] for various compositions, as well as the Bathia-Thornton structure factors. The isothermal compressibilities versus concentration were also evaluated from the Kirkwood-Buff equations.

A few years ago Varotsos and Alexopoulos [3] suggested a simple macroscopic model that permits the evaluation of the bulk modulus B of an alloy for various concentrations, provided that the bulk moduli of the two end components are experimentally known. We check the validity of this model that has already successfully been applied in a large variety of solid alloys, such as mixed ionic crystals and metal alloys [3 to 11], on the afore-mentioned liquid mixtures.

2. Theory

According to the Varotsos and Alexopoulos model [3], the introduction of an impurity atom into a pure material with mean atomic volume Ω_0 results 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

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

where V_{n+N}, V_0 are the volume of the alloy and the host material, respectively. We stress that, as already mentioned by Varotsos and Alexopoulos [3], u^d is not necessarily equal to the difference between the mean atomic volumes of the two components, and is derived

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from density measurements. We notice that the molar fraction χ is connected to the ratio n/N by

$$\frac{n}{N} = \frac{\chi}{1 - \chi}. \tag{2}$$

Assuming that the alloy is a hard spheres model, i.e.,

$$u^{\mathrm{d}} = u_1 - u_0, \tag{3}$$

where u denotes the molar volume and the subscripts 0 and 1 refer to the host material and the added component, respectively. Equation (3) in combination with (2) gives

$$V_{n+N} = (1 - \chi) V_0 + xV_1, \tag{4}$$

where $x = n/(n + N)$ and V_1 is the volume of the added component. Differentiating (4) with respect to pressure we get

$$\varkappa V = (1 - \chi) \varkappa_0 V_0 + \chi \varkappa_1 V_1, \tag{5}$$

where $\varkappa$ and $\varkappa_0$ is the isothermal compressibility of the alloy and the host material, respectively. From (4) and (5), taking into account that the bulk modulus is given by $B = 1/\varkappa$, we get

$$B = B_0 \frac{1 + \chi[(V_1/V_0) - 1]}{1 + \chi[(B_0 V_1)/(B_1 V_0) - 1]}. \tag{6}$$

This relation is just based on the assumption that the hard sphere model holds also for the mixed system. A liquid can be considered [2] as a hard sphere model, so it fulfils the afore-mentioned assumption of the Varotsos-Alexopoulos model (that makes no distinction between solid and liqud alloys).

3. Results and Discussion

The isothermal bulk modulus $B = 1/\varkappa$ may be evaluated from density and sound velocity measurements. Kim et al. [12] have measured the densities of liquid alkali metals at various temperatures, while Kim and Letcher [13] have published sound velocity data in liquid mixtures of K–Rb, Na–Cs versus temperature.

The isothermal compressibility $\varkappa$ may be calculated using the relation

$$\varkappa = \frac{C_p}{C_v} \frac{1}{\varrho v_s^2}, \tag{7}$$

where ϱ is the density of the alloy and v_s denotes the sound velocity. The ratio C_p/C_v at 100 °C can be set equal to 1.13 for the Na–Cs mixture [14]. For the K–Rb system the isothermal compressibilities have already been calculated by Gopala Rao and Bandyopadhyay [1].

The input parameters for the Varotsos and Alexopoulos model are listed in Table 1. These data were extracted at $T = 373$ K from [12] and [13].

Table 1
Input parameters for the Varotsos and Alexopoulos model

constituent	V (cm^3/mol)	B (GPa)
Cs	73.76	1.472
Na	24.83	5.204
Rb	58.82	1.948
K	47.67	2.497

The experimental and the theoretical isothermal bulk moduli versus the atomic concentration of the added component are shown in Fig. 1a and b for Cs–Na and K–Rb liquid alloys, respectively. The corresponding values are listed in Tables 2 and 3.

Table 2
Theoretical and experimental data for Na–Cs liquid alloys at 373 K

χ (at% Na)	B_{theor} (GPa)		B_{exper} (GPa)
	Varotsos model	[2]	
0.00	–	1.303	1.472
4.73	1.490	1.331	1.491
20.25	1.560	1.441	1.620
29.00	1.612	1.524	1.693
35.98	1.662	1.610	1.733
53.61	1.842	1.885	1.996
62.90	1.991	2.150	1.946
68.76	2.119	2.364	2.296
75.13	2.580	2.612	2.306
79.96	3.114	2.879	2.500
89.84	3.178	3.658	3.733
100.00	–	5.059	5.204

Table 3
Theoretical and experimental data for K–Rb liquid alloys at 373 K. The experimental values were both derived in [1] and in our work

χ (at% K)	B_{theor} (GPa)		B_{exper} (GPa)	
	Varotos model	[1]	[1]	present work
0.00	–	1.723	1.948	1.938
10.08	1.985	1.743	1.929	1.996
19.04	2.020	1.760	1.902	2.023
32.29	2.076	1.831	1.907	2.089
40.11	2.112	1.908	1.919	2.125
52.58	2.175	2.011	1.971	2.201
67.71	2.262	2.207	2.076	2.295
74.02	2.302	2.430	2.054	2.249
89.72	2.413	2.615	2.134	2.236
100.00	–	2.844	2.497	2.501

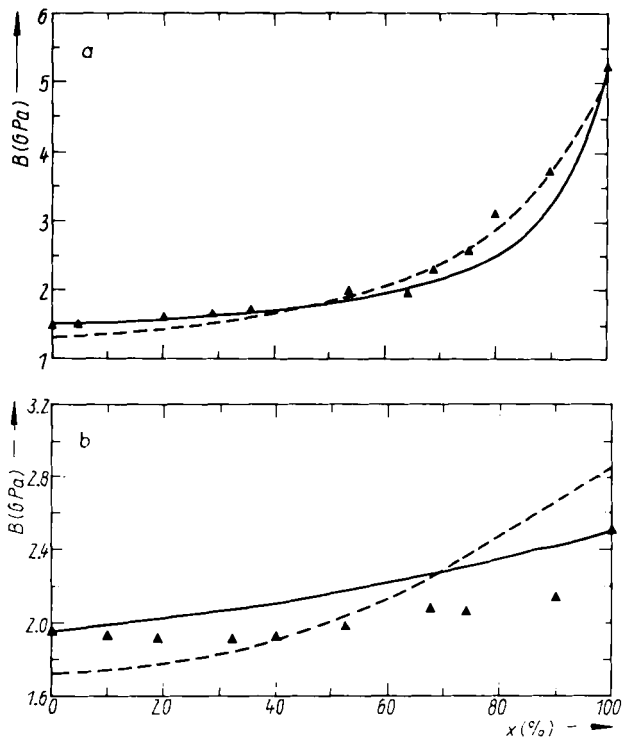

Fig. 1. The isothermal bulk modulus B vs. the atomic fraction of a) Na for the Na–Cs b) K for the K–Rb liquid alloys at 373 K. ▲ Experimental points (in b) from [1]), ——— calculated from the Varotsos-Alexopoulos model, – – – computed by Gopala Rao and Satpathy [2] (in a), Gopala Rao and Bandyopadhyay [1] (in b)

For the first mixture Cs–Na (Fig. 1a) we point out that the Varotsos-Alexopoulos model fits well to the experimental values. The calculated ones by Gopala Rao and Satpathy are also in agreement.

In Fig. 1b a similar diagram is designated for the latter mixture K–Rb using the experimental values given by Gopala Rao and Bandyopadhyay [1]. The Varotsos-Alexopoulos model overestimates the experimental values no more than 13% and the dependence of B upon χ is similar to the experiment. Supposing that the ratio C_p/C_v is around 1.13, slightly different experimental values are estimated which are also listed in Table 3 and a third diagram may be drawn as in Fig. 2. In this case the Varotsos-Alexopoulos

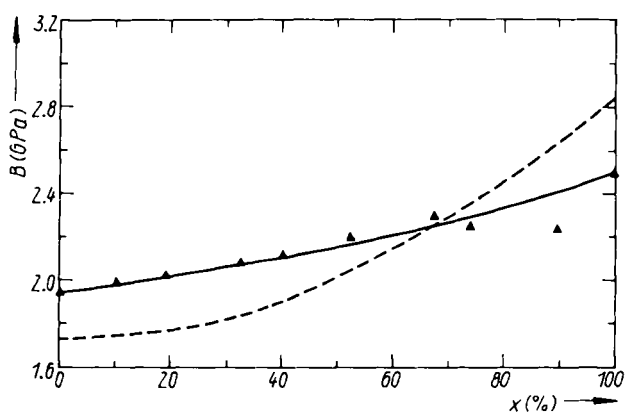

Fig. 2. The isothermal bulk modulus B vs. the atomic fraction of K for the K–Rb liquid alloy at 373 K. ▲ Experimental points obtained assuming that $C_p/C_v \approx 1.13$, ——— calculated from the Varotsos-Alexopoulos model, – – – computed by Gopala Rao and Bandyopadhyay [1]

model is in good agreement with the experiment. Anyway, the above small deviations are less than the total error of the bulk modulus due to experimental uncertainties and assumptions made in order to extract the values of B.

We conclude that the Varotsos and Alexopoulos model can predict with high accuracy the bulk modulus at any composition of the above mixtures if we know the compressibilities of the end components.

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