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Summary. - The correlations between long-wavelength fluctuations of concentration in a liquid binary alloy are determined by a balance between an elastic strain free energy and an Ornstein - Zernike effective interaction. The latter is extracted from thermodynamic data in the case of the Li - Pb system, which is well known to chemically order with stoichiometric composition corresponding to Li_4Pb. Strong attractive interactions between concentration fluctuations near the composition of chemical ordering originate from electronic charge transfer, which is estimated from the electron-ion partial structure factors as functions of composition in the liquid alloy.

1. - Introduction.

A class of liquid alloys formed by combining an alkali metal with an electronegative metallic element such as Au or Pb shows chemical short-range order of the component elements ([1-3]). Ordering is believed to arise from electronic charge transfer ([4]) and is signalled by extrema in the composition dependence of transport coefficients and thermodynamic properties, occurring at stoichiometric compositions given by the ratio of the chemical valences of the constituents. A well known example is the Li - Pb system, with stoichiometric composition corresponding to Li_4Pb. The Li - Pb system has been studied by measurements of electronic transport properties ([5,6]), magnetic susceptibility ([7]), Knight shifts ([8]) and thermodynamic properties ([9,10]), as well as by neutron diffraction ([11,12]). Charge transfer and local order have been evaluated on the basis of tight binding models ([13,14]).

We present below an analysis of thermodynamic properties for a liquid binary alloy with a specific illustration on the Li - Pb alloy. The analysis uses the well known relationships between thermodynamic properties of the alloy and the ion-ion ([15,16]) and ion-electron ([17]) partial structure factors at long wavelengths. It is aimed at obtaining the Ornstein - Zernike effective interaction between fluctuations of concentration as a function of composition and at estimating from the data the amount of charge transfer between the components of the alloy.

2. - Effective interaction between concentration fluctuations.

The ion-ion partial structure factors are defined by

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + (n_\alpha n_\beta)^{1/2}\int dr\, [g_{\alpha\beta}(r) - 1] \exp(i\mathbf{k}.\mathbf{r}) \qquad (1)$$

where a Greek suffix denotes an ionic component of the alloy in concentration c_α and partial density $n_\alpha = c_\alpha n$, n is the total number density and $g_{\alpha\beta}(r)$ are the partial radial distribution functions. Inversion of the matrix of partial structure factors yields the Ornstein - Zernike direct correlation functions,

$$c_{\alpha\beta}(k) = \delta_{\alpha\beta} - S^{-1}_{\alpha\beta}(k) \quad . \qquad (2)$$

The Ornstein - Zernike functions expressing direct correlations between total number density and concentration fluctuations are constructed as

$$c_{NN}(k) = c_1c_{11}(k) + c_2c_{22}(k) + 2(c_1c_2)^{1/2}c_{12}(k) \quad , \qquad (3)$$

$$c_{cc}(k) = c_2c_{11}(k) + c_1c_{22}(k) - 2(c_1c_2)^{1/2}c_{12}(k) \qquad (4)$$

and

$$c_{Nc}(k) = c_{11}(k) - c_{22}(k) + (c_2 - c_1)(c_1c_2)^{-1/2}c_{12}(k) \quad . \qquad (5)$$

These definitions are analogous to those given by Bhatia and Thornton ([16]) for the density - concentration structure factors.

The Kirkwood-Buff relations ([15]) express the partial structure factors in the long wavelength limit $k \to 0$ through thermodynamic properties of the liquid alloy. These are the isothermal compressibility K_T, the composition dependence of the molar volume $V^{-1}(\partial V/\partial c_2)_{T,P,N}$ or equivalently the quantity $n(v_2 - v_1)$ where v_α is the partial molar volume of component α, and the activity coefficient $(\partial\mu_2/\partial c_2)_{T,P,N}$. From the Kirkwood-Buff relations it is easily found ([18]) that the Ornstein - Zernike functions for $k \to 0$ can be determined from the same thermodynamic quantities through the expressions

$$n\, k_B T\, K_T = (1 - c_{NN})^{-1} \quad , \qquad (6)$$

$$n\,(v_2 - v_1) = c_{Nc}\,(1 - c_{NN})^{-1} \qquad (7)$$

and

$$\left(\frac{\partial\mu_2}{\partial c_2}\right)_{T,P,N} = -\,c_1\,\frac{n\,(v_2 - v_1)^2}{K_T} + \frac{k_B T}{c_2}\,(1 - c_{cc}) \quad . \qquad (8)$$

In particular, it follows from eqn (8) that the concentration-concentration structure factor S_{cc} at long wavelength can be written as ([19])

$$S_{cc} = c_1 k_B T \left[\left(\frac{\partial\mu_2}{\partial c_2}\right)_{T,P,N}\right]^{-1} = \frac{c_1c_2}{1 - 2c_1c_2w/k_BT} \qquad (9)$$

where

$$w = \frac{n(v_2 - v_1)^2}{2K_T} + \frac{k_B T}{2c_1 c_2} c_{cc} \quad . \qquad (10)$$

Equation (10) gives an exact definition of the so-called "interchange free energy" entering approximate theories of concentration fluctuations in a binary alloy, such as the theories of regular or conformal solutions. The first term on the right-hand side of eqn (10) is the free energy change from the elastic strain associated with the interchange process. This contribution is intrinsically positive and favours phase separation. The second term, involving the direct correlations of concentration fluctuations, describes an effective interaction between them in the Ornstein - Zernike sense. It has been shown ([19]) that in Na - K alloys the two contributions to w cancel each other to a large extent, leaving a small positive residue of order $k_B T$.

In a chemically ordered alloy one expects w to be a strong function of composition, reaching large negative values in the region of stoichiometric composition where fluctuations in concentration are strongly suppressed. This is evident from the values of S_{cc} that have been obtained as a function of concentration from electromotive force measurements for instance in the Li - Pb system ([10]). Around stoichiometry S_{cc} shows a strong depression below the value $c_1 c_2$ appropriate to an ideal mixture.

Figure 1 reports c_{cc} as a function of composition in Li - Pb at 932 K. Use has been made of the ionic partial structure factors constructed for the alloy by Saboungi *et al.* ([10]) from electromotive force data in combination with compressibility and density data ([9]). To understand the origin of such strong attractive interactions between concentration fluctuations, we turn below to the ion-electron structure factors and to their interpretation in terms of electronic charge transfer.

3. - Ion-electron structure factors and charge transfer.

The ion-electron and electron-electron structure factors can be directly obtained from the ion-ion structure factors through the condition of perfect screening in the liquid metal alloy ([17]). With definitions similar to eqn (1) and denoting by the suffix e the electronic component, one has

$$S_{1e} = (n_1/n_e)^{1/2} z_1 S_{11} + (n_2/n_e)^{1/2} z_2 S_{12} \quad , \qquad (11)$$

$$S_{2e} = (n_2/n_e)^{1/2} z_2 S_{22} + (n_1/n_e)^{1/2} z_1 S_{12} \qquad (12)$$

and

$$S_{ee} = (n_1/n_e) z_1^2 S_{11} + 2(n_1 n_2/n_e^2)^{1/2} z_1 z_2 S_{12} + (n_2/n_e) z_2^2 S_{22} \quad . \qquad (13)$$

Here, z_α is the valence of the ionic component α in the alloy.

From eqns (11)-(13) and the data of Saboungi *et al.* ([10]) for the ion-ion structure factors, we show in Figure 2 the electronic structure factors in the Li - Pb alloy system at 932 K (with the choice $z_{Li} = 1$ and $z_{Pb} = 4$). Although there is appreciable scatter in the results, the general features of the redistribution of electronic charge density in the alloying process are clear. Very substantial electronic rearrangements accompany the addition of small quantities of Pb to molten Li, as electrons pile up on the Pb ions at the expense of the electron density on the Li ions. Consistently with this interpretation, the electron-electron structure factor closely follows the changes of the Pb-electron correlations with composition.

Tamaki *et al.* ([20]) have used the electron-ion structure factors in the Mg - Sn system for a phenomenological estimate of the charge transfer between the two components of the alloy. They questioned the applicability of their method to strongly compound-forming alloys, and indeed we have found that it is not useful in the present instance of the Li - Pb system. The specific assumption at fault is that the electron density attains its average value immediately outside the Wigner-Seitz sphere of an ion. With reasonable values of the Wigner-Seitz volumes, this assumption leads to the incorrect sign for the electronic charge transfer.

A crude estimate of the charge transfer from Li to Pb can nevertheless be obtained from the data in Figure 2. According to its definition, $S_{\alpha e}$ gives the average deviation of the number of pairs of α-type ions and electrons over a "macroscopic" volume from its uncorrelated value,

$$S_{\alpha e} = (n_\alpha n_e)^{1/2} \int [g_{\alpha e}(r) - 1] \, dr = \frac{\langle N_\alpha N_e \rangle - \langle N_\alpha \rangle \langle N_e \rangle}{(\langle N_\alpha \rangle \langle N_e \rangle)^{1/2}} \quad . \qquad (14)$$

For "macroscopic" volume in the present context one should understand a volume whose size is appreciably larger than the Wigner-Seitz radii (of order 2 Å).

We see from Figure 2 that S_{Pbe} reaches its largest value in the Li-rich region of the compo-

sition range ($S_{Pbe} \approx 1$ at $c_{Pb} = 0.1$), the corresponding value of $(n_e/n_{Pb})^{1/2}S_{Pbe}$ as $c_{Pb} \to 0$ being approximately + 4. Similarly, S_{Lie} reaches its extremal value in the Pb-rich region ($S_{Lie} \approx -0.2$ at $c_{Li} \approx 0.15$), the corresponding value of $(n_e/n_{Li})^{1/2}S_{Lie}$ as $c_{Li} \to 0$ being - 1 approximately. At such compositions the Pb (or Li) ions are in sufficiently small concentration that a "macroscopic" volume may still be taken to be available to each of them. The above values of the ion-electron structure factors then suggest that (i) a Pb impurity in Li metal retains a local excess of four valence electrons over the average, while a Li impurity in Pb metal loses one electron relative to the average; and (ii) the electron transfer at small but finite concentrations of solutes is of the order of one electron from Li to Pb. Values of such magnitude have been obtained in earlier theoretical estimates ([13,14]).

4. - Concluding remarks.

We have in the foregoing emphasized the information of microscopic import that can be obtained on a chemically ordering liquid metal alloy from thermodynamic data as functions of composition, giving an illustration for the Li - Pb system. Thermodynamic data yield the effective Ornstein - Zernike interactions between concentration fluctuations and give evidence for the electronic charge transfer from the electropositive to the electronegative component of the alloy. Electronic charge transfer cannot be uniquely defined, but may be sensibly estimated through a phenomenological interpretation of the ion-electron structure factors near the ends of the composition range.

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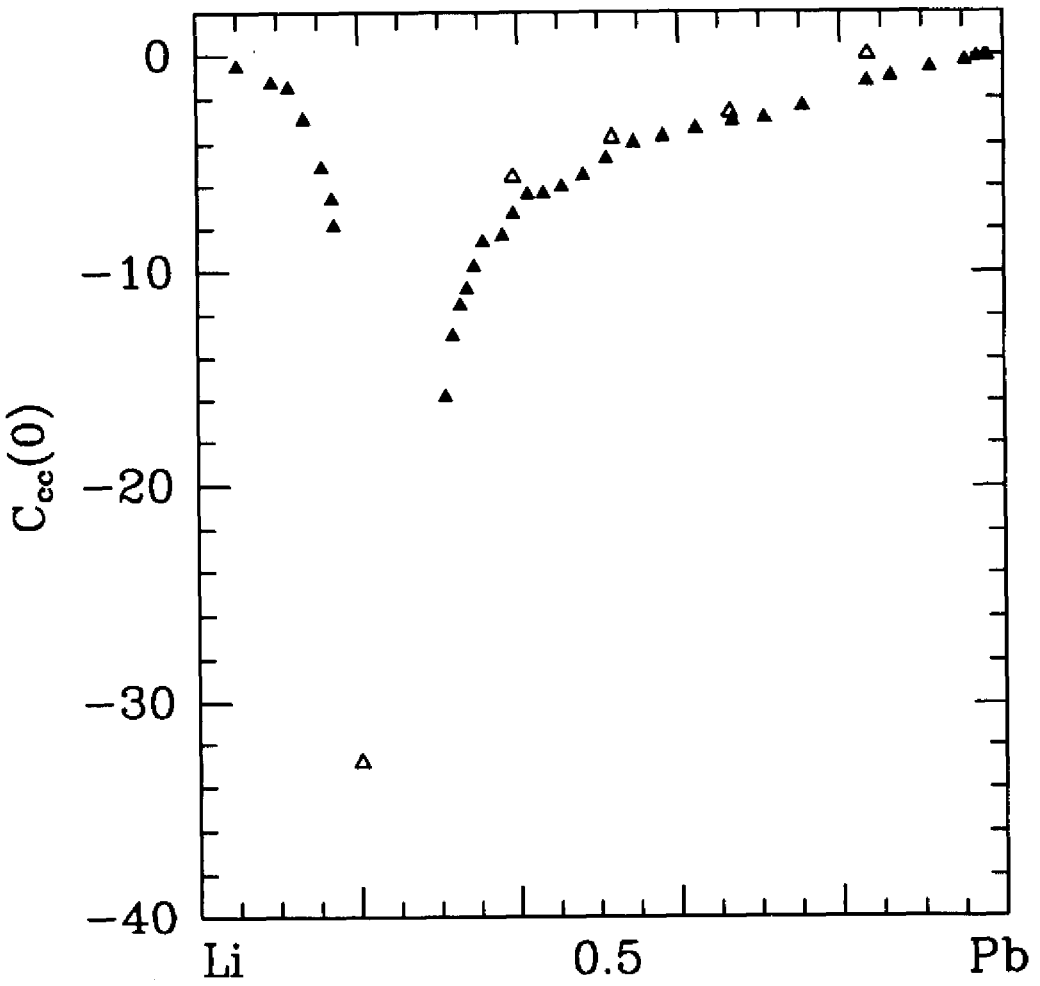
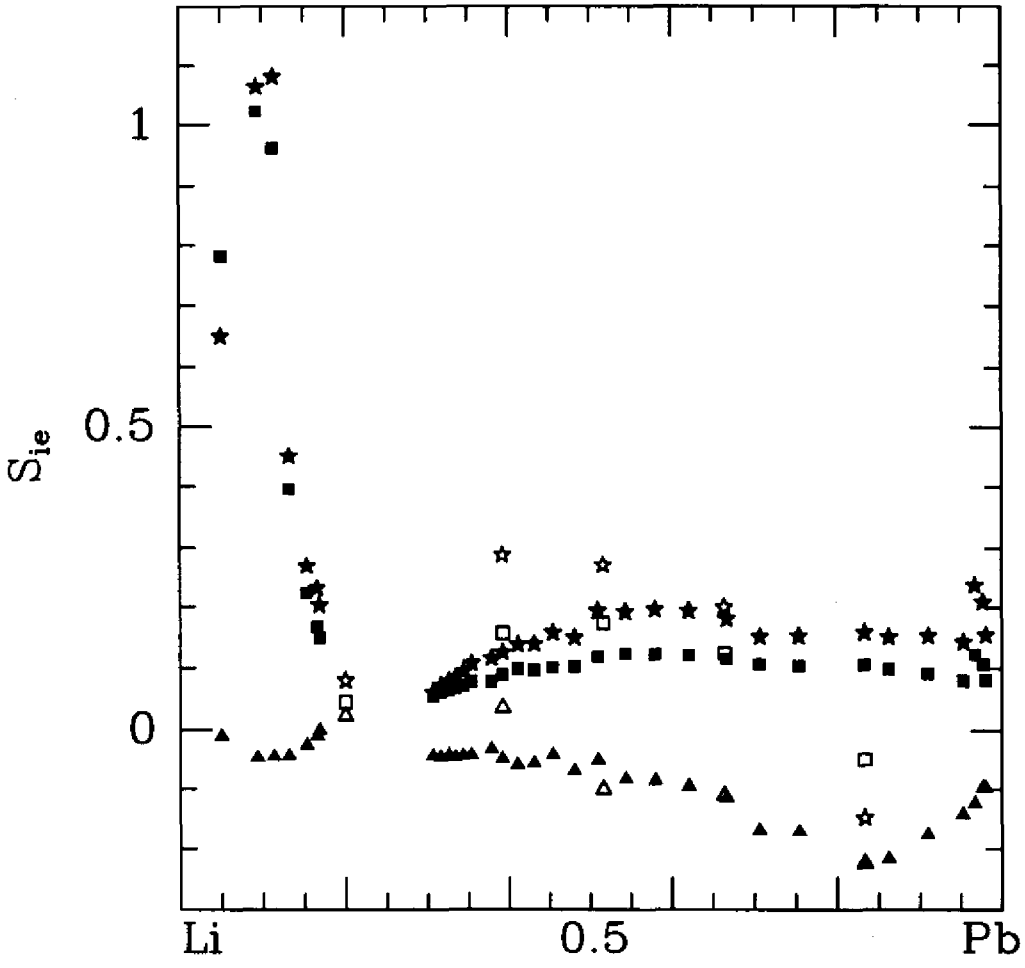
Figure captions

Figure 1. - Direct correlations between concentration fluctuations at long wavelength *versus* concentration in the Li - Pb system at 932 K. Filled triangles, from the partial ionic structure factors obtained from thermodynamic data by Saboungi *et al.* ([10]); empty triangles, from neutron diffraction data of Ruppersberg and Egger ([11]).

Figure 2. - Ion- electron and electron-electron structure factors at long wavelength *versus* concentration in the Li - Pb system at 932 K, from thermodynamic data (filled symbols) and from neutron diffraction data (empty symbols). Triangles: S_{Lie}; squares, S_{Pbe}; stars, S_{ee}.




1
0.5
0
S_{ie}
Li
0.5
Pb