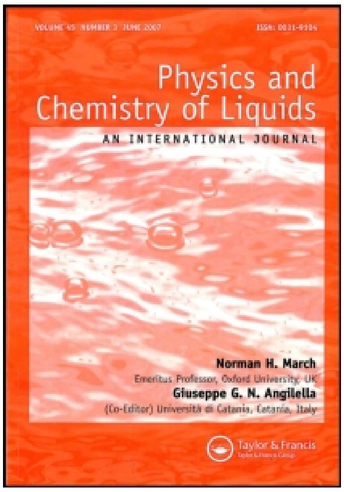

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CONFORMAL MIXTURES WITH CONCENTRATION-DEPENDENT INTERACTIONS; APPLICATION TO LIQUID Li–Mg

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The conformal model for binary liquids is extended to the case when the interaction energies are linear in the concentration, c. It is found that a suitably defined c-dependent ordering energy w is the single most important indication of the general character of the alloy, in particular of the behaviour of the excess free energy ΔF^{XS} and of the concentration fluctuation function S_{cc}. There are three cases:

I) w is of fixed sign and varies by less than a factor of 2. Then ΔF^{XS} and $S_{cc} - c(1 - c)$ both have opposite sign from w. The latter functions are largest (absolutely) in roughly the same region of c.

II) w changes sign. Then ΔF^{XS} and $S_{cc} - c(1 - c)$ are of opposite sign from w at each end of the diagram (much as one would expect on the basis of I).

III) w is of fixed sign but varies by more than a factor of 2. Then ΔF^{XS} is of opposite sign from w and $S_{cc} - c(1 - c)$ is mainly so. The latter function is, however, (marginally) of the same sign as w in a limited range of c at the end where w (and ΔF^{XS}) is absolutely smallest. The alloy system Li–Mg appears to be of this type.

KEY WORDS: Conformal solution theory, excess free energy, ordering energy.

1 INTRODUCTION

The conformal model[1] or the regular solution model in zeroth approximation,[2] was first applied to the thermodynamic description of binary liquid metal alloys by Bhatia and co-workers.[3–5] Thereby much valuable insight has been obtained and a central feature of this work was the postulation of a concentration independent ordering energy, the sign of which determined the system's general character (its tendency to phase separation or compound formation).

Unfortunately, the theory, as worked out as indicated above, is of limited applicability* because the use of a constant ordering energy leads to calculated thermodynamic data which are symmetrical about the equiatomic concentration. Measured data are, however, asymmetric in general, so quantitative success of the theory, in this simple form, is the exception rather than the rule.

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* We exclude from this work the generalisation of the theory that requires the postulation of chemical complexes[5].

When the atomic volumes of the components are very different, Bhatia and March[6] have shown that an early semi-empirical description due to Flory[8] can be successfully applied. The method has recently been placed on a more rigorous basis,[8,9] showing how the concentration dependence of the interaction constants, and therefore of the ordering energy, occurs through the variation in the mean atomic volume. In Cs–Na, for example, where the volume ratio is 3, the method works well.[6]

But there are asymmetric systems in which the specific volumes of the component fluids are very similar. Mg–Li is one such case; at 1000 K (the temperature at which this system is studied below), the specific volume ratio is 1.05 and, furthermore, there is little variation of the mean volume per atom across the whole composition diagram.[10] For such systems we need a new mechanism.

In the following work, we assume that a concentration dependence in the interaction constants arises from the variation in the density of the ambient free electron gas, this being entirely understandable on the basis of pseudopotential theory. For example, in the above Mg–Li case, although the atomic number density changes little across the composition diagram, the valence electron density varies by a factor of about 2. Such a mechanism was suggested by Bhatia[5] but, as far as we know, it has not hitherto been pursued.

2 GENERAL DEFINITIONS

Consider a mixture of $c_1N = cN$ atoms of type 1 and $c_2N = (1 - c)N$ atoms of type 2. If F is the Helmholtz free energy, the free energy of mixing is

$$\Delta F = F - c_1F(c_1 = 1) - c_2F(c_2 = 1) \tag{1}$$

But for the ideal case (randomly distributed non-interacting particles on a lattice), the free energy of mixing is $-TS_c$, where S_c is the ideal entropy expression†

$$S_c = -k_B(c_1 \ln c_1 + c_2 \ln c_2) \tag{2}$$

Therefore, relative to this system, the excess free energy of mixing[11] is

$$\Delta F^{XS} = \Delta F + TS_c \tag{3}$$

Likewise, if $S = -(\partial F/\partial T)_\Omega$ is the entropy,

$$\Delta S = S - c_1S(c_1 = 1) - c_2S(c_2 = 1) \tag{4}$$

and the excess entropy of mixing[11] is

$$\Delta S^{XS} = \Delta S - S_c \tag{5}$$

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† Per atom, here and for all other extensive thermodynamic quantities in this paper.

The Bhatia–Thornton[3] concentration fluctuation function $S_{cc} = k_B T/(\partial^2 G/\partial c^2)_{T,N}$ is also an object of prime interest.‡ The ideal value of this is $c_1 c_2$ and, in the following, it will be convenient to focus on the quantity

$$D \equiv [S_{cc}^{-1} - (c_1 c_2)^{-1}] k_B T, \tag{6}$$

which is closely related to the Darken[12] stability function $(\partial^2 G/\partial c^2)_{T,N}$. In fact D, as defined here, is the excess Darken stability function relative to the ideal value. By Eqs. (1)–(3), we have‡

$$D = (\partial^2 \Delta F^{XS}/\partial c^2)_{T,N} \tag{7}$$

The physical meaning of S_{cc} and D is as follows. If $S_{cc} > c_1 c_2$, i.e. $D < 0$, we have enhanced concentration fluctuations relative to the ideal description and we can define this as a phase separating tendency. On the other hand, if $S_{cc} < c_1 c_2$, i.e. $D > 0$, we have suppressed fluctuations and this can be defined as a compound forming tendency.

3 BHATIA MODEL

In this section, we briefly review those parts of the conformal model, as used by Bhatia and coworkers[3–5], that we will find of subsequent use.

For simplicity, we adhere to the static lattice model§ introduced above, in which the volume Ω is assumed to be independent of concentration. Then the free energy is postulated to be

$$F = E_c - TS_c, \tag{8}$$

where S_c is as in (2) and

$$E_c = \tfrac{1}{2}(c_1^2 W_{11} + 2c_1 c_2 W_{12} + c_2^2 W_{22}) \tag{9}$$

The quantity $W_{ij}(= W_{ji})$ is such that $c_j W_{ij}$ is the average interaction energy of an i-type atom with the totality of surrounding atoms of j-type.

Despite the external form of (8), S_c and E_c are not to be regarded as the entropy and internal energy respectively. For, to assume this would be contradictory (for unequal W_{ij}), because the interactions produce some degree of order not reflected in

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‡ Because Ω and P are constant, as c varies, the Helmholtz free energy F can replace the Gibbs free energy G, without approximation, in the calculation of S_{cc}. Furthermore, because P is so small (1 atm.), calculated F's can be compared with measured G's with negligible approximation.

§ For fluids, gas kinetic terms can be included in the absolute expressions, but these cancel in the excess quantities. This cancellation is exact under the assumption of this paper that the alloy volume is independent of c.

the random configuration corresponding to the ideal entropy expression S_c. Rather, we must regard S_c and E_c as the leading terms of the true expressions, the missing parts of which can be described through the T-dependence of the W_{ij}. In this way, explicit forms for the entropy $S = -(\partial F/\partial T)_\Omega$ and the internal energy $E = F + TS$ are found from (8) to be[13]

$$S = S_c - (\partial E_c/\partial T)_\Omega \tag{10}$$

and

$$E = E_c - T(\partial E_c/\partial T)_\Omega \tag{11}$$

Because only two of F, E and S are independent we will, in the later sections, focus on the free energy and entropy only.

Finally, within the general context of this section, let us introduce an ordering energy, defined by

$$W = W_{11} - 2W_{12} + W_{22} \tag{12}$$

This quantity is a measure of the degree of homo- or heterocoordination in the system and it could have suggested itself, a priori, as an alternative candidate to (6) for quantitatively defining a phase separating or compound forming tendency. To see this more precisely, note that (9) can be rewritten

$$E_c = -\tfrac{1}{2}c_1c_2W + \tfrac{1}{2}(c_1W_{11} + c_2W_{22}) \tag{13}$$

For fixed W_{11} and W_{22}, the effect of $W < 0$ is to raise E_c and, therefore, the free energy (8), while $W > 0$ lowers E_c and (8).

In the elementary form of the theory, when the W_{ij} are independent of c, it turns out (as can be seen by specialising the theory of the following section) that

$$D = W \qquad (\textit{c-independent case}) \tag{14}$$

and the two indicators (Eq. (6) and (12)) are effectively equivalent. But under any other circumstances (in particular, those below) this identity disappears and the relationship of W to our basic index (6) requires clarification.

4 CONCENTRATION-DEPENDENT INTERACTIONS

In earlier work, the interaction energies were assumed to be independent of concentration. Now, in the present paper, we suppose they are linear. This is the simplest generalisation. It keeps the number of disposable constants to a minimum and yields formulae which are elementary enough to yield some general insight as well as, on occasion, to provide a semi-quantitative description.

Accordingly, we write

$$W_{ij} = c_1 W_{ij}^1 + c_2 W_{ij}^2 \tag{15}$$

where W_{ij}^k is the (i, j)th interaction parameter in a medium of k-type atoms. (Here, of course, $k = i$ or j or both). Under such circumstances, the ordering energy (12) in the alloy becomes

$$W = c_1 W^1 + c_2 W^2 \tag{16}$$

where

$$W^k = W_{11}^k - 2W_{12}^k + W_{22}^k \tag{17}$$

is the ordering energy in medium k.

Substitution of (8) into Eqs. (1) and (3) gives

$$\Delta F^{XS} = -\tfrac{1}{2} c_1 c_2 f \tag{18}$$

where

$$f = \tfrac{1}{2}(W^1 + W^2) - W_0 + (W^1 - W^2)(c - \tfrac{1}{2}) \tag{19}$$

and

$$W_0 = W_{11}^2 + W_{22}^1 - W_{11}^1 - W_{22}^2 \tag{20}$$

Note that the latter expression does not depend on the unlike interactions. Eq. (18) can now be used to evaluate other thermodynamic quantities; using (5), we have

$$\Delta S^{XS} = \tfrac{1}{2} c_1 c_2 (\partial f / \partial T)_\Omega \tag{21}$$

and (7) becomes

$$D = \tfrac{1}{2}(W^1 + W^2) - W_0 + 3(W^1 - W^2)(c - \tfrac{1}{2}) \tag{22}$$

If $W_{ij}^1 = W_{ij}^2 = W_{ij}$, independent of c, then $W^1 = W^2 = W$, also independent of c and, furthermore, $W_0 = 0$. Thus (22) reduces to the simple result (14), indicated at the end of the previous section. Generally, however, $W_{ij}^1 \neq W_{ij}^2$ and $W^1 \neq W^2$ and, for this case, the role of the ordering energy in (22) needs to be investigated.

First note, from Eqs. (19) and (22) respectively, that the asymmetries of ΔF^{XS} and S_{cc} are governed by $dW/dc = W^1 - W^2 \equiv \Delta W$, the variation of ordering energy with concentration. Now, the signs of ΔF^{XS} and D might change but, in each case, this can happen at most once.

The matter can be pursued further by referring the ordering energy to a new zero.

We do this by writing

$$w^k = W^k - W_0 \tag{23}$$

so that the new ordering energy, to replace (16), is

$$w \equiv c_1 w^1 + c_2 w^2 = W - W_0 \tag{24}$$

It is also convenient to introduce the mean value

$$\bar{w} = \tfrac{1}{2}(w^1 + w^2) \tag{25}$$

and the variation with concentration

$$dw/dc = w^1 - w^2 \equiv \Delta w \tag{26}$$

Observe (for analysis below of Cases I–III) that

$$\frac{w^2}{w^1} = \frac{2 - (\Delta w/\bar{w})}{2 + (\Delta w/\bar{w})} \tag{27}$$

In terms of these quantities, expression (19), describing ΔF^{XS}, becomes

$$f = \bar{w} + \Delta w(c - \tfrac{1}{2}) \tag{28}$$

and (22) can be rewritten

$$D = \bar{w} + 3\Delta\omega(c - \tfrac{1}{2}) \tag{29}$$

Examination of Eqs. (28) and (29) shows that there are three distinct cases:

Case I $|\Delta w/\bar{w}| < \frac{2}{3}$. Here, w^1 and w^2 are of the same sign and differ by less than a factor of 2. Then ΔF^{XS} and D are nodeless and $f < 0$ ($\Delta F^{XS} > 0$) implies $D < 0$ ($S_{cc} > c_1c_2$), while $f > 0$ ($\Delta F^{XS} < 0$) implies $D > 0$ ($S_{cc} < c_1c_2$). There is a clear similarity with the earlier result for c-independent ordering energies. Curves I(a) and I(b) of Figure 1 illustrate the effect.

Case II $|\Delta w/\bar{w}| > 2$. Here, w^1 and w^2 have opposite signs. Then each of ΔF^{XS} and D has a node. In general, these occur at different concentrations so no longer, for a given c, are the signs of ΔF^{XS} and D invariably opposite. However, the nodes occur in the same half of the composition range, and the end that corresponds to $f < 0$ ($\Delta F^{XS} > 0$) also corresponds to $D < 0$ ($S_{cc} > c_1c_2$) and, similarly, the end at which $f > 0$ ($\Delta F^{XS} < 0$) is also that at which $D > 0$($S_{cc} < c_1c_2$). This is also, in large measure, what our intuition, based on earlier experience might suggest. Curves II in Figure 1 provide an illustration.

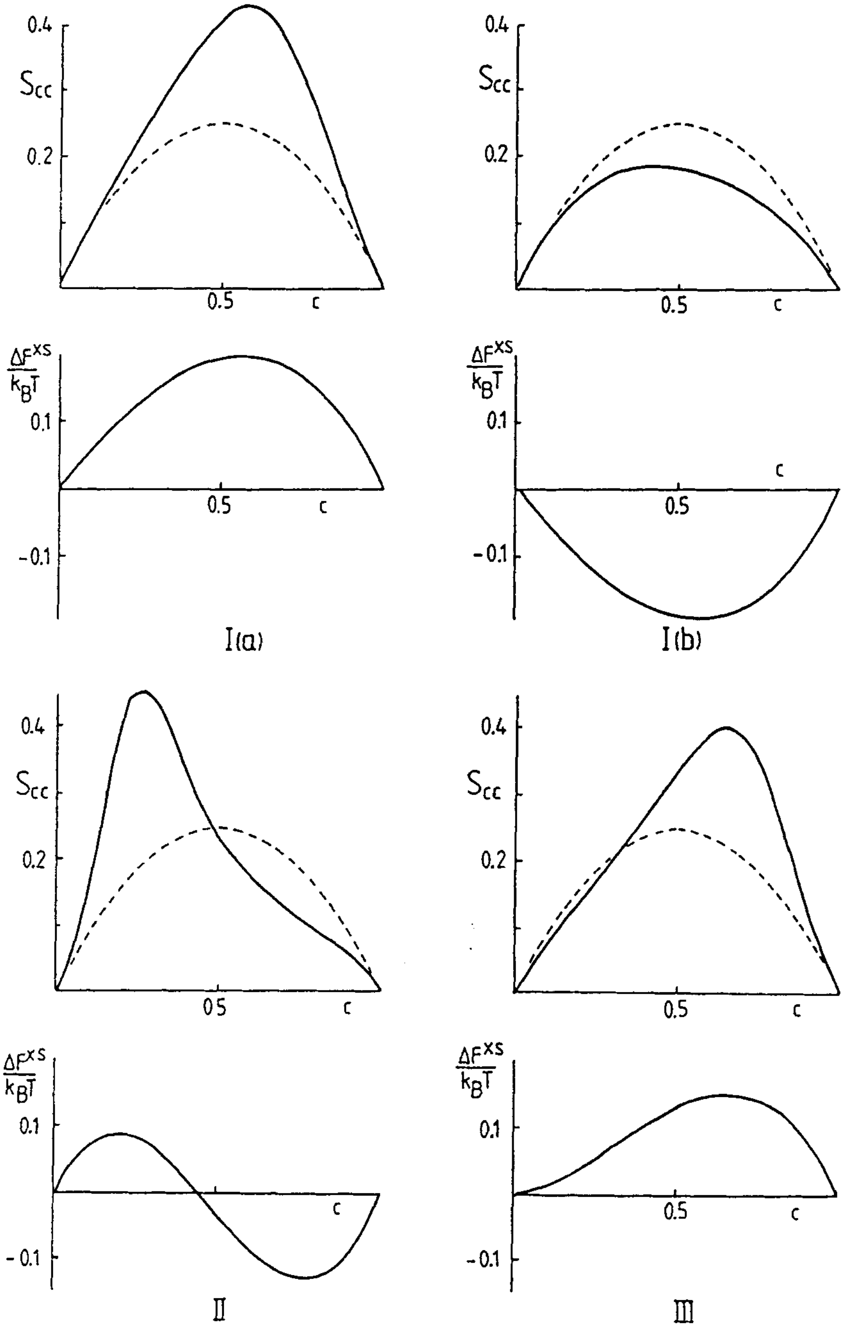

Figure 1 $\Delta F^{XS}/k_BT$, as given by Eqs. (18) and (28), and S_{cc}, as given by Eqs. (6) and (29). These curves illustrate the general cases I–III specified in the text. *Case I(a)*: $(w^1, w^2)/k_BT = (-2.0, -1.1)$; $\Delta w/\bar{w} = 0.58$. *Case I(b)*; $(w^1, w^2)/k_BT = (2.0, 1.1)$; $\Delta w/\bar{w} = 0.58$. *Case II*; $(w^1, w^2)/k_BT = (2.5, -2.0)$; $\Delta w/\bar{w} = 18.0$. *Case III*; $(w^1, w^2)/k_BT = (-2.0, -0.1)$; $\Delta w/\bar{w} = 1.81$.

Case III $\frac{2}{3} < |\Delta w/\bar{w}| < 2$ (the intermediate case). Here, w^1 and w^2 are of the same sign and differ by more than a factor of 2. Then D has a node but ΔF^{XS} does not. This is not so intuitively obvious on the basis of our past experience. Curves III of Figure 1 show such a case, in which both w^1 and w^2 are negative. Despite a wholly positive ΔF^{XS}, there is a portion of S_{cc} marginally below the ideal value. Likewise, if we choose w^1 and w^2 both suitably positive, we obtain a wholly negative ΔF^{XS} with a portion of S_{cc} marginally above the ideal value. A physical example of the latter type is given next.

5 THE CASE OF Li–Mg

$Mg_{c_1}Li_{c_2}$, at $T = 1000$ K, illustrates the new case III. If we choose $(w^1, w^2) = (2.4, 6.0)k_BT \equiv (2400, 6000)$K and use Eqs. (18) and (28) for ΔF^{XS} and Eqs. (6) and (29) for S_{cc}, we calculate the results shown in Figure 2. These reproduce rather well the

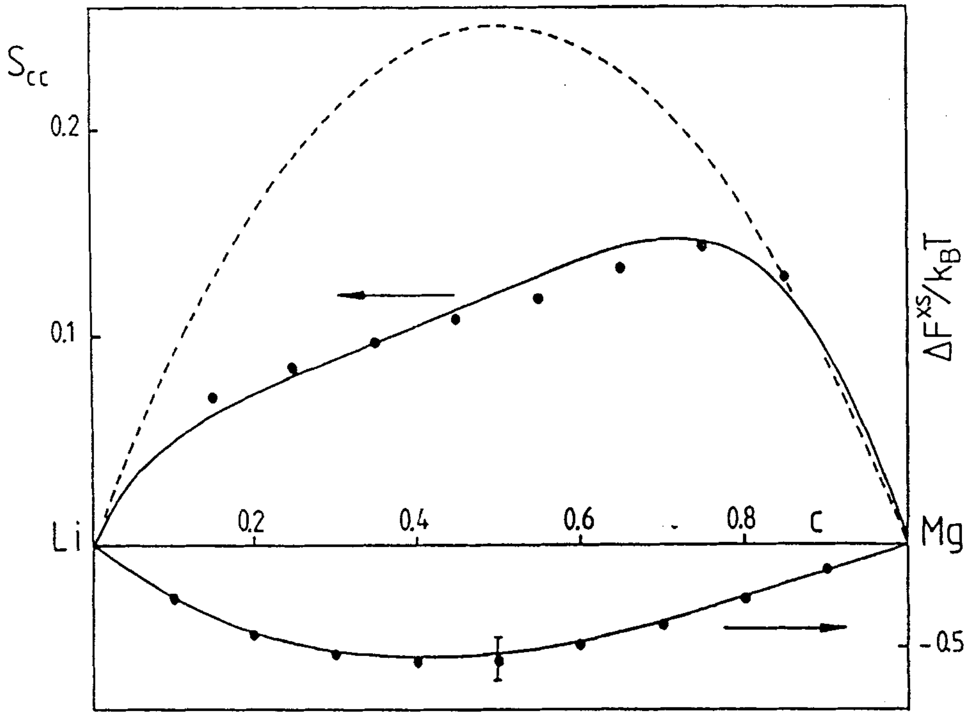

Figure 2 Excess free energy, ΔF^{XS}, and concentration fluctuation function, S_{cc}, for Li–Mg at 1000 K. Experimental data (points) from ¶ Hultgren *et al.*[11], while the theory (lines) is based on Eqs. (18) and (28), for ΔF^{XS}, and Eqs. (6) and (29) for S_{cc}, with w^1 (for Mg) $= 2.4k_BT = 2400k_B$ and w^2 (for Li) $= 6.0\,k_BT = 6000k_B$.

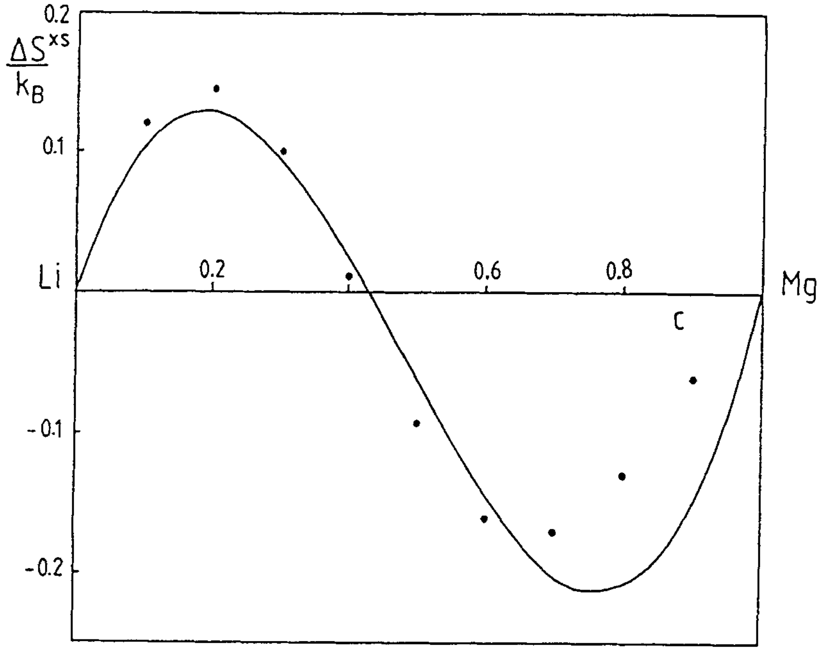

Figure 3 Excess entropy, ΔS^{XS}, for Li–Mg at 1000 K. Experimental data (points) are taken from Hultgren *et al.*[11], who specify the error at $c=0.5$ to be given by $(0.09 \pm 0.3)k_B$—too large to be recorded conveniently on the figure. The theoretical results (lines) follow from Eqs. (21) and (28) with $(\partial w^1/\partial T)_\Omega = -4k_B$, $(\partial w^2/\partial T)_\Omega = 3k_B$.

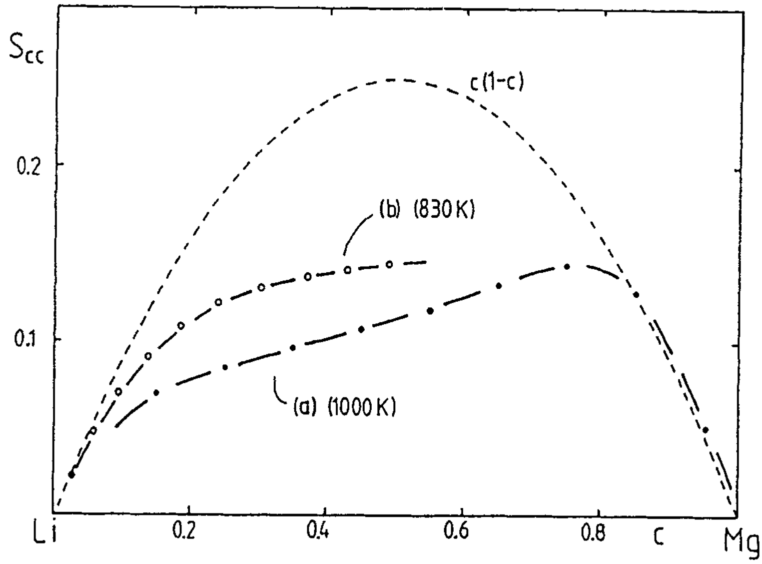

Figure 4 Experimental S_{cc} data for Li–Mg: (a) from Hultgren *et al.*[11] at 1000 K (same as in Figure 2), (b) from Saboungi and Blander[13] at 830 K.¶ The results (b) agree well with the neutron diffraction results of Ruppersberg *et al.*[10] for the particular case $c = 0.3$.

experimental data obtained from ¶ the compilation of Hultgren *et al.*[11] Although the effect is small, both the experimental and theoretical results for S_{cc} exceed the ideal values at sufficiently high Mg concentration (from about $c_1 = 0.85$ upwards).

It should also be noted that Eqs. (21) and (28) provide a theoretical expression for the corresponding excess entropy of mixing. By choosing $(\partial(w^1, w^2)/\partial T)_\Omega = (-4, 3)k_B$, the experimental results can be qualitatively described. The quantitative comparison leaves room for improvement, although it should be noted that the errors quoted for the measured data are large ($\Delta S^{XS}/k_B = 0.09 \pm 0.3$ at $c = 0.5$).

To conclude this section, it should be mentioned that some activity measurements over incomplete ranges of concentrations have been made on this alloy system by Saboungi and Blander[14], and S_{cc} inferred for $0 < c < 0.55$ at $T = 830$ K. This result is shown in Figure 4 and it agrees, for the particular alloy $Mg_{0.3}Li_{0.7}$, with the neutron diffraction results of Ruppersberg *et al.*[10] It will be seen that, although there is a suggestion of qualitative agreement with the earlier curve in shape, there is a basic incompatibility, because the higher temperature results should be nearer to the ideal. Application of our theoretical description to the Saboungi-Blander curve segment suggests that in this case the mean ordering energy $\bar{w}$ is equivalent to about 2400 K (compared with the previous 4200 K). There are insufficient data to obtain a value for Δw but this too is likely to be smaller than before.

6 SUMMARY AND CONCLUSIONS

We have generalised the conformal model to the case of interactions linear in the concentration and find that, as before, the ordering energy is a central concept. This ordering energy w, however, has a suitably redefined zero. There are three cases:

Case I w is of fixed sign and weakly varying (by less than a factor of 2). If $w < 0$, we get the types of results shown in Figure 1, I(a): $\Delta F^{XS} > 0$, $S_{cc} > c_1c_2$ and ΔF^{XS} and $S_{cc} - c_1c_2$ maximise in roughly the same region. If $w > 0$, we get the types shown in Figure 1, I(b); $\Delta F^{XS} < 0$, $S_{cc} < c_1c_2$ and ΔF^{XS} and $S_{cc} - c_1c_2$ minimise in roughly the same region.

Case II w changes sign. Then results of the type shown in Figure 1, II are obtained. Towards the end where $w < 0$, we find $\Delta F^{XS} > 0$, $S_{cc} > c_1c_2$ and towards the end where $w > 0$, we find $\Delta F^{XS} < 0$, $S_{cc} < c_1c_2$. This is much as one would intuitively expect from the case I results.

Case III w is of fixed sign but strongly varying (by more than a factor of 2). If $w < 0$, we get the type of results shown in Figure 1, III. There, $\Delta F^{XS} > 0$ everywhere, but $S_{cc} - c_1c_2$ changes sign. In the part of the composition diagram where w is most negative, ΔF^{XS} maximises and $S_{cc} - c_1c_2 > 0$. At the other end of the diagram, $S_{cc} - c_1c_2$ is marginally negative. On the other hand, if $w > 0$, we get the type of

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¶ (To obtain S_{cc}, we take a numerical derivative with respect to concentration of the activities quoted.

results shown for Li–Mg in Figure 2. There, $\Delta F^{XS} < 0$ everywhere, but $S_{cc} - c_1c_2$ changes sign. In the region where w is most positive, ΔF^{XS} minimises and $S_{cc} - c_1c_2 < 0$. At the other end of the diagram, $S_{cc} - c_1c_2$ is marginally positive.

The theory propounded here is of rather restricted applicability in that the specific volume per atom is supposed not to vary significantly with concentration. Nevertheless, the importance of concentration-dependent interactions would appear to be demonstrated. On the other hand, the theory of Bhatia and March allows for changes in specific volume but not (otherwise) in the interactions. The next step, which we hope to undertake, is to combine these two approaches. If this is done, we should obtain a rather general description with wide applicability.

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