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Metal–non-metal transition in liquid alloys with polyvalent components

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Abstract. The metal–non-metal transitions that occur in certain alloy systems as a function of concentration have been investigated in three alloys that have polyvalent components, using a calculational model that was applied previously to the gold–alkali alloys. The important elements of the model, charge transfer and local chemical order, are treated self-consistently and the equilibrium state of the system is found by minimising the free energy. It is found that the transitions predicted by the model agree well with a variety of experimental results. The Cs–Sb and Na–Sb systems are found to have a high degree of local chemical order and a charge transfer of about 2.5 electrons per atom in the concentration region near stoichiometry where the transitions occur. At other concentrations the alloys are found to be random and the charge transfer drops to about 1/4 electron per atom. For the Li–Pb system, which is known to remain metallic for all concentrations, an intermediate degree of local order and a charge transfer of about 1.5 electrons per atom appear to be consistent with experimental results in the concentration region near stoichiometry. Differences between these alloys and the gold–alkali systems are discussed.

1. Introduction

A number of liquid alloy systems are known that exhibit metal–non-metal transitions as a function of concentration. Among these the group of alloys that are formed from two metallic components is characterised by the following: the transition from metallic to non-metallic and back to metallic occurs in a narrow concentration region near a stoichiometric composition, and a large charge transfer and local ordering occur throughout this same concentration region. One of these systems that has received considerable attention, both experimental and theoretical, is caesium–gold. As a result of these studies it is generally accepted that, near stoichiometry, Cs–Au is a highly ionic liquid with properties very similar to those of molten salts.

Recently reported experimental results have shown that alloys of alkali metals with polyvalent metals, such as Sb, Pb or Bi, have electronic properties which are qualitatively different from Cs–Au. In order to gain insight into the nature of the metal–non-metal transition in these materials, we have applied a calculational technique similar to that reported in Franz *et al* (1980). We have chosen Cs–Sb, Na–Sb and Li–Pb as prototype systems, because a wide variety of experimental results are available for these systems. In this paper we compare our results to some of the experimental results and discuss the similarities and differences between our results for these alloys and those for Cs–Au.

2. Calculation model

The calculation makes use of a tight-binding, Green function technique, applied to the Cayley tree approximation, and is quite similar to that used in Franz *et al* (1980) and Holzhey *et al* (1981), which will be referred to as I and II. As before, we consider an alloy $A_x B_{1-x}$ and write:

$$G_{ii} = x G_{ii}^A + (1 - x) G_{ii}^B \qquad (1)$$

where

$$G_{ii}^A(\varepsilon) = (\varepsilon - \varepsilon_A - \Delta_A)^{-1} \qquad G_{ii}^B(\varepsilon) = (\varepsilon - \varepsilon_B - \Delta_B)^{-1} \qquad (2)$$

are the two partial Green functions corresponding to either an A atom or B atom occupying the site *i*. Δ_A and Δ_B are self-energies and ε_A and ε_B are atomic energy levels chosen so that their difference, $\varepsilon_B - \varepsilon_A$, is scaled to the electronegativity difference between the metals.

In contrast to the previous work, however, there now exists an asymmetry between the two energy bands that did not occur when both bands were taken to be pure s bands. In this work the polyvalent band (A band) is taken to be an s–p band with eight states per atom, $N_A = 8$, while the alkali band (B band) remains an s band with $N_B = 2$. The increased number of orbitals per A atom must be accounted for since an electron can hop into any of these orbitals, which increases the ratio of hopping amplitudes to an A atom by a factor of 8/2. The expressions for Δ_A and Δ_B thus become:

$$\Delta_A = 4Z_{AA}t_{AA}^2/(\varepsilon - \varepsilon_A - \Delta_A^A) + Z_{AB}t_{AB}^2/(\varepsilon - \varepsilon_B - \Delta_B^A)$$
$$\Delta_B = Z_{BB}t_{BB}^2/(\varepsilon - \varepsilon_B - \Delta_B^B) + 4Z_{BA}t_{AB}^2/(\varepsilon - \varepsilon_A - \Delta_A^B) \qquad (3)$$

where the Z_{AB} is the number of B atoms surrounding an A atom, the self-energies Δ_A^B are defined as in I, and the *t* are the hopping parameters, with t_{AA} and t_{BB} chosen so that pure materials have the appropriate band widths (see §3).

The degree of local chemical order is introduced as in I by means of a short-range order parameter, σ_{sr}, which determines the probabilities for the various nearest-neighbour pairs. In terms of σ_{sr}:

$$Z_{AA} = [x + (1 - x)\sigma_{sr}]Z \qquad Z_{AB} = [(1 - x)(1 - \sigma_{sr})]Z \qquad (4)$$

where Z is the average number of nearest neighbours and is taken to be ten. The range of possible values of σ_{sr} is

$$\begin{aligned} -x/(1 - x) \leqslant \sigma_{sr} \leqslant 0 & \qquad \text{for } x \leqslant 1/2 \\ -(1 - x)/x \leqslant \sigma_{sr} \leqslant 0 & \qquad \text{for } x \geqslant 1/2 \end{aligned} \qquad (5)$$

where the lower limit corresponds to the maximum possible order for a given concentration and the upper limit, zero, indicates a random distribution.

Charge transfer is expected to be large in the alloy systems under consideration, so that it is necessary to correct both the atomic energy levels, ε_A and ε_B, and also the internal energy, E, to take account of it. As in I the energy shift $\Delta\varepsilon_A = \varepsilon_A - \varepsilon_A^0$ is written:

$$\Delta\varepsilon_A(x,\sigma_{sr}) = [(N_A - 1)/N]\delta n_A(x,\sigma_{sr})U + Z_{AA}(x,\sigma_{sr})\delta n_A(x,\sigma_{sr})V + Z_{AB}(x,\sigma_{sr})\delta n_B(x,\sigma_{sr})V \qquad (6)$$

where $\delta n_{A(B)}$ is the average charge transfer on an A(B) atom and U and V are parameters giving the size of the intra- and inter-atomic parts of the Coulomb interaction.

The charge on an ion is calculated self-consistently from the density of states, $g(\varepsilon)$:

$$g_{A(B)}(\varepsilon) = -(1/\pi)N_{A(B)} \operatorname{Im} G_{ii}^{A(B)}(\varepsilon + i\eta) \qquad \eta \to 0 \qquad (7)$$

$$n_{A(B)} = \int_{-\infty}^{E_F} g_{A(B)}(\varepsilon)\,d\varepsilon. \qquad (8)$$

E_F is determined from charge conservation as in I. Then $\delta n_{A(B)} = n_{A(B)} - n_{A(B)}^0$, where $n_{A(B)}^0$ is the number of valence electrons per atom in the pure metal.

The internal energy is written

$$E(x,\sigma_{sr}) = E_{HF}(x,\sigma_{sr}) - E_{el}^{intra}(x,\sigma_{sr}) + [E_{ion}^{inter}(x,\sigma_{sr}) - E_{el}^{inter}(x,\sigma_{sr})] \qquad (9)$$

where the first two terms are the Hartree–Fock energy and the correction to it from the intra-atomic Coulomb interactions and are identical to those in I. The last two terms are corrections due to the inter-atomic Coulomb interactions. Because the A atoms have an s–p valence band rather than an s band these corrections are somewhat different from those in I so we write them in their entirety here:

$$E_{ion}^{inter} - E_{el}^{inter} = \tfrac{1}{2}V\{xZ_{AA}(2n_A^0\delta n_A + \delta n_A^2) + (1-x)Z_{BB}(2n_B^0\delta n_B + \delta n_B^2)$$

$$+ [xZ_{AB} + (1-x)Z_{BA}](n_A^0\delta n_B + \delta n_A\,\delta n_B + n_B^0\delta n_A)\}. \qquad (10)$$

As in I and II, the degree of local order at each concentration is determined by finding the value of σ_{sr} that minimises the free energy, $F = E - TS$. The entropy, S, is calculated in the pair approximation as in I and II.

3. Choice of parameters

The parameters used in the calculations reported here are given in table 1. As in II, the hopping parameters, t_{AA} and t_{BB}, are chosen so that the Cayley tree half-band width in the pure metal reproduces the free-electron Fermi energy of a half-filled band. This is calculated using the experimentally measured density for the temperature for which the calculations are performed, in this case $T = 1000$ K. The hopping parameter, t_{AB}, is adjusted to include the known volume contraction of the alloys as in I and II. The

Table 1. Model parameters for the $A_x B_{1-x}$ alloys. The subscript A refers to the polyvalent atoms and B refers to the alkali atoms.

| Parameter (units)	Cs–Sb	Na–Sb	Li–Pb
t_{AA} (Ryd)	0.057	0.057	0.055
t_{BB} (Ryd)	0.017	0.035	0.045
t_{AB} (Ryd)	0.036	0.052	0.055
Electronegativity difference	1.3	1.2	0.85
$\varepsilon_B - \varepsilon_A$ (Ryd)	0.17	0.16	0.11
n_A^0	5	5	4
n_B^0	1	1	1
U (Ryd)	0.15	0.15	0.15
V/U (Ryd)	0.4	0.4	0.4
T (K)	1000	1000	1000

energy difference $\varepsilon_B - \varepsilon_A$ is scaled to the electronegativity difference of the two metals, using the Pauling scale.

The intra-atomic Coulomb interaction parameter, U, was chosen to be in agreement with generally accepted estimates of its size. The ratio of V, the inter-atomic Coulomb interaction parameter, to U, V/U, is the one adjustable parameter in the calculation, and although it was taken to be the same for the three alloy systems, the specific value was chosen so that the calculated results would best agree with the full range of experimental measurements that have been reported. The value chosen, $V/U = 0.4$, is larger than that used in I for the Cs–Au system, but smaller than the theoretical estimate given by Giner *et al* (1976). The effect of this parameter on the calculations will be discussed further in §4.

4. Numerical results

4.1 Cs–Sb

Figure 1 shows the calculated free energy as a function of local order for Cs–Sb for various Cs-rich concentrations. It can be seen that in a concentration region surrounding $x = 0.25$, which corresponds to the stoichiometric concentration for the compound Cs_3Sb, the system will be highly ordered, whereas for higher antimony concentrations the system will become random. At low Sb concentrations the system also tends to become random but the differences in free energy between random and ordered shrinks as the alkali concentration decreases. Figure 2 shows the value of the short-range order parameter that minimises the free energy as a function of concentration. The broken curve indicates regions in which the free energy does not have a
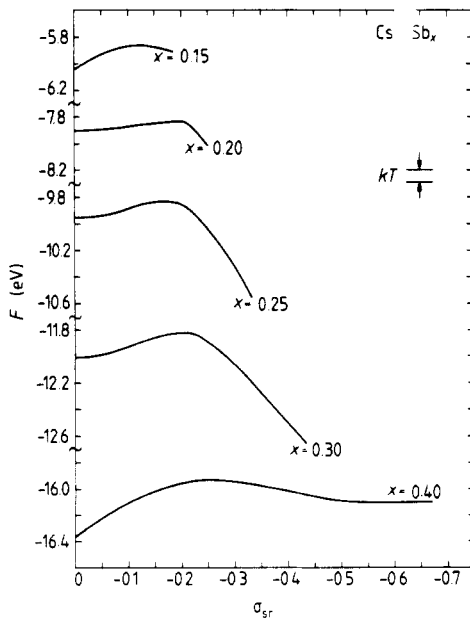
Figure 1. Free energy as a function of local order parameter for various Sb concentrations, x, in the Cs–Sb alloy system. For each concentration the maximum local order occurs for a value $\sigma_{sr} = -x/(1-x)$.
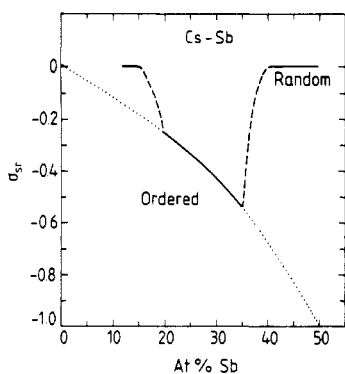
Figure 2. Local order parameter that minimises the free energy as a function of Sb concentration. The full curves indicate regions where a definite minimum exists in the free energy. The broken curves show a possible way of interpolating between these regions. The dotted curve indicates values of σ_{sr} for maximum local order.
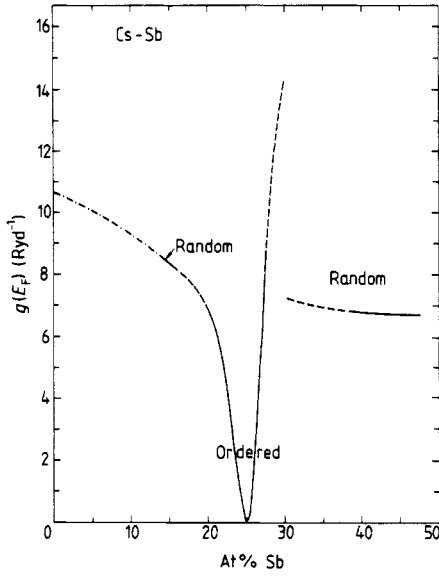
unique minimum; in these regions the free energy versus σ_{sr} curves have minimum values at both $|\sigma_{sr}|_{max}$ and $\sigma_{sr} = 0$, and they lie within kT of each other.

Several observations can be made from these results. First, they are qualitatively different from equivalent calculations in Cs–Au. For all concentrations of the Cs–Au system the graphs of the free energy as a function of σ_{sr} had a single minimum that lay between the extreme values of σ_{sr}; they were more similar to the inverse of those for Cs–Sb. Second, in the concentration regions where the Cs–Sb system is crossing over from highly ordered to random, small changes in parameters have a large effect. In particular, increases in V/U enlarge the 'ordered' region, while decreases contract it. It is also in these regions that temperature changes have the largest effect. Our calculations predict large temperature variations in the charge transfer in the region $0.16 < x < 0.20$ and $0.33 < x < 0.38$, and large temperature variations in the density of states at the Fermi surface in the latter region. In the intermediate region $0.20 < x < 0.33$, the system is predicted to remain highly ordered over the full range of experimentally obtainable temperatures.

Figure 3 shows the density of states at the Fermi energy, $g(E_F)$, as a function of concentration, calculated for the values of σ_{sr} that minimise the free energy. The most evident feature is the very sharp dip in the density of states at $x = 0.25$. It is important to note that, although the bands are only partly overlapping, if the system had no local chemical order, no gap would open in the density of states and the dip in figure 3 would disappear. The peak in the 'ordered' density of states in the region $x > 0.28$ is caused by a singularity in the numerical calculations in this region for $|\sigma_{sr}| = |\sigma_{sr}|_{max}$. The results shown in the 'ordered' region were calculated with $|\sigma_{sr}| = 0.98 |\sigma_{sr}|_{max}$. It is expected that if the randomness caused by the liquid atomic motions were included in this calculation, it would reduce the size of this peak. The average charge transfer for both the Cs and Sb atoms are shown as a function of concentration in figure 4. The charge transfer remains large throughout the 'ordered' region, but drops rapidly as the system disorders.

4.2. Na–Sb

The results for the Na–Sb alloy system are quite similar to those for Cs–Sb. As seen from the values of the parameters in table 1, the main difference between the systems

Figure 3. Density of states at the Fermi energy as a function of Sb concentration. The full curves indicate regions where a definite minimum exists in the free energy. The broken curves show a possible way of interpolating between these regions. A possible extrapolation to pure Cs is also shown.
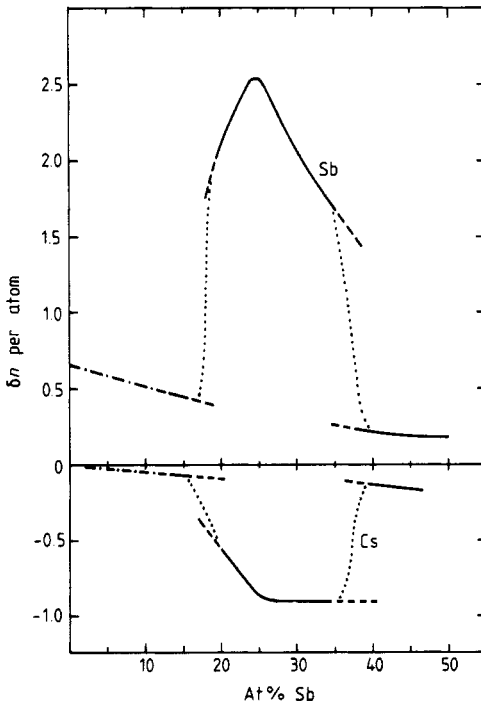
Figure 4. Average charge transfer per atom for Sb and Cs atoms as a function of Sb concentration. The full curves indicate regions where a definite minimum exists in the free energy. The broken curves are extrapolations of these regions. The dotted curves show a possible way of interpolating between these regions. Possible extrapolations to pure Cs are also shown.
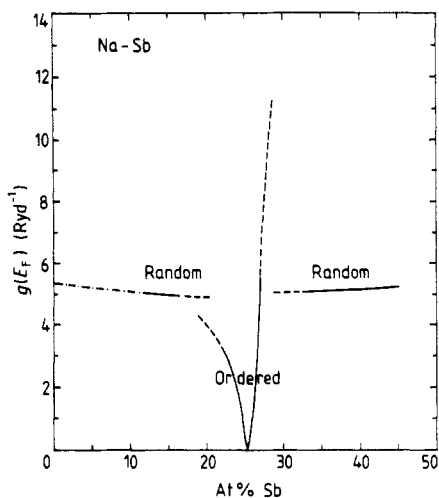
Figure 5. As figure 3 but for the Na–Sb system.

within our model is that Na has a larger value of t_{BB} than Cs, reflecting its larger Fermi energy and band width. Figures 5 and 6 show the calculated $g(E_F)$ and charge transfer as a function of concentration. From a comparison of these figures with figures 3 and 4 for Cs–Sb, it can be seen that Na–Sb remains 'ordered' throughout a smaller concentration range and that the charge transfer is somewhat less. Once again the crossover regions (broken curves) are the most sensitive to V/U and T. Due to the high melting point of Na–Sb alloys near Na_3Sb, experiments in this region have been performed at somewhat higher temperatures than the value $T = 1000$ K that was used for comparative purposes in calculating the results shown in figures 5 and 6.
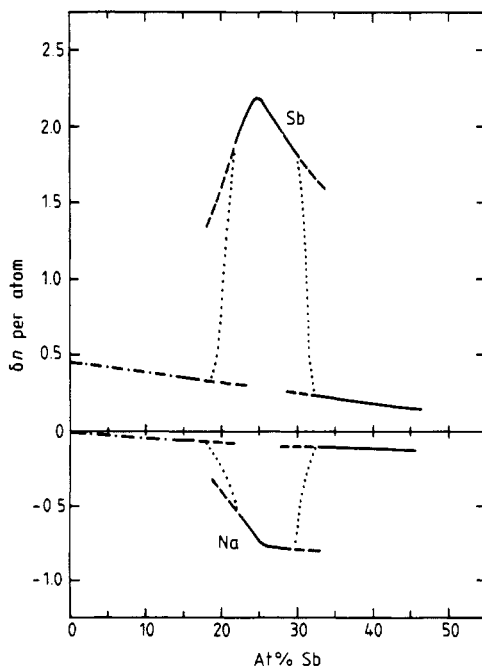

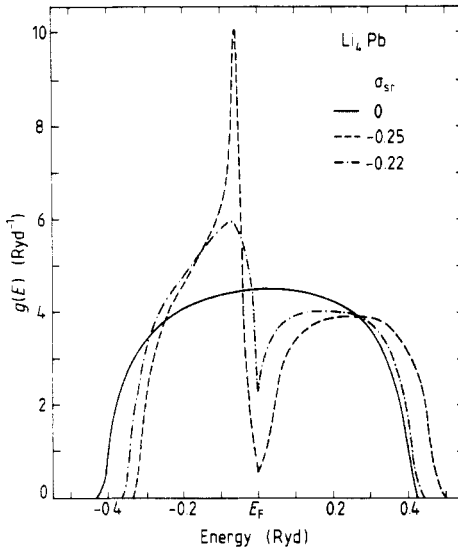**Figure 6.** As figure 4 but for the Na–Sb system.

Figure 7. Density of states as a function of energy for the composition Li_4Pb for three different values of σ_{sr}.

Although the 'ordered' region narrows with an increase of temperature, an increase of 100–200 K would not make a noticeable change in our results, which are not well defined anyway in the crossover regions between 'ordered' and random.

4.3. Li–Pb

The parameters for the Li–Pb system reflect the fact that Li has a larger Fermi energy than the heavier alkalis while Pb is less electronegative than Sb. The Li and Sb bands are thus both quite broad and overlap in energy almost completely. Figure 7 shows the calculated density of states as a function of energy with zero and maximum local order for concentration $x = 0.20$ (Li_4Pb). The dip in $g(E)$ occurs at the Fermi energy for 20 at% Pb rather than 25 at%, as for Sb, since the Pb s–p band has 4 electrons per atom rather than 5. It is evident that a large degree of local order is needed to cause any gap in the density of states. Figures 8 and 9 show $g(E_F)$ and charge transfer as a function of concentration. In the region near $x = 0.20$, curves are shown for both the 'ordered' and the random states. It is not possible to determine the degree of local order from our calculations in this region since the free energy for both 'ordered' and
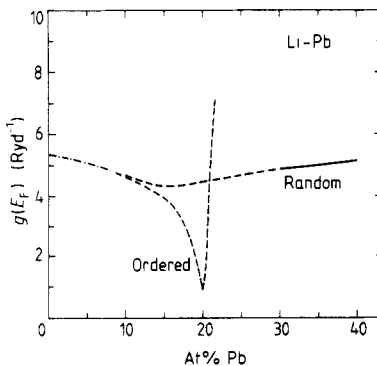

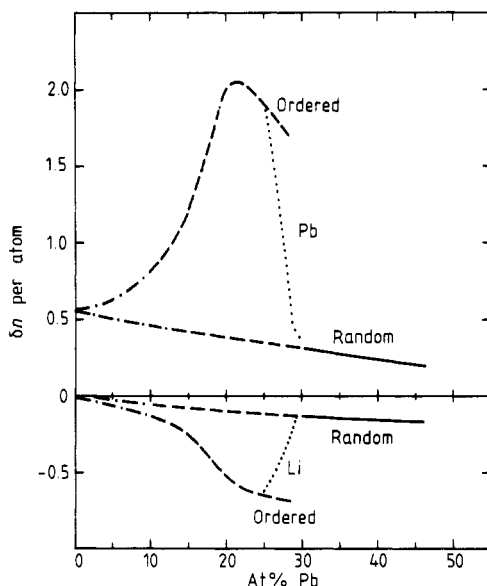**Figure 8.** Same as figure 3 but for the Li–Pb system.

Figure 9. Same as figure 4 but for the Li–Pb system.

random lie within kT of each other. The tendency to order is greatest near $x = 0.20$, and an increase of 5% in V/U is sufficient to make $F(|\sigma_{sr}|_{max}) - F(0) > kT$ at this point. For the same reasons as discussed earlier, large temperature-dependent effects are expected in the concentration region around $x = 0.20$.

5. Discussion

5.1. Cs–Sb

A wide variety of experimental measurements have been reported for Cs–Sb: measurements of the Knight shift and nuclear spin relaxation time (Kirby 1981), measurements of the volume contraction, conductivity, magnetic susceptibility and thermopower (Redslob *et al* 1982) and neutron diffraction measurements (Martin *et al* 1978). It is useful to discuss our calculated results in relation to these measurements.

The most obvious connection between our results and those from experiments can be seen by comparing our calculation of the density of states at the Fermi energy to the conductivity measurements (Redslob *et al* 1982). In the intermediate conductivity (or diffusion) regime, in which our tight-binding model should be a good approximation, the conductivity, σ, can be approximated by the Kubo–Greenwood equation,

$$\sigma = \frac{2\pi e^2}{3\hbar\Omega} g^2(E_F) \sum_{ij} \langle r_{ij}^2 t_{ij}^2 \rangle. \tag{11}$$

Over a narrow concentration region, all factors other than the density of states can be assumed to remain fairly constant, so that $\sigma \propto g^2(E_F)$. Using this relation, we find that our results are in excellent agreement with the experimental results for $0.23 < x < 0.28$, the region of the metal–non-metal transitions. Our model is thus able to give a good description of the system throughout this critical region, indicating that the self-consistently calculated charge transfer and local order are sufficient to account for the metal–non-metal transition. A more sophisticated model that included

electronic screening explicitly would be expected only to sharpen the transition further (Holzhey *et al* 1982). Other evidence supporting this general description comes from the large measured volume contraction (Redslob *et al* 1982) which reaches a maximum of 42% in the region, $0.25 < x < 0.33$. Such a large volume contraction is usually indicative of a highly ionic system. Evidence in opposition to a highly ionic system comes from the magnetic susceptibility measurements (Freyland and Steinleitner 1976). Although these results show a dip in χ at $x = 0.25$, it is not as large as would be expected for a purely ionic system or even for the highly ionic system predicted here. The extremely rapid variation of $g(E_F)$ with concentration in this region, however, indicates that an error of 1% in the concentration would have a very large effect on χ, introducing a significant metallic component. Simultaneous measurements of conductivity and susceptibility would help to clarify this point.

For lower Sb concentrations our calculations predict that the system makes a transition from highly ordered to random. This has little effect on $g(E_F)$ but causes a rapid change in the charge transfer. The variation of the free energy with σ_{sr} in this region is not much larger than kT, however, and it is quite probable that the order–disorder transition, if it occurs, is quite smeared out. Such a transition should lead to temperature-dependent effects in experiments that depend on the charge distribution rather than the density of states. Different experiments yield different temperature dependences throughout this region. Measurements of the Knight shift (Kirby 1981), which does depend strongly on charge distribution, show a large temperature variation for Sb concentrations less than that at the metal–non-metal transition. Further investigation of an order–disorder transition in this region is needed.

For Sb concentrations greater than about 28%, the agreement between theory and experiment is poor and our model is clearly insufficient for a description of the system. Our results, however, do give additional insight into the electronic behaviour of the system by indicating that with increasing Sb concentration, it becomes energetically unfavourable to maintain a highly ordered, large charge transfer state. It is easy to understand this by considering the huge Coulomb repulsion that would exist between two neighbouring Sb ions with large negative charges. What our calculations cannot predict, but which seems evident from many experiments, is that as the system disorders, it becomes energetically favourable for the Sb atoms to form covalently bonded chains, similar to those found in solid Cs_3Sb. The highly polarisable Cs atoms undoubtedly play an important role in the covalent bonding since pure liquid Sb does not exhibit such bonding. The large temperature dependence which is observed in many experiments in the region $x > 0.30$ is probably caused by the change in average length of the Sb–Sb chains. For $x \approx 0.30$, an additional temperature dependence may occur that is caused by the change-over in bonding from highly ionic to highly covalent.

5.2. Na–Sb

Fewer experimental results are available for Na–Sb than for Cs–Sb. In addition to the results for conductivity and magnetic susceptibility reported by Redslob *et al* (1982) there are also magnetic susceptibility results reported by Hackstein *et al* (1980). The metal–non-metal transition in Na–Sb is reported to be qualitatively similar to that in Cs–Sb but somewhat sharper, in good agreement with our calculated results. For Sb concentrations greater than 27%, the region in which covalently bonded Sb chains are expected to occur, the two systems behave quite differently. Whereas the conductivity

of Cs–Sb has a broad dip for $0.35 \lesssim x \lesssim 0.75$, that of Na–Sb has a small dip at $x \approx 0.30$. The fact that the onset of the dip occurs at a lower concentration in Na–Sb agrees with our prediction that the region of high local order for this system ends at a smaller Sb concentration. The smaller dip in Na–Sb indicates that the covalent bonding is much less prevalent in this alloy, which is expected since the polarisability of Na atoms is a factor of two less than that of Cs atoms while for the positive ions the ratio is about 15.

5.3. Li–Pb

Although Li–Pb does not undergo a metal–non-metal transition as do Cs–Sb and Na–Sb, it does become a poor metal in the region near stoichiometry, 20 at% Pb. The change in conductivity is considerably larger than can be explained by a Faber–Ziman diffraction model (van der Marel 1981), yet not sufficient for the system to enter a regime where a tight-binding model is expected to give quantitatively good results. Because the Li–Pb system has been studied by a large number of investigators and many experimental results have been reported for it, we decided, nevertheless, to apply our model to it to see if a self-consistent picture of the electronic properties could be obtained. We mention here just a few of the experiments that have been done: resistivity (Nguyen and Enderby 1977), Knight shift (van der Marel *et al* 1980), neutron diffraction study of structure (Ruppersberg and Egger 1975), volume contraction (Ruppersberg and Speicher 1976), and Gibbs free energy of mixing (Saboungi *et al* 1978). All of these results can be interpreted by assuming that charge transfer and local order effects are important in the region near stoichiometry.

Our results indicate that because the Li and Pb bands overlap in energy almost completely, a high degree of local order must occur for a gap to form. We find, however, that neither the 'ordered' nor the random states is energetically favoured so that an intermediate state is expected to exist. One way to check this is to compare our results with the conductivity measurements of Nguyen and Enderby (1977). We do this by using our results to calculate the ratio of the conductivities at two different concentrations and then compare this ratio to the ratio taken from their measurements. For the values of the parameters used in our calculations and taking the system to have the maximum possible order, we calculate a ratio of $g(E_F)$ ($x = 0.20$) to $g(E_F)$ ($x = 0.15$) of about 1/4 which leads to a ratio in conductivity of about 1/16. Comparing this to the ratio of about 1/2 obtained from the measured values, we find that the assumption of maximum possible order considerably overestimates the dip which indicates that the local order in the system is less than the maximum, as expected. In order for our calculated results to be in reasonable agreement with the conductivity measurements, we find that a value of $\sigma_{sr} \approx 0.88 |\sigma_{sr}|_{max} \approx -0.22$ must be used. For this value we calculate for the composition Li_4Pb a ratio $g(E_F)/g(E_F)_{\text{free electron}} \approx 1/2$. An independent estimate of this ratio can be obtained from measurements of the nuclear spin lattice relaxation time of Li in Li–Pb (Heitjans *et al* 1980). The relaxation rate is expected to be enhanced by a factor proportional to $1/g(E_F)$ (Warren 1971) which yields a value of $g(E_F)/g(E_F)_{\text{free electron}} \sim 1/2$ in good agreement with our calculated value.

Using the same value of σ_{sr}, we calculate for 20 at% Pb a value for the charge transfer per Pb atom of $\delta n_{Pb} \approx 1.5$. This value is somewhat larger than those estimated by others, $\delta n_{Pb} = 0.8$ in calculations by Schirmacher (1980) and $\delta n_{Pb} \approx 1.0$ used by R Evans (1981, private communication), but is not unreasonable. It is thus possible

to find a set of self-consistent parameters that agree well with experimental results. The $g(E)$ calculated using these parameters is shown together with the 'ordered' and random cases in figure 7.

Many of the experiments mentioned above yielded large temperature-dependent effects for Pb concentrations between 15 at% and 25 at% with the temperature dependence sharply peaked at 20 at% Pb. This temperature dependence is also in good agreement with our supposition that the alloy is in a state of intermediate order.

6. Conclusions

We have shown that our model calculations, which include chemical short-range order and charge transfer in a self-consistent way, are able to describe well the metal–non-metal transitions that occur in some liquid alloy systems with polyvalent components. Although these systems appear to be similar to Cs–Au, the functional relationship that we find between the free energy and local order is quite different. For polyvalent alloys the systems prefer either a highly ordered or a random state rather than a state of intermediate local order as for Cs–Au. We have treated three systems, Cs–Sb, Na–Sb and Li–Pb in some detail and find that in each case a high degree of local order and a large charge transfer occur in the transition region, so that the bonding in this region is highly ionic.

For Cs–Sb and Na–Sb with Sb concentration in the range of 20–30%, we find that it is energetically favourable for the alloy to achieve as ordered a state as is possible for a liquid, causing the average charge transfer to the Sb atoms in this range to be 2–2.5 electrons. As the Sb concentration increases further, however, the average Sb–Sb distance decreases and the Coulomb repulsion between Sb ions makes it energetically favourable for the system to disorder, causing the charge transfer to drop rapidly to about 1/4 electron. In this concentration region, experiments have shown that covalent bonding can be favoured. Thus the bonding in these systems appears to vary drastically with concentration, exhibiting ionic, covalent and metallic bonding, each in a different concentration region.

For Li–Pb we are unable to determine the degree of local order by minimising the free energy. Our calculations are able, however, to give a self-consistent description of the system in the concentration region near Li_4Pb that is in agreement with a variety of experimental results. We find that at stoichiometry the system has a high degree of local order and a charge transfer of about 1.5 electrons per atom.

All of the calculations reported here treat the local atomic environment in an average way, each atom experiencing the same environment as all the others. It is not possible to include covalent bonding in a straightforward way within such a scheme. A calculation of the type carried out by Jonson and Franz (1980) that employs a Monte-Carlo method to treat the local atom configurations accurately would overcome this problem. Such a calculation is planned for the future.

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