Thermodynamic properties of the liquid Na–Bi system under high pressures

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Abstract. The EMF of the liquid Na–Bi system has been measured as a function of temperature and pressure in detail by the method of an electrochemical cell using β-alumina as the electrolyte. We have obtained the associated thermodynamic quantities of mixing such as the free Gibbs energy ΔG, entropy ΔS, enthalpy ΔH, excess specific heat ΔC_p and excess volume ΔV. The isothermal compressibility χ_T and the concentration–concentration fluctuation $S_{cc}(0)$ in the long-wavelength limit are obtained. From these, a strong short-range order was found at the composition of Na_3Bi and a rather weak short-range order was found around the composition of $NaBi$.

1. Introduction

It is well known that the liquid Na–Bi system has a strong compound-forming character at around 75 at.% Na in the electronic properties such as transport properties (Pfeifer *et al* 1981) and magnetic susceptibilities (Hackstein *et al* 1980). The electromotive force (EMF) measurements of this system have been carried out by Fischer *et al* (1967) and Yih and Thompson (1982), and some thermodynamic quantities of mixing such as the Gibbs free energy ΔG, entropy ΔS, enthalpy ΔH and concentration–concentration fluctuation $S_{cc}(0)$ in the long-wavelength limit have already been obtained under 1 atm. However, these measurements are restricted to less than 80 at.% Na and no measurement has been done in the sodium-rich region beyond 80 at.% Na. This is only because of technical difficulties; the boiling point of sodium is 888 °C, while the melting temperature of Na_3Bi is 848.1 °C (Johnson and Fischer 1970).

The purpose of this paper is to report all the thermodynamic quantities of mixing in liquid Na–Bi alloys including the concentration–concentration fluctuation $S_{cc}(0)$ in the long-wavelength limit, the volume changes and the isothermal compressibility by measuring the EMF of a concentration cell under pressure.

2. Experimental procedure

The electrochemical cell has been used to measure the chemical potential difference between a liquid alloy and liquid sodium. The EMF of a concentration cell has been measured using an electrochemical cell with a sodium β-alumina as the electrolyte. A

description of the EMF cell and the apparatus under a high pressure has already been given by Neale and Cusack (1982) in detail, and the apparatus is essentially identical with the design used in earlier work (Neale and Cusack 1982). So we shall not repeat the methods of those experimental techniques; however, we refer briefly to the essence and schematic procedure of those experiments. We could obtain the EMF in the following way. The cell used in the present experiment was Mo wire, Na (liq)|β-alumina, Na$^+$|Na$_x$Bi$_{1-x}$ alloy (liq), Mo wire. The values of EMF and the pressure applied to the alloy sample were all measured with a high-precision digital voltmeter with an input impedance greater than 100 GΩ in the range $c = c_{Na} = 0.10$–0.92; the lowest and highest temperatures were 300 °C $< T <$ 800 °C and pressures up to 272 bar were applied.

At each concentration c, the variation in EMF with increasing temperature was measured under the constant pressure (from 1 bar to 68, 102, 204 and 272 bar). The Na and Bi were of purities 99.99 at.% and 99.999 at.%, respectively.

3. Results and discussion

The observed values of EMF are shown in figure 1 as a function of temperature at given concentrations and at constant pressure. As shown in this figure, it should be emphasized that most of the $(\partial E/\partial T)_{c,p}$ are not constant with increasing temperature. The pressure dependence of the EMF of these alloys at several temperatures is shown in figure 2. This figure also indicates that most of the $(\partial E/\partial p)_{c,T}$ are not always constant. These facts indicate that the variation in the specific heat of this system deviates from the linear concentration dependence and the curve of isothermal compressibility deviates from the ideal curve; these points will be discussed later.

The following equations were used to derive the thermodynamic quantities of mixing:

$$\Delta G = (1 - c) \int_0^c \frac{(-zFE)}{(1 - c')^2} \, dc' \tag{1}$$

$$\Delta S = (1 - c) \int_0^c \frac{zF(\partial E/\partial T)_{c'}}{(1 - c')^2} \, dc' \tag{2}$$

$$\Delta H = \Delta G + T \Delta S \tag{3}$$

$$S_{cc}(0, c, T) = -RT(1 - c)/zF(\partial E/\partial c)_{p,T} \tag{4}$$

$$\Delta C_p = \left(\frac{\partial(\Delta H)}{\partial T}\right)_p = (1 - c)T \int_0^c \frac{zF(\partial^2 E/\partial T^2)_{c'}}{(1 - c')^2} \, dc' \tag{5}$$

where F is the Faraday constant and z is the valence number of Na. The molar volume V and isothermal compressibility χ_T of the alloy composition are given by the formulae (Neale *et al* 1981)

$$V = (1 - c)V_1^0 + cV_2^0 - (1 - c) \int_0^c \frac{zF(\partial E/\partial p)_{c',T}}{(1 - c')^2} \, dc' \tag{6}$$

$$\chi_T = -(1/V)(\partial V/\partial p)_T = \frac{1}{V}[(1 - c)\chi_{T1}^0 V_1^0 + c\chi_{T2}^0 V_2^0] + \frac{1 - c}{V} \int_0^c \frac{F(\partial^2 E/\partial p^2)_{c',T}}{(1 - c')^2} \, dc' \tag{7}$$
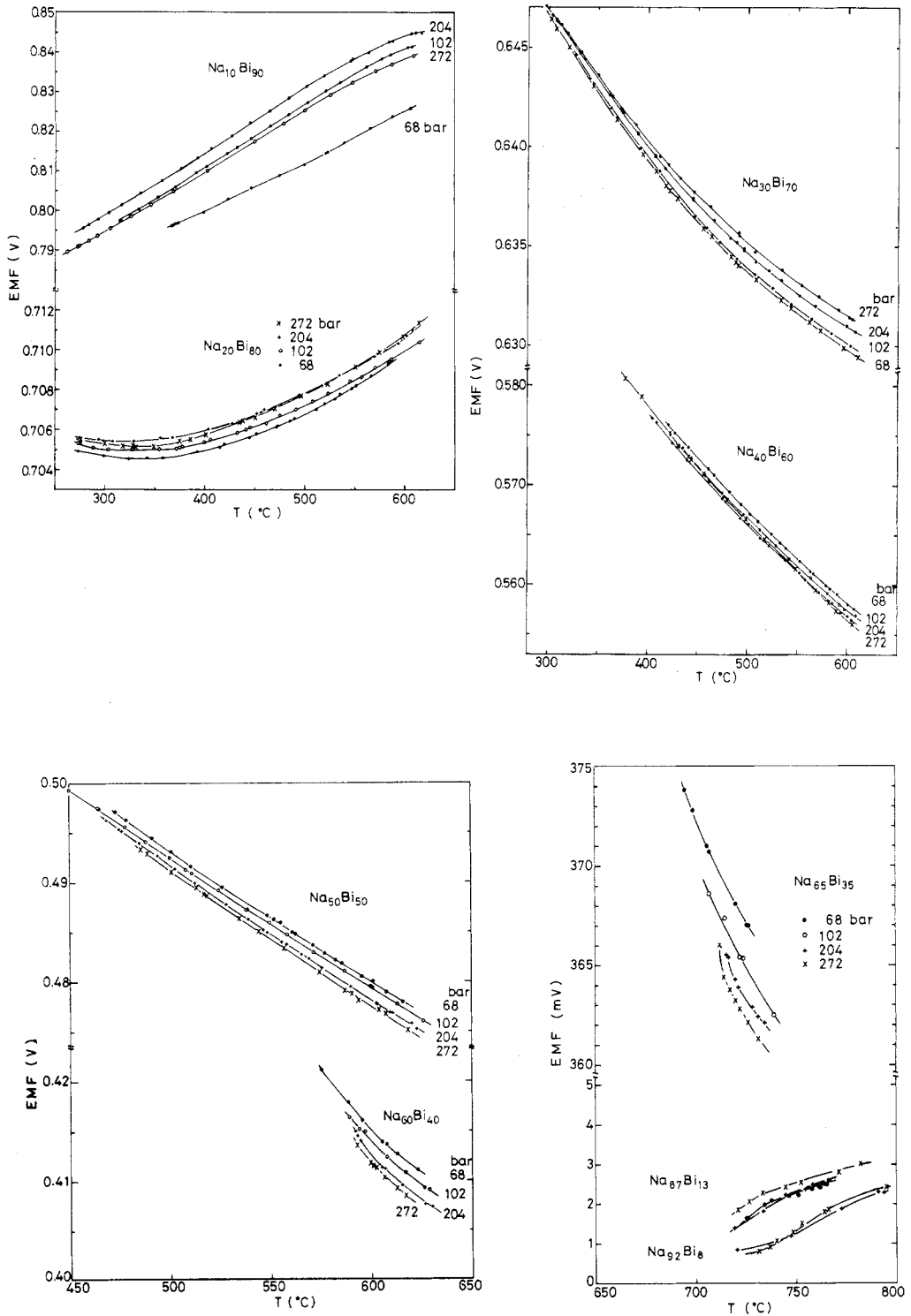
Figure 1. Observed EMF as a function of temperature at different pressures and different compositions in atomic per cent as indicated in the figures.
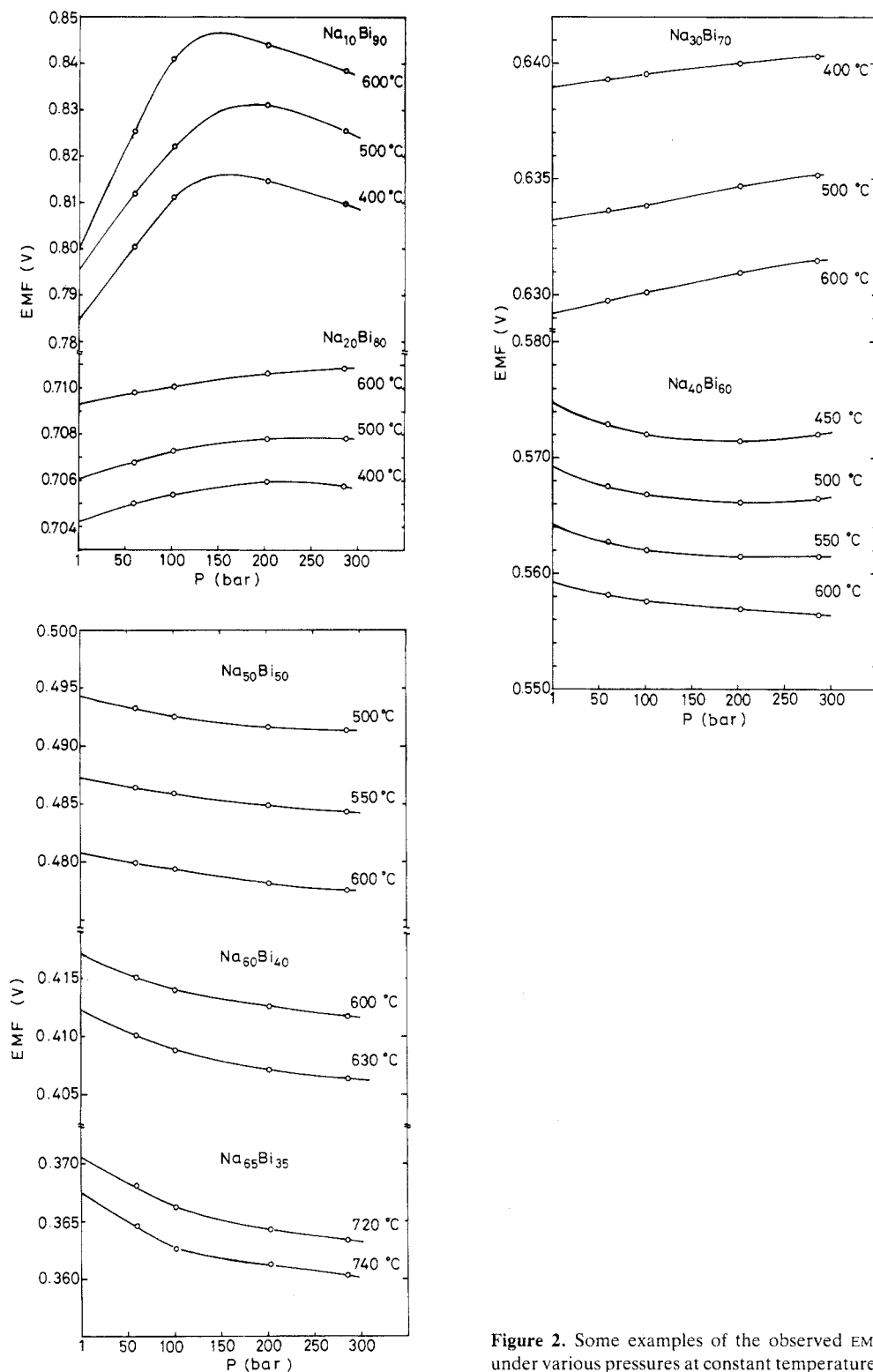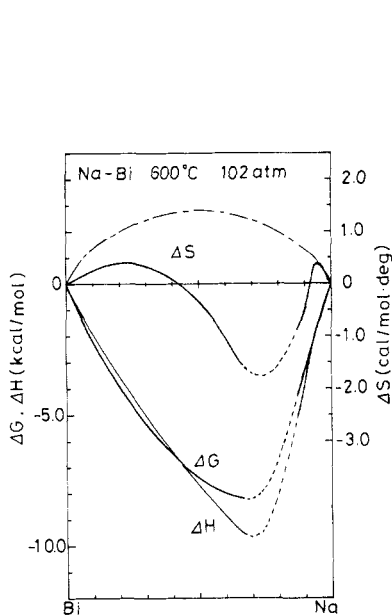
Figure 2. Some examples of the observed EMF under various pressures at constant temperature.

Table 1. Thermodynamic properties of pure sodium and pure bismuth at 1 bar.

	V $(\text{cm}^3\,\text{mol}^{-1})$	χ_T $(10^{-12}\,\text{dyn}^{-1}\,\text{cm}^2)$
Na	28.35 (at 600 °C)	19.0
Bi	21.61 (at 600 °C)	4.21

Figure 3. Typical example of the observed Gibbs free energy, entropy and heat of mixing at 600 °C and 104 bar for liquid Na–Bi. Values in the concentration range $0.65 \leqslant C_{\text{Na}} \leqslant 1$ are taken from the data at 725 °C.
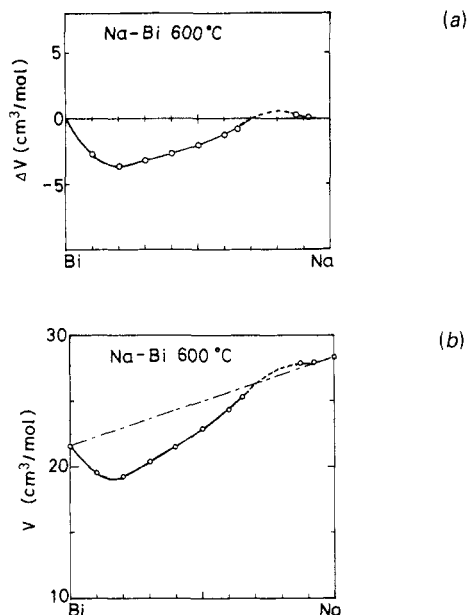
Figure 4. Composition dependences of (a) the excess molar volume and (b) the molar volume for liquid Na–Bi alloys.

where the superscript zeros refer to the properties of pure Bi (subscripts 1) and pure Na (subscripts 2) and listed for convenience in table 1. Typical examples of thermodynamic quantity of mixing such as ΔG, ΔH and ΔS of the alloys at 600 °C are given in figure 3, although those alloys at the concentration range $0.65 \leqslant C_{\text{Na}} \leqslant 1$ are taken from the data at 725 °C. In what follows, all thermodynamic quantities are drawn in a similar way. All these thermodynamic quantities of mixing have minima at a composition of around Na_3Bi and this may result from the formation of the complex Na_3Bi in the liquid state. The absolute values of the free energy ΔG of mixing slightly increase with increasing pressure in the Bi-rich region. This trend is easily acceptable if the excess volume ΔV is negative on mixing, because we have the following relation:

$$[\partial(\Delta G)/\partial p]_T = \Delta V.$$

The excess molar volumes of the alloys are shown in figure 4(a) and the molar volumes, using the volume listed in table 1, shown in figure 4(b). The curve of molar
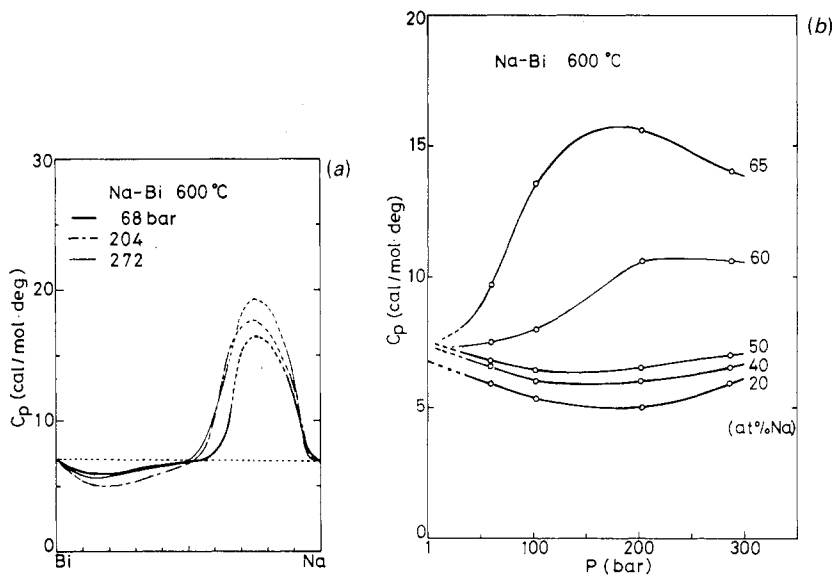
Figure 5. (a) Concentration dependence and (b) pressure dependence of excess specific heat for liquid Na–Bi.

volume deviates negatively from the ideal behaviour especially in the Bi-rich region. The ratio $\Delta V/V_{id}$ of volume contraction to the ideal volume is estimated to be a minimum value of about -16% at a composition of around $NaBi_4$ and it may be the most compact packing structure in the present system.

A deviation from Kopp's law in the specific heats of the alloys can be found in figure $5(a)$. The concentration dependence of specific heat has a maximum value at around Na_3Bi corresponding to the minimum in ΔG. This fact may result from the dissociation of chemical complex of Na_3Bi in the liquid state. The pressure dependences of the specific heats are shown in figure ($5b$) for different Na concentrations. It is interesting that the degree of dissociation of complexes, which is expressed by the specific heat C_p is small for the concentration range $0 < C_{Na} < 0.5$. Beyond 50 at.% Na, this dissociation seems to be larger and the specific heat strongly depends on the applied pressure.

The concentration–concentration fluctuation $S_{cc}(0)$ in the long-wavelength limit is shown in figure 6 at 1 and 272 bar. $S_{cc}(0)$ at $p = 1$ bar quantitatively agrees with the former result (Yih and Thompson 1982). As shown in the figure, the concentration fluctuation $S_{cc}(0)$ seems to have a minimum at around Na_3Bi and a broad minimum at around equiatomic concentration. It is clear that a chemical complex of Na_3Bi forms in the liquid state, which is also supported by the increase in the specific heat at around this composition. On the other hand, there is no anomalous behaviour in the curve of specific heat at around equiatomic concentration. So there may remain some kind of short-range order at around the equiatomic concentration, although its bonding nature is not changed with increasing temperature.

The height of $S_{cc}(0)$ at a concentration of around 80 at.% Na decreases with increasing pressure. In other words, the phase separation tendency decreases with increasing pressure. The curve of $S_{cc}((0)$ at a concentration of around 20 at.% Na decreases slightly
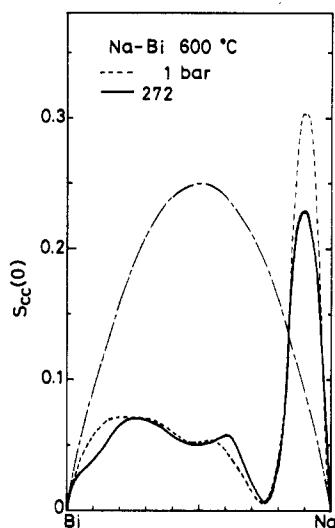
Figure 6. Concentration–concentration fluctuation $S_{cc}(0)$ in the long-wavelength limit for liquid Na–Bi alloys.

with increasing pressure. The pressure derivative of $S_{cc}(0)$ is expressed as follows (Hoshino and Endo 1982):

$$[\partial S_{cc}(0)/\partial p]_{T,c} = -[S_{cc}(0)^2/RT](\partial^2 V/\partial c^2)_T. \tag{8}$$

Since the signs of pressure dependence of concentration fluctuation $[\partial S_{cc}(0)/\partial p]_{T,c}$ is negative for 20 and 90 at.% Na and positive at around 62 at.% Na, the curvature $(\partial^2 V/\partial c^2)_{T,c}$ of molar volume could be positive at 20 and 90 at.% Na and negative at around 62 at.% Na. These are quite consistent with the concentration variation of the molar volume, as shown in figure 4.

The isothermal compressibilities, determined by the volume data, is shown in figure 7(a). It is found that the curve deviates almost positively from the ideal behaviour (chain line). Since the molar volume contracts by alloying, the compressibility is expected to decrease, but the present result contradicts to the usual sense. However, this may be understood in the following way. The terms on the right-hand side in equation (7) can be rewritten as three terms:

$$\chi_T = \chi_T^{id} + \Delta\chi_T^A + \Delta\chi_T^B$$

$$\chi_T^{id} = (1/V_0)[(1-c)\chi_{T_1}^0 V_1^0 + c\chi_{T_2}^0 V_2^0]$$

$$\Delta\chi_T^A = [(1-c)\chi_{T_1}^0 V_1^0 + c\chi_{T_2}^0 V_2^0](1/V - 1/V_0)$$

$$\Delta\chi_T^B = \frac{l-c}{V}\int_0^c \frac{F(\partial^2 E/\partial p^2)_{c',T}}{(1-c')^2}\,dc'. \tag{9}$$

The first term χ_T^{id} in equation (9) indicates the compressibility in the case of ideally mixed, the second term $\Delta\chi_T^A$ indicates the compressibility variation due to the volume change, and the third term $\Delta\chi_T^B$ indicates the compressibility variation in the mixture by the pressure dependence of free energy in mixing. The concentration curve χ_T^{id} is shown in figure 7(a) by the chain curve. The concentration curves of the second and third terms in equation (9) are shown in figure 7(b). The second term becomes a positive value whenever the alloy system contracts by mixing, while the last term has a negative value.
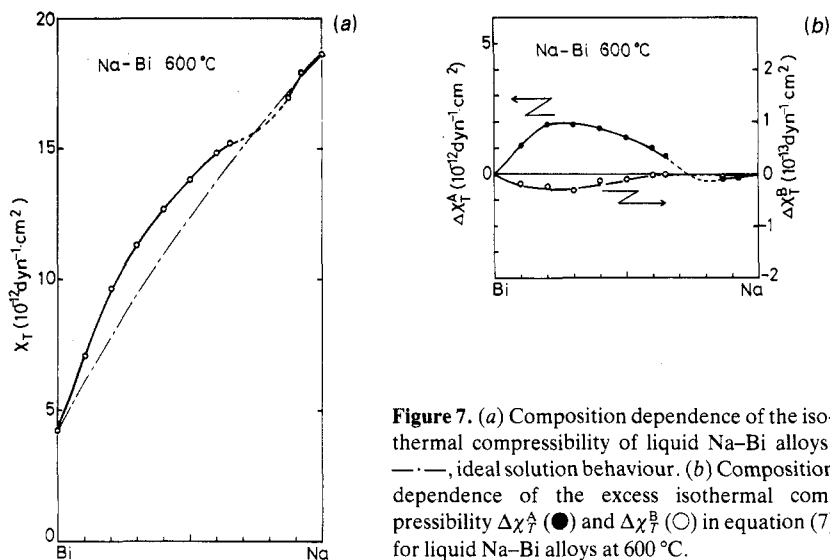
Figure 7. (a) Composition dependence of the iso-thermal compressibility of liquid Na–Bi alloys: — · —, ideal solution behaviour. (b) Composition dependence of the excess isothermal compressibility $\Delta\chi_T^A$ (●) and $\Delta\chi_T^B$ (○) in equation (7) for liquid Na–Bi alloys at 600 °C.

However, the values of the third term $\Delta\chi_T^B$ are much smaller than those of the second term $\Delta\chi_T^A$ by almost one order. Thus it becomes clear that the compressibility of the present system is governed by the first and second terms in equation (9).

Let us consider the origin of the large negative excess volume in the Bi-rich region and also the unusual variation in isothermal compressibility in this system. The large negative excess volume may be due to the electron charge transfer from the Na atom to the Bi atom when Na atoms are put into Bi atoms. That is, the ionic radii of Na ions are contracted by charge transfer in the alloy system. The negative excess volume in the polyvalent-metal-rich region has been reported for many liquid Na–polyvalent metal systems such as Na–Hg (Ishiguro *et al* 1984), Na–Cd, Na–Ga (Hoshino and Endoh 1982), Na–In (Tamaki *et al* 1989) and Na–Pb (Hesson *et al* 1968, McAlister 1972). The large negative excess volume yields the positive excess compressibility as a result.

4. Fluctuations

As mentioned in the preceding section, a hollow region can be seen in $S_{cc}(0)$ at around 15 at.% Na with increasing pressure, and this may corresponding to the decrease in $S_{cc}(0)$ with decreasing temperature. The phase separation tendency in the Na-rich region, which is indicated by the large peak in $S_{cc}(0)$, decreases with increasing pressure and, therefore, the fluctuation in the Na-rich region decreases with increasing pressure. A similar pressure effect has also been observed for Na–Cs (Neale and Cusack 1982), Na–Cd, Na–Ga (Hoshino and Endoh (1982) and Na–In alloys (Tamaki *et al* 1989). This pressure effect in the Na-rich region may be due to a positive value in the ordering energy (Hoshino and Young 1989); this determines the phase separation tendency, which decreases with increasing pressure.

From the observed data on $S_{cc}(0)$, $\delta = (1/V)(\partial V/\partial C)_T$ and χ_T, we can derive the three types of partial structure factor in the long-wavelength limit, although the error bars become larger on going to Na-rich concentrations: the Faber–Ziman type, $a_{ij}(0)$
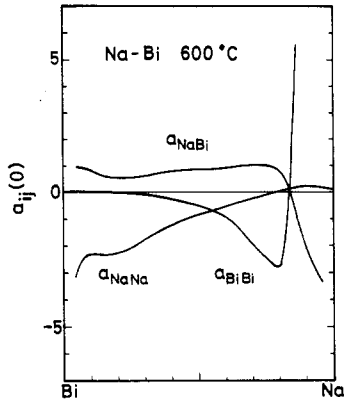
Figure 8. The Faber–Ziman-type structure factors in the long-wavelength limit for $a_{ij}(0)$ (i, j = Na, Bi) for liquid Na–Bi.
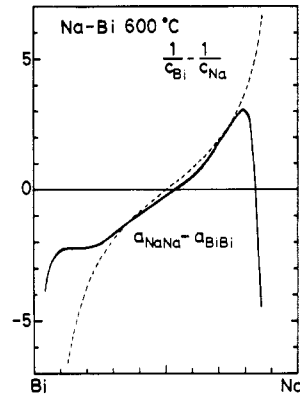

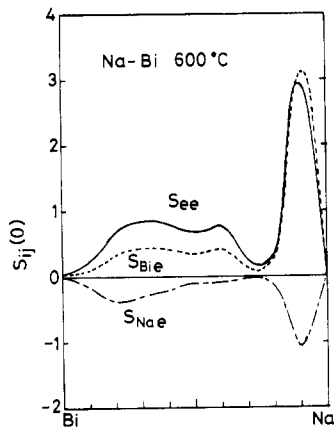**Figure 9.** Stillinger–Lovett condition for liquid Na–Bi alloys.

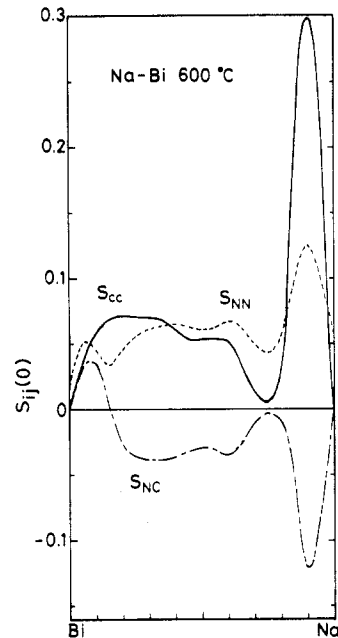**Figure 10.** Observed correlation functions $S_{ie}(0)$ (i = Na, Bi, e) for liquid Na–Bi.

Figure 11. Observed correlation functions $S_{ij}(0)$ (i, j = C, N) for liquid Na–Bi.

(i, j ≡ Na, Bi), the Bhatia–Thornton type, S_{ij} (i, j ≡ C, N) and the March–Tosi–Bhatia type S_{Ae} (A ≡ Ba, Bi, e) which are all derivable from one another (March *et al* 1973).

The Faber–Ziman-type structure factors $a_{ij}(0)$ in the long-wavelength limit are obtained as shown in figure 8. If charge transfer occurs strongly between the atoms in

the present liquid alloys, then it may be useful to examine the so-called Stillinger–Lovett (1968) condition, which indicates local charge neutrality:

$$a_{\text{NaNa}}(0) - a_{\text{BiBi}}(0) - (1/c_{\text{Bi}} - 1/c_{\text{Na}}) = 0. \tag{10}$$

This is a good measure of the local order in the liquid state. In figure 9, we see that the Stillinger–Lovett condition is satisfied at around Na_2Bi and Na_3Bi, and a rather small deviation from equation (10) gives a wide concentration range around the equiatomic fraction where the curve of $S_{cc}(0)$ has a shallow minimum region.

The March–Tosi–Bhatia-type partial structure factors are shown in figure 10. These behaviours suggest that charge transfer from Na to Bi may occur to some extent, similar to the case of liquid Na–In alloys (Tamaki *et al* 1989).

For reference, the partial structure factors of Bhatia–Thornton type are also shown in figure 11. All $S_{ij}(0)$-values have a complicated concentration dependence and have minimum values at around Na_3Bi and large values in the Na-rich region.

In conclusion, liquid Na–Bi alloys have a strong short-range order in Na_3Bi and a rather weak short-range order at around NaBi, to some extent owing to an electron charge transfer from Na to Bi because of the large difference in their electronegativities.

Acknowledgments

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