Thermodynamic properties of liquid Na-In alloys under high pressure

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Abstract. We report detailed data on the EMF of Na in molten Na–In alloys under high pressure. The measurements employed an electrochemical cell with β-alumina as the electrolyte. The associated thermodynamic quantities of mixing, such as the free energy ΔG, entropy ΔS, enthalpy ΔH, excess specific heat ΔC_p, excess volume ΔV, compressibility χ_T and concentration–concentration fluctuation in the long-wavelength limit $S_{cc}(0)$, are obtained. From these, a kind of short-range order was found at the composition of Na_4In under pressure, in addition to the other short-range orders, corresponding to β and γ phases in the solid state. Using $S_{cc}(0)$, ΔV and χ_T, the various kinds of partial structure factors in the long-wavelength limit are also obtained.

1. Introduction

Thermodynamic measurements and theoretical interpretations of thermodynamic properties of mixing for liquid Na–polyvalent metal alloys have frequently been made over a long period of time. Some of these alloys show interesting variations with concentration in their thermodynamic quantities such as the Gibbs free energy ΔG, entropy ΔS, enthalpy ΔH and concentration–concentration fluctuation in the long-wavelength limit $S_{cc}(0)$. From the viewpoint of electronic properties, the concentration dependence of the properties of Na–X (X = non-transition polyvalent metal of valence z) alloy is governed largely by the valence z of X. If $z \le 2$, NEF theory for these alloys appears to be valid and the problem is to understand how a suitable kind of order emerges in the liquid state (Tamaki *et al* 1982). If $z \ge 4$, ideas beyond NFE theory are necessary for the transport properties, and 'complex' formation is currently the most favoured explanation (Tamaki 1987, Van der Lugt and Geertsma 1987). It is not clear whether liquid Na–In alloys, in which $z = 3$, are covered by NFE theory or not, and this is what prompted us to measure their thermodynamic properties. In a previous paper (Harada *et al* 1988), we reported that the liquid Na–In alloys have a kind of short-range order around the concentration of 50 at.% Na, while there exists a tendency towards phase separation in the Na-rich region.

On the other hand, Neale *et al* (1981) and Neale and Cusack (1982) introduced a new method to obtain all the thermodynamic quantities associated with mixing in liquid binary alloys, including concentration–concentration fluctuation in the long-wavelength

limit $S_{cc}(0)$, volume changes and isothermal compressibilities by measuring the electromotive force (EMF), $E(c, T, P)$ of a concentration cell under pressure.

In the present study, we have applied the method of Neale et al (1981) and Neale and Cusack (1982) to liquid Na–In alloys in order to obtain the more interesting and detailed thermodynamic properties. Where this work overlaps that of previous papers (Bartlett et al 1970, Rais et al 1982, Iwase et al and Harada et al 1988) the agreement is moderately satisfactory.

2. Experimental procedure

The thermodynamic properties were all determined by measuring the EMF, $E(c, T, P)$, in a concentration cell incorporating a sodium β-alumina electrolyte separator. The cell used was

Mo wire, Na(liquid)$|\beta$-alumina, Na$^+|$alloy(liquid), Mo wire.
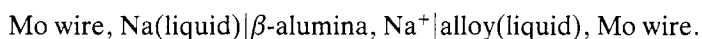
The apparatus is essentially identical to the design used in earlier work by Neale and Cusack (1982). A detailed description of the apparatus is given in their paper and so it is not duplicated here. The values of the EMF, temperature of the alloy and pressure applied to the alloy sample were all measured by a high-precision digital voltmeter (Schlumberger Solartron 7065) with an input impedance greater than $100\,\mathrm{G\Omega}$ in the range $c = c_{Na} = 0.10$–0.90; $T \simeq 300$–$500\,^{\circ}\mathrm{C}$, $p \simeq 1$–280 bar.

At each concentration of c, the variation of EMF with increasing temperature was measured under constant pressure (from 1 to 50, 100, 150, 200, 250, 280 bar). The Na and In were of purities 99.99 and 99.999 at.%, respectively.

3. Results

Values of the EMF at given concentrations and at constant pressure are plotted as a function of temperature and shown in figure 1(a) to 1(d). It should be emphasised that the majority of the $(\partial E/\partial T)_{c,p}$ are not constant with temperature. From these figures, the pressure dependence of the EMF of the alloys at constant temperature was obtained and figure 2 is a typical example. From this figure, it is apparent that $(\partial E^2/\partial p^2)_{c,T}$ is also not constant, which indicates that the compressibilities of the present system depend on composition; this point will be discussed later.

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

$$\Delta G = (1-c)\int_0^c (-zFE)/(1-c')^2\, \mathrm{d}c' \tag{1}$$

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

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

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

$$\Delta C_p = (\partial \Delta H/\partial T)_p = (1-c)T\int_0^c zF(\partial^2 E/\partial T^2)_{c'}/(1-c')^2\, \mathrm{d}c' \tag{5}$$
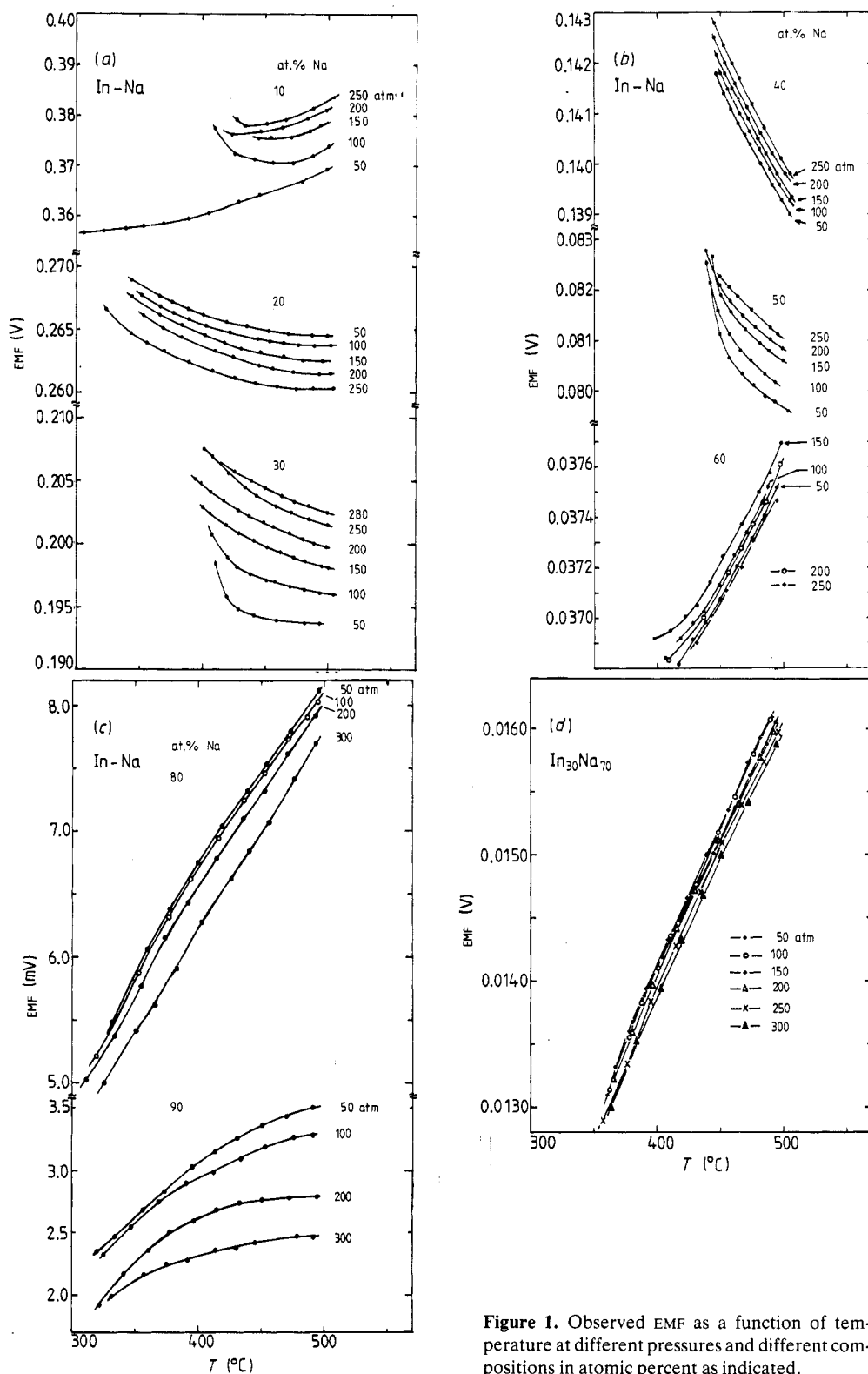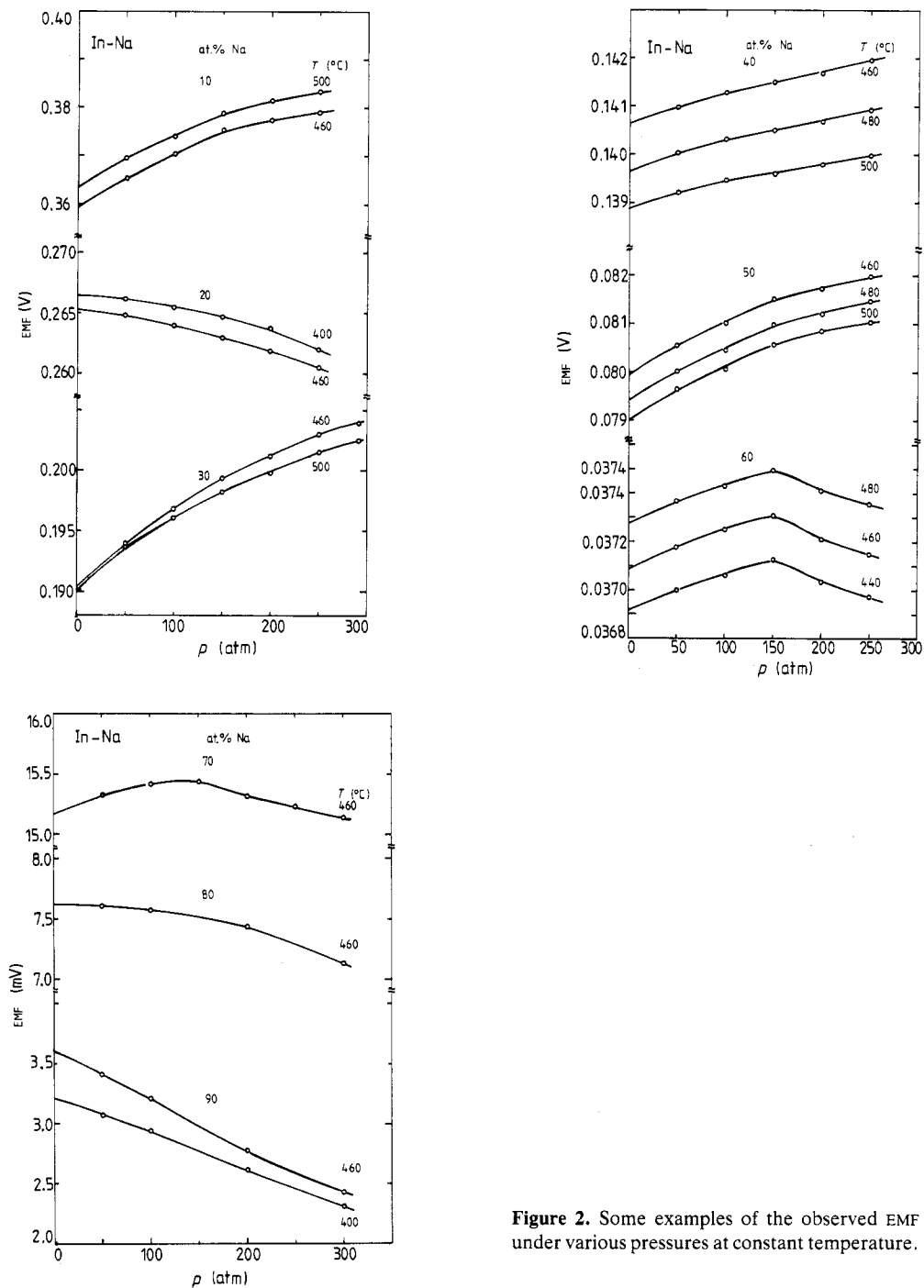
Figure 1. Observed EMF as a function of temperature at different pressures and different compositions in atomic percent as indicated.

Figure 2. Some examples of the observed EMF under various pressures at constant temperature.

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

Table 1. Thermodynamic properties of pure sodium and pure indium at their melting temperature and 1 bar.

	V cm^3 mol^{-1}	χ_T (10^{-12} dyn cm^{-2})
Na	24.863	19.0
In	16.3	2.96
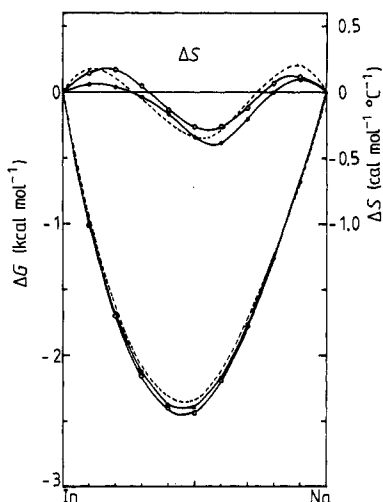
Figure 3. Observed Gibbs free energy and entropy of mixing at 460 °C under various pressures for liquid Na–In. – – –, 1 atm; —●—, 100 atm; —○—, 250 atm.

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

$$\chi_T = (1/V)[(1 - c)\chi_1^0 V_1^0 + c\chi_2^0 V_2^0]$$
$$+ (1 - c)/V \int_0^c F(\partial^2 E/\partial p^2)_{c',T}/(1 - c')^2 \, dc' \tag{7}$$

where the subscript zero refers to the properties of pure In($=1$) and pure Na($=2$), listed for convenience in table 1. In figure 3, the ΔG and ΔS of the alloys at 460 °C under various pressures are given. It is clear that absolute values of ΔG increase with increasing pressure. This trend is easily acceptable if $\Delta V < 0$, because we have the following relation:

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

Using the volumes listed in table 1, the molar volumes of the alloys at 460 °C are estimated as shown in figures 4(a) and 4(b). Davies (1972) measured the molar volumes of liquid Na–In alloys up to 7 at.% In in the Na-rich region, and observed a negative deviation in ΔV, which agreed qualitatively with our results. The curve of ΔV has a minimum at the mixture In$_8$Na$_5$. This result suggests that the complex of liquid In$_8$Na$_5$ is formed, and this corresponds to the intermetallic compound in the solid state. It may be the most compact packing structure in the present system. The minimum position of ΔG around In$_8$Na$_5$ may result from the formation of the complex In$_8$Na$_5$.
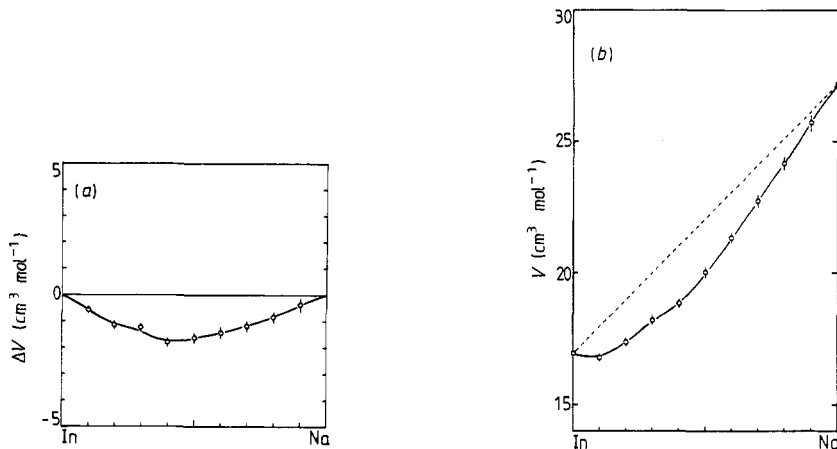
Figure 4. (*a*) Composition dependence of volume contraction on mixing for liquid Na–In alloys at 460 °C. (*b*) Composition dependence of the volume contraction for liquid Na–In alloys at 460 °C.
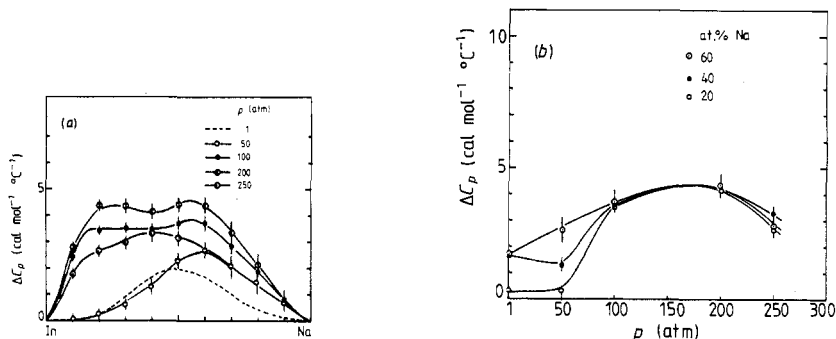
Figure 5. (*a*) Concentration dependence of excess specific heat for liquid Na–In. (*b*) Pressure dependence of excess specific heat for some alloy composition of liquid In–Na.

The minimum in ΔS at constant pressure is located at 55 at. % Na, while the minimum value of ΔV is at about 40 at. % Na. This difference may be explained as follows. The isothermal compressibility of the alloys increases with the Na concentration as will be shown later; so the minimum value of ΔS shifts towards the Na-rich region, because we have a thermodynamic relation $\Delta S \simeq \Delta V \alpha_v / \chi_T$, where α_v is the thermal expansion coefficient.

As seen in figure 5(*a*), a large deviation from Kopp's law in the specific heats of the alloys was found. At $p = 1$ atm the peak of ΔC_p is located around 45 at. % Na corresponding to the minimum in ΔG. Then its peak shifts towards 60 at. % Na with increasing pressure. This fact may result from a complicated change in $\Delta H(p, T)$ around these concentrations. By 100 to 200 atm the curve of ΔC_p develops two maxima at the concentration of 20 at. % Na and 57 at. % Na, respectively. The maximum at 20 at. % Na may suggest that the alloy system forms a kind of complex In_4Na under moderate pressure. The pressure dependence of ΔC_p obtained from figure 5(*a*) is shown in figure 5(*b*). It is interesting that the readiness of the complexes to dissociate, which is measured
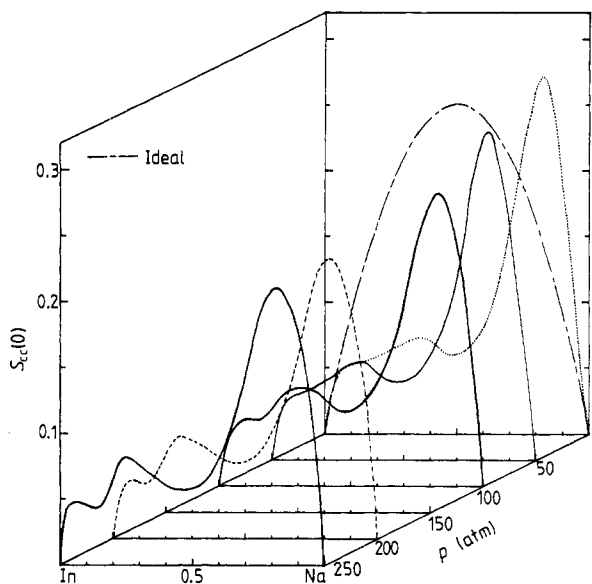
Figure 6. Concentration–concentration fluctuation $S_{cc}(0)$ in the long wavelength limit for liquid Na–In alloys at 460 °C.

by ΔC_p, is independent of composition for the pressure range above 100 atm and its maximum lies at about $p = 180$ atm.

The change of concentration–concentration fluctuation in the long wavelength limit, $S_{cc}(0)$, is shown in figure 6. $S_{cc}(0)$ at $p = 1$ atm agrees with the former result (Harada *et al* 1988) and it is clear that a complex of InNa forms. However, the curve of $S_{cc}(0)$ around the concentration of In_4Na varies with increasing pressure and a new minimum appears at higher pressure. We believe that this is caused by some slight formation of In_4Na as already suggested by ΔC_p.

As discussed above, the complexes In_4Na, In_8Na_5 and InNa are formed in the present alloys to a greater or lesser extent. However the minima of $S_{cc}(0)$ are located only at the compositions In_4Na and InNa. To understand these facts consistently, we assume that the formation of In_8Na_5 is limited to atomic scale short-range ordering, whilst the clusters of In_4Na and InNa are much bigger with an intermediate range ordering.

The depth of $S_{cc}(0)$ at the equiatomic fraction is scarcely changed by applying the pressure. However, the height of the peak around the concentration of 80 at.% Na decreases with increasing pressure. In other words, the tendency toward phase separation decreases with increasing pressure.

Using the volume data, the isothermal compressibilities are also obtained as shown in figure 7. Since the molar volume contracts by alloying, as seen in figure 6, the first term on the right-hand side of equation (7) deviates positively, although the last term in equation (7) is somewhat negative for the whole concentration range.

All the quantities derived from equations (1) to (7) are subject to uncertainty arising from the errors of measurement in E, p, c and T, those in c and T being the most important. The error bars in figures 3 to 7 represent our estimate of errors in the derived quantities.
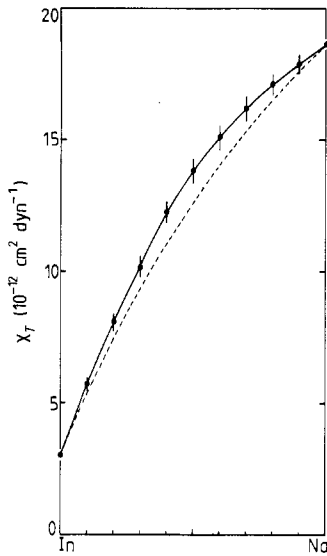
Figure 7. Composition dependence of the isothermal compressibility of liquid Na–In alloys at 460 °C. The broken curve represents the ideal solution behaviour.

4. Discussion

As described in the preceding section, a small minimum in $S_{cc}(0)$ forms in the In-rich region with increasing pressure, and this may correspond to the behaviour of S_{cc} 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. A similar pressure effect has been observed in liquid Na–Cs alloys (Neale and Cusack 1982). If the phase-separation tendency in liquid alloys is fully described in terms of the ordering potential (see, for example, Young 1987), then this fact suggests that the positive value of the ordering potential decreases with pressure.

Another interesting fact is that, although the volume is lower, the isothermal compressibility is higher than the ideal solution of the same composition (see figures 4(b) and 7). This fact is unusual, if not unique. By a contraction of the volume, the sodium and indium atoms are more closely packed and it is natural to expect the compressibility of the system to become smaller if the atomic behaviour of the system is unchanged. From this, we expect that the electronic structure of liquid Na–In alloys are appreciably changed by alloying. In other words, it is somewhat doubtful to apply straightforward NFE theory to these alloys, even if their constituents could be interpreted in terms of simple NFE theory.

Using the data of $S_{cc}(0)$, $\delta = (1/V)(\partial V/\partial c)_T$ and χ_T, we can derive three types of partial structure factors in the long-wavelength limit: the Faber–Ziman type, $a_{ij}(0)$ ($i, j =$ In, Na); the Bhatia–Thornton type $S_{ij}(0)$ ($i, j = c, N$) and the March–Tosi–Bhatia type, S_{Ae} (A = In, Na, e), which are all derivable from one another.
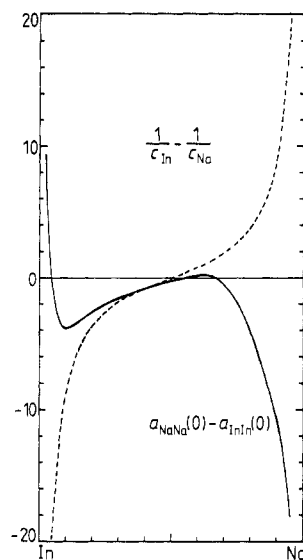
If charge transfer occurs strongly between atoms in the present liquid alloys, then we have the so-called Stillinger–Lovett conditions, which indicate local charge neutrality:

$$a_{NaNa}(0) - a_{InIn}(0) - (1/c_{In} - 1/c_{Na}) = 0. \tag{8}$$

This is a measure of local ordering.
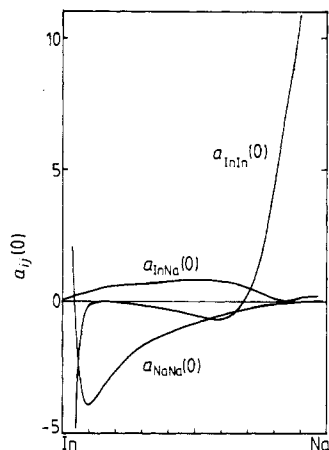
Figure 8. Long-wavelength limit for the Faber–Ziman type structure factor $a_{ij}(0)$ (i, j = Na, In) for liquid Na–In.

Figure 9. Stillinger–Lovett condition for liquid Na–In alloys.

In figure 8 the $a_{ij}(0)$ are shown. Using these values, equation (8) is examined as seen in figure 9—equation (8) is only satisfied around the compound In_8Na_5. A small amount of deviation from the Stillinger–Lovett condition is found at the equiatomic fraction where the curve of $S_{cc}(0)$ has the minimum.

The March–Tosi–Bhatia-type (M-T-B) partial structure factors are shown in figure 10. The M-T-B partial structure factors are a good indication of charge transfer (Tamaki 1987). March *et al* (1973) and Takeda and Tamaki (1986) have obtained S_{Nae}, S_{Ke} and S_{ee} of liquid Na–K alloys and they have found a trend such that S_{Nae} and S_{Ke} have positive and negative values, respectively. This trend is related to the fact that a charge transfer occurs from K to Na, which was qualitatively recognised by the study of structure factors in liquid Na–K alloys (Hoshino *et al* 1981). Taking this trend into account, charge transfer from Na to In may occur to some extent, similar to the case of liquid Na–Sn alloys (Takeda *et al* 1984).

For reference, partial structure factors of the Bhatia–Thornton type are also shown in figure 11, although only to point out that for the present alloys they are quite different from those of liquid Na–K alloys (see for example Young (1987)) so the straightforward application of simple theory to the In–Na seems unpromising.

In conclusion, liquid In–Na alloys have a charge transfer from Na to In. Their thermodynamic properties are not easy to explain by a simple model and a theory more complicated than NFE theory will be required.
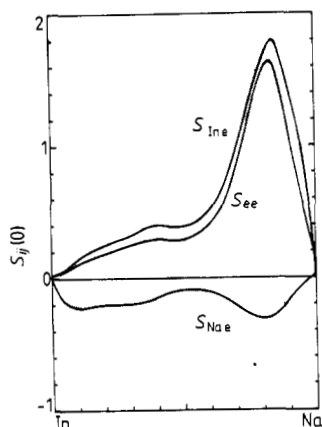
Acknowledgments

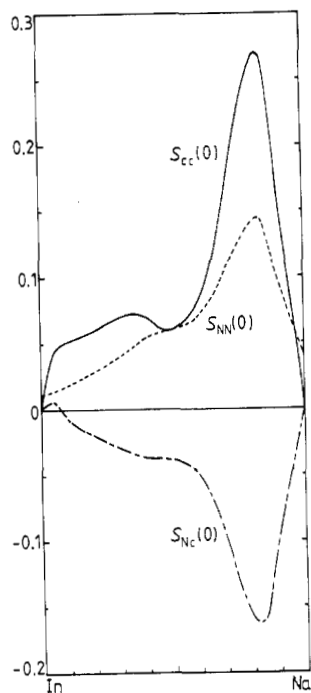**Figure 10.** Observed correlation functions, $S_{ie}(0)$, (i = Na, In, e) for liquid Na–In.

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

enabled an extension of his stay at the University of East Anglia and he wishes to thank Miss T Tamaki for her helpful assistance in Norwich.

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