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Structure of liquid Li–Ga alloys

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Abstract. We have carried out neutron diffraction measurements for two Li–Ga samples: $\text{Li}_{0.50}\text{Ga}_{0.50}$ at 750 °C and $\text{Li}_{0.77}\text{Ga}_{0.23}$ at 475 °C. The Li–Ga system is an example of a system forming ionic alloys. The temperatures were chosen to be slightly above the respective melting points. The composition of the latter sample is not only close to that at which a maximum in the resistivity is observed, it corresponds also to the 'zero-alloy' composition. For both samples evidence for chemical short-range order is found while for the equiatomic composition evidence is obtained that the arrangement of atoms in the first coordination shell as observed in the solid state is preserved upon melting. A simple model using the mean spherical approximation yields structure factors that are in satisfactory agreement with the measured ones.

1. Introduction

In the last years the liquid alkali–group IIIb alloys have been studied extensively. For a brief review the reader is referred to sections 7 and 12 of a paper by Van der Lugt and Geertsma (1987). Since there is a considerable difference between the electronegativities of the constituent elements (1.25 eV for Li–Ga on the Miedema scale (Boom *et al* 1976)), electron transfer takes place during alloying from the less electronegative to the more electronegative element. This results in alloys with an ionic character. Recently, several properties of the Li–Ga system have been studied. The resistivity and the Knight shift were measured (Itami *et al* 1988) and the phase diagram was determined (Itami *et al* 1989, see figure 1). The maximum value of the resistivity is obtained at 32 at. % Ga and does not exceed values appropriate for the nearly-free-electron (NFE) model. Indeed a calculation of resistivity values based on the diffraction model is in fair agreement with experiment (Itami *et al* 1988), though the peak positions of the calculated isotherm of the resistivity is shifted slightly to the Li-rich side. Clear evidence for electron transfer comes from the Knight shift measurements, which show a rapid decrease of the Knight shift of ^7Li with the addition of Ga up to 30 at. % Ga. Beyond this Ga concentration the Li Knight shift becomes constant.

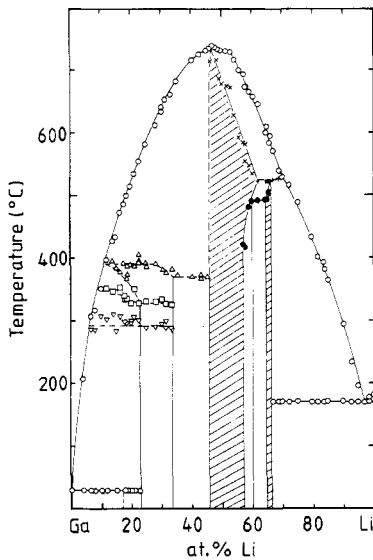


Figure 1. Phase diagram of the Li–Ga system determined by Itami *et al* (1989).

The crystal structure of several Li–Ga alloys has been determined (Zintl and Brauer 1933, Müller and Stöhr 1977, Stöhr and Schäfer 1982, Belin 1984). In the Ga-rich alloys Ga polyanions are formed (Belin and Ling 1982). The equiatomic alloy is a nice example of a Zintl phase. The Li atoms donate an electron to the Ga atoms so that in an ionic picture (which is not entirely appropriate) the Ga atoms change into singly-charged negative ions, iso-electronic to Si for example. According to Zintl and Brauer (1933) the Ga ions form a lattice similar to that of Si, i.e. a diamond lattice. The Li ions occupy the remaining empty sites which together constitute a diamond lattice as well. The resulting B32 lattice (NaTl structure) has indeed been observed (Zintl and Brauer 1933).

To find further evidence for ordering in Li–Ga alloys we decided to perform neutron diffraction measurements. For this purpose the Li–Ga alloy containing 77 at.% ^7Li is the best sample to investigate from the point of view of neutron diffraction technique because it is a zero alloy. This is an alloy of which the average scattering length is zero, so that there is no coherent scattering. Only a diffuse scattering pattern is observed determined by the concentration fluctuations. The other alloy, $\text{Li}_{0.50}\text{Ga}_{0.50}$, has been selected because it corresponds to the Zintl phase LiGa mentioned before. Besides we want to compare the scattering of the zero alloy with that of a Li–Ga alloy which contains in addition a contribution of coherent scattering.

2. Experimental procedure

The neutron diffraction experiments were performed on the Liquids and Amorphous Materials Diffractometer (LAD) of the pulsed neutron source at the Rutherford Appleton Laboratory (RAL) (Chilton, UK). Four scintillation detectors positioned symmetrically with respect to the incident beam were used for the measurements. A temperature-controlled vacuum furnace was available for heating the samples. The sample containers were made of $\text{Ti}_{0.67}\text{Zr}_{0.33}$. Apart from being a zero alloy, this material proves to be strongly resistant against corrosive liquid alloys. The sample height was 40 mm, the

Table 1. The scattering lengths, coherent scattering cross sections σ_{coh} , total scattering cross sections σ_{sca} , absorption cross sections σ_{abs} for 2200 m/s-neutrons, the average atomic weight $\langle M \rangle$ and estimated density ρ of the Li-Ga alloys. For ${}^7\text{Li}$ we used the specified enrichment of 99.971 at. % to calculate the scattering lengths and the cross sections.

Alloy	$\langle b \rangle$ (10^{-1} cm)	σ_{coh} (b)	σ_{sca} (b)	σ_{abs} (b)	$\langle M \rangle$	ρ (g cm^{-3})
$\text{Li}_{0.50}\text{Ga}_{0.50}$	0.253	3.647	4.011	1.614	38.36	3.00
$\text{Li}_{0.77}\text{Ga}_{0.23}$	-0.003	2.012	2.549	0.914	21.44	1.65

inner diameter of the container was 9 mm and its wall thickness 0.5 mm. The Li-Ga samples were prepared in a He-filled glove box in which the oxygen level was less than 1 ppm. The ${}^7\text{Li}$ isotope (enrichment 99.971%) was delivered by Oak Ridge National Laboratory. Gallium (purity 99.99%) was obtained from Highways International. The following procedure was used to prepare the alloys: first a tungsten crucible was filled with the appropriate amounts of the pure metals, next the crucible was heated up, and after the metals had alloyed the contents of the crucible was quenched on a copper plate. The crystallised pieces of the alloy were brittle and could be easily crushed. The pieces were subsequently put one by one in the sample container, which was kept at a temperature exceeding the melting point of the alloy so that the pieces immediately melted. By filling the containers in this way it was ensured that no empty space or He bubbles could be formed.

After that the sample cells were put in a glass tube that was closed and evacuated. Then they were transported from the glove box to the laser welding department. Here the lids were welded to the cans. Since the absorption of the laser light by the glass walls is very low, the sample containers can be welded *in situ* in the tubes.

3. Data reduction

A set of programs developed at RAL (Howells 1986) was used to correct the data for absorption and multiple scattering, due to both sample and container, and for normalisation. The scattering cross sections were taken from Sears (1986) and are shown in table 1. Since no density data on liquid Li-Ga alloys are available we have calculated the densities from those of an ideal mixture assuming a volume contraction of 15%. This is a guess to be compared with the volume contraction of 18% of the more strongly ionic compound Li-Pb at 600 °C (Ruppersberg and Speicher 1976). The average differential scattering cross-section per atom was corrected for incoherent scattering and yielded the structure factor after normalisation by $\langle b^2 \rangle$. Here $\langle \dots \rangle$ denotes an average over the concentrations of the components.

To perform the Fourier transformation the maximum entropy method as implemented by an algorithm of Soper (1986) has been used. We have preferred this method to a straightforward Fourier transformation of the measured structure factor because of the possible presence of systematic errors caused by both the experimental circumstances (drift in the detectors proved not to be insignificant) and the correction procedures, which are only approximately known. All these sources of error will in some way influence the structure factor calculated from the raw data. Starting from a structureless system the pair correlation function $g(r)$ is modified in an iterative scheme

in such a way that the following conditions are fulfilled: (i) the structure factor $S(q)$ calculated from $g(r)$ must represent the measured one without reproducing the statistical noise present in the original data, and (ii) the calculated $g(r)$ must satisfy known constraints, e.g. the compressibility limit for $S(q)$ at $q = 0$, and furthermore $g(r) = 0$ and $g(\infty) = 1$.

In each step $g(r)$ is chosen such that it has the least amount of structure in it, i.e. contains a minimum of information. Because of condition (i), each step yields a better agreement between the measured and calculated $S(q)$. The procedure is repeated until the regenerated $S(q)$ agrees satisfactorily with the measured one. The amount of information contained by $g(r)$ is measured by the entropy. In each step the entropy corresponding to $g(r)$, being considered as a probability distribution function, is maximised consistent with conditions (i) and (ii). Full details can be found in the papers by Root (1986) and Soper (1986). We confined ourselves here to mentioning the parameters that have been used: the number of iteration steps was 24, the feedback factor was 0.1, the 'smoothness parameter' λ was 1 and the power of the repulsive potential as occurring in the above-mentioned paper of Soper was 6. The zero-wavevector limit of $S(q)$ although unknown was taken to be 0.05. This is a typical value for metals (see e.g. Blairs 1978). It was established that a different value of $S(0)$ hardly influenced the final results.

Let us define a pair correlation function $g(r)$ related to $S(q)$ as follows:

$$g(r) - \frac{\langle b \rangle^2}{\langle b^2 \rangle} = \frac{1}{2\pi^2 r \rho_0} \int_0^\infty q [S(q) - 1] \sin(qr) dq \quad (1)$$

As before, $\langle \dots \rangle$ denotes an average over the concentrations over the components and ρ_0 is the number density. Let us also define a radial distribution function $N(r)$

$$N(r) = 4\pi r^2 \rho_0 g(r). \quad (2)$$

The total structure factor $S(q)$ can be written as a linear combination of Bhatia–Thornton partial structure factors (Bhatia and Thornton 1970)

$$S(q) = w_{NN} S_{NN}(q) + w_{NC} S_{NC}(q) + w_{CC} S_{CC}(q) \quad (3)$$

with

$$w_{NN} = \langle b \rangle^2 / \langle b^2 \rangle \quad w_{NC} = 2 \langle b \rangle \Delta b / \langle b^2 \rangle \quad w_{CC} = (\Delta b)^2 / \langle b^2 \rangle. \quad (4)$$

Here NN , NC and CC are pairs of variables, where N is the mean number density and C the concentration, and $\Delta b = b_1 - b_2$. A similar expression holds for $g(r)$.

For a zero alloy $\langle b \rangle = 0$, so that all terms in (3) except the last one vanish. Furthermore it can be shown that $w_{CC} = 1/(c_1 c_2)$. In case of a zero alloy, equation (1) gives us directly the radial concentration correlation function $4\pi r^2 \rho_{CC}(r)$, introduced by Ruppertsberg and Egger (1975) in their work on Li–Pb and defined as

$$4\pi r^2 \rho_{CC}(r) = \frac{2}{\pi} r \int_0^\infty q \left(\frac{s_{CC}(q)}{c_1 c_2} - 1 \right) \sin(qr) dq. \quad (5)$$

Note that for a zero alloy $N(r) = 4\pi r^2 \rho_{CC}(r)$. One can show (see e.g. Ruppertsberg and Egger 1975, Harris and Lewis 1983) that

$$\rho_{CC}(r) = c_2(\rho_{11}(r) + \rho_{12}(r)) + c_1(\rho_{22}(r) + \rho_{21}(r)) - \rho_{12}(r)/c_2 \quad (6)$$

in which $\rho_{ij}(r)$ is the density of j atoms at distance r from an i atom. From (6) it follows that the area A under the first peak of $4\pi r^2 \rho_{CC}(r)$ can be written as

$$A = c_2 N_1 + c_1 N_2 - N_{12}/c_2 \quad (7)$$

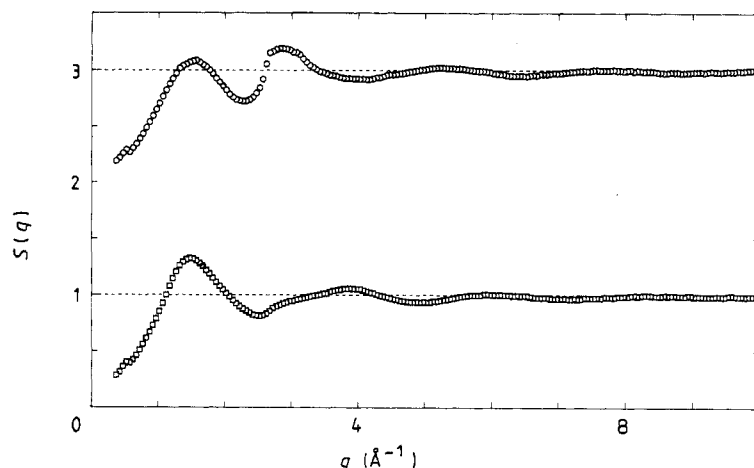


Figure 2. Measured structure factors of $\text{Li}_{0.50}\text{Ga}_{0.50}$ at 750 °C (○) and $\text{Li}_{0.77}\text{Ga}_{0.23}$ at 475 °C (□). For the structure factor of $\text{Li}_{0.50}\text{Ga}_{0.50}$ the zero of the ordinate has been shifted by +2. q is the scattering vector.

where N_{ij} is the partial coordination number of j atoms in the first coordination shell of an i atom, while $N_i = \sum_j N_{ij}$ is the total coordination number of an i atom. Equation (7) allows us to define the so-called generalised Warren (1969) chemical short-range order (CSRO) parameter α as

$$\alpha = A/N \quad N = c_2 N_1 + c_1 N_2. \quad (8)$$

This parameter was originally introduced by Cowley (1950) in the theory of order and disorder in solid binary systems and was later on generalised to liquid and amorphous binary systems (Chieux and Ruppertsberg 1980, Ruppertsberg *et al* 1980a). Its sign determines whether there is heterocoordination (preference for unlike neighbours) or self-coordination (preference for like neighbours). Simple arguments will make this statement clear. For a random system $N_{ij} = c_j N_i$ so that $\alpha = 0$. In case of heterocoordination $N_{12} > c_2 N_1$ and $N_{21} > c_1 N_2$, thus $N_{12} + N_{21} > c_2 N_1 + c_1 N_2$, or equivalently $N_{12}/c_2 > N$. Here we have used the identity $c_1 N_{12} = c_2 N_{21}$. This implies that α is negative. Conversely, a positive value of α is obtained in case of self-coordination. The limiting values of α are obtained in case of maximum ordering and in case of total self-coordination. In the former case $N_1 = N_2 = N_{12}$ if $c_2 > c_1$ ($N_1 = N_2 = N_{21}$ if $c_1 > c_2$) so that $\alpha = c_1/c_2$ ($\alpha = -c_2/c_1$). In the latter case $N_{12} = N_{21} = 0$ and thus $\alpha = 1$ according to (8).

4. Results

Figure 2 shows the structure factors (SFs) of $\text{Li}_{0.50}\text{Ga}_{0.50}$ at 750 °C and $\text{Li}_{0.77}\text{Ga}_{0.23}$ at 475 °C over a restricted range up to 12 \AA^{-1} . The range covered by the complete data sets goes up to 20 \AA^{-1} . Table 2 contains the peak positions and heights of the first, second and third peaks. For comparison those of the SFs of pure Li and Ga, measured at resp. 452 °C and 565 °C, have also been included. The Li data were taken from a compilation of Van der Lugt and Alblas (1985), the Ga data from the work of Bizid *et al* (1978). In contrast to the SFs of the pure components where the first peak occurs at approximately 2.5 \AA^{-1} ,

Table 2. Peak positions and heights of the first, second and third maxima of the structure factors of $\text{Li}_{0.50}\text{Ga}_{0.50}$ (750 °C) and $\text{Li}_{0.77}\text{Ga}_{0.23}$ (475 °C) as well as of pure Ga (565 °C) and Li (452 °C).

	1st max		2nd max		3rd max	
	q (\AA^{-1})	$S(q)$	q (\AA^{-1})	$S(q)$	q (\AA^{-1})	$S(q)$
Ga	2.58	1.87	4.98	1.24	7.38	1.10
$\text{Li}_{0.50}\text{Ga}_{0.50}$	1.57	1.088	2.87	1.190	5.23	1.025
$\text{Li}_{0.77}\text{Ga}_{0.23}$	1.48	1.325	3.88	1.059	5.87	1.006
Li	2.45	2.32	4.55	1.15	6.85	1.02

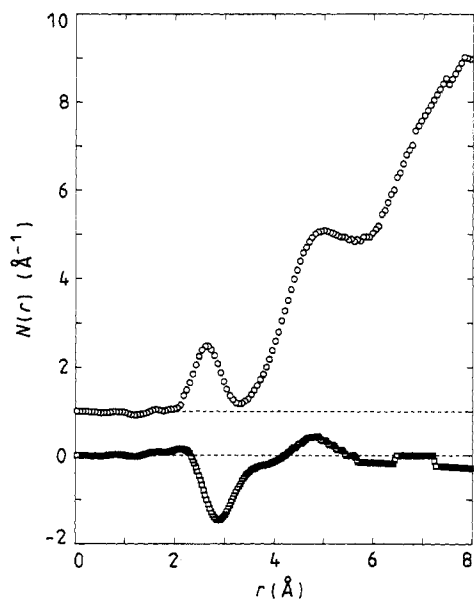


Figure 3. Radial distribution functions found by application of the maximum entropy method to the structure factors in figure 2. For the radial distribution function of $\text{Li}_{0.50}\text{Ga}_{0.50}$ the zero of the ordinate has been shifted by +1. \circ , $\text{Li}_{0.50}\text{Ga}_{0.50}$; \square , $\text{Li}_{0.77}\text{Ga}_{0.23}$.

the first peak in the sfs of both alloys is at about 1.5 \AA^{-1} . Since in $\text{Li}_{0.77}\text{Ga}_{0.23}$ the only contribution to $S(q)$ is from $S_{CC}(q)$ we can conclude that this peak is an S_{CC} peak, the position of which is associated with the periodicity of the concentration fluctuations. Comparing the sfs of $\text{Li}_{0.77}\text{Ga}_{0.23}$ and $\text{Li}_{0.50}\text{Ga}_{0.50}$ we find that in the latter the height of the prepeak has decreased, that an additional peak at 2.9 \AA^{-1} occurs and that the high- q oscillations are out of phase with those of $\text{Li}_{0.77}\text{Ga}_{0.23}$. Because the Li and Ga atoms are of similar size (Müller and Stöhr 1977, Itami *et al* 1988), it is a reasonable approximation to neglect the S_{NC} contribution (see e.g. Reiter *et al* 1977, Alblas *et al* 1984). This implies that the second peak in the sf of $\text{Li}_{0.50}\text{Ga}_{0.50}$ is essentially an S_{NN} peak, which is related to the nearest-neighbour distance.

The corresponding radial distribution functions (RDFs) found by applying the maximum entropy method to the measured sfs up to 20 \AA^{-1} are shown in figure 3. The RDF of $\text{Li}_{0.77}\text{Ga}_{0.23}$ shows a distinct negative minimum at 2.9 \AA which is an indication of chemical short-range order, i.e. a preference for unlike neighbours in the first coordination shell. Its area is related to the Warren CSRO parameter α as has been pointed out before. The small second peak is positive, implying that in the second coordination

Table 3. Parameters of Gaussian fits to the two peaks of the radial distribution functions: distance d around which the peak is centred, the half width σ of the peak and the area A under the peak.

	d (Å)	σ (Å)	A	d (Å)	σ (Å)	A
$\text{Li}_{0.50}\text{Ga}_{0.50}$	2.648	0.254	0.961	4.883	0.630	6.388
$\text{Li}_{0.77}\text{Ga}_{0.23}$	2.891	0.234	-0.919	4.824	0.290	0.318

Table 4. Properties of various Li-based zero alloys showing a tendency towards hetero-coordination: electronegativity difference $\Delta\varphi$ on the Miedema scale (Boom *et al* 1976), Li concentration at which the resistivity shows a maximum c_{\max} , prepeak position q_p , the maximum resistivity ρ_{\max} and the Warren CSRO parameter α . From the first-mentioned reference c_{\max} and ρ_{\max} were taken, from the second-mentioned the value of α was taken.

	$\Delta\varphi$ (eV)	c_{\max}	ρ_{\max} ($\mu\Omega$ cm)	q_p (\AA^{-1})	α
$\text{Li}_{0.70}\text{Mg}_{0.30}$ ^{a,b}	0.60	0.60	60.3	1.5	-0.04
$\text{Li}_{0.72}\text{Ag}_{0.28}$ ^c	1.60	—	—	1.8	-0.15
$\text{Li}_{0.73}\text{Sn}_{0.27}$ ^{d,e}	1.30	0.80	850	1.6	-0.16
$\text{Li}_{0.77}\text{Ga}_{0.23}$ ^{f,g}	1.25	0.67	161.1	1.5	-0.09
$\text{Li}_{0.80}\text{Pb}_{0.20}$ ^{h,i}	1.25	0.80	480	1.5	-0.25

^a Feitsma *et al* (1978)^f Itami *et al* (1988)^b Ruppertsberg *et al* (1980b)^g Present work^c Reiter *et al* (1977)^h Nguyen and Enderby (1977)^d Van der Marel *et al* (1982)ⁱ Ruppertsberg and Egger (1975)^e Ablas *et al* (1984)

shell the like atoms slightly outnumber the unlike ones compared with a random distribution. The deep minimum at 3.3 Å in the RDF of $\text{Li}_{0.50}\text{Ga}_{0.50}$ is still a remnant of the dip in the RDF of $\text{Li}_{0.77}\text{Ga}_{0.23}$. However, two strong peaks have arisen at both sides of this minimum which are supposed to be dominated by the g_{NN} contribution. Table 3 contains the parameters of Gaussian fits to the peaks: the distance d around which the peak is centered, the half width σ of the peak and the area A under the peak.

5. Discussion

Let us first discuss the zero alloy $\text{Li}_{0.77}\text{Ga}_{0.23}$. The oscillating behaviour of the measured SF suggests that there is considerable ordering in the liquid. The first peak of the corresponding RDF is due to Li–Ga correlations. Its position (2.89 Å) agrees with the average Li–Ga distance found in the crystal structure (2.96 Å, see Müller and Stöhr 1977). From the area under the first peak of the RDF of $\text{Li}_{0.77}\text{Ga}_{0.23}$ we find a Warren CSRO parameter $\alpha = -0.092$, assuming 10 nearest neighbours. This implies that a Li atom has 2.5 Ga neighbours on the average in comparison to 2.3 in a random distribution. We can compare the Li–Ga system with other Li-based zero alloys that show a tendency towards hetero-coordination. Table 4 summarises some properties of interest of alloys that belong to this group. All these alloys are characterised by a prepeak in the SF the position of which varies from 1.5 to 1.8 Å⁻¹. The Warren CSRO parameter has been

Table 5. The ratio of the positions of the first and second peak of the measured structure factors of several equiatomic alloys.

	q_1/q_2	Reference
$\text{Li}_{0.5}\text{Sn}_{0.5}$	0.64	Alblas <i>et al</i> (1984)
$\text{Li}_{0.5}\text{Pb}_{0.5}$	0.64	Ruppersberg and Egger (1975)
$\text{Li}_{0.5}\text{Ga}_{0.5}$	0.55	Present work
$\text{Na}_{0.5}\text{Sn}_{0.5}$	0.46	Alblas <i>et al</i> (1983)
$\text{K}_{0.5}\text{Pb}_{0.5}$	0.46	Reijers <i>et al</i> (1987, 1989)

calculated assuming a mean value of 10 nearest neighbours. Its value lies between -0.04 and -0.25 .

When comparing the values of α in table 4, one should keep in mind that they are not a proper measure of the tendency to compound formation or ordering. In systems like Au–Cs and Li–Pb distinct compounds occur at well-defined stoichiometric compositions, respectively AuCs and Li_4Pb , which are easily predictable from simple chemical valence rules. According to the work of Holzhey *et al* (1981) and Holzhey (1982) this composition coincides with those for the maximum order, resistivity and volume contraction. For example in Au–Cs α is reduced to half its value in $\text{Au}_{0.50}\text{Cs}_{0.50}$ by a concentration deviation from the equiatomic composition of no more than 10%. Obviously a comparison of α values is most meaningful when only stoichiometric compositions are considered, which is not the case for four of the alloys in table 4. Even when the comparison is restricted to stoichiometric compounds, it follows from the elementary theory of order and disorder that the degree of order depends on the stoichiometric composition itself and thus on the valencies: an equiatomic mixture will show up its order more clearly than a mixture of metals of strongly different valencies.

The origin of the short-range order in $\text{Li}_{0.80}\text{Pb}_{0.20}$ is explained by a rearrangement of the electronic states on mixing the pure components which leads to a transfer of charge from the Li towards the Pb atoms (Ruppersberg and Egger 1975). This idea is supported by the fact that the above Li–Pb composition corresponds with the octet composition. Although the Li–Ga system has the same electronegativity difference as Li–Pb, the $(8 - N)$ -rule is hard to satisfy. This would imply that five electrons are donated to the Ga atoms which is very unlikely because of the on-site Coulomb interactions. That this does not occur follows from the resistivity measurements (Itami *et al* 1988). They do not find the composition of maximum resistivity at a Li : Ga concentration ratio of 5 : 1, but at a ratio close to 2 : 1. The resistivity maximum is broad indicating that there is no sharply defined stoichiometric composition. Undoubtedly, electron transfer plays an important role in the Li–Ga system as follows from the Knight shift measurements (Itami *et al* 1988). On the other hand the resistivity maximum is definitely in the NFE range. Thus in the Li–Ga system aspects of NFE behaviour and of compound formation due to charge transfer are present simultaneously, which makes Li–Ga intermediate between liquid metals and ionic semiconducting alloys like $\text{Li}_{0.80}\text{Pb}_{0.20}$.

The SF of $\text{Li}_{0.50}\text{Ga}_{0.50}$ reveals an interesting property. If we compare the ratio of the prepeak position and the position of the S_{NN} peak next to it, we find that the ratio for $\text{Li}_{0.5}\text{Ga}_{0.5}$ lies between those of $\text{Li}_{0.5}\text{Sn}_{0.5}$ and $\text{Li}_{0.5}\text{Pb}_{0.5}$ on the one hand, and $\text{Na}_{0.5}\text{Sn}_{0.5}$ and $\text{K}_{0.5}\text{Pb}_{0.5}$ on the other hand (see table 5). The value 0.64 for $\text{Li}_{0.5}\text{Sn}_{0.5}$ and $\text{Li}_{0.5}\text{Pb}_{0.5}$ is close to the value 0.67 that has been experimentally observed for the alkali–halide series (Chieux and Ruppersberg 1980). In $\text{Na}_{0.5}\text{Sn}_{0.5}$ and $\text{K}_{0.5}\text{Pb}_{0.5}$ poly-anions $(\text{Sn}_2)^{4-}$

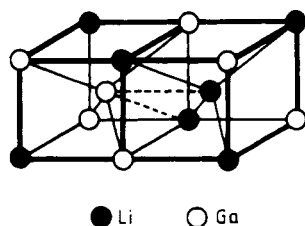


Figure 4. The crystal structure of LiGa (B32 lattice).

and $(\text{Pb}_4)^{4-}$ are respectively assumed to exist (Alblas *et al* 1983, Reijers *et al* 1987, 1989). This suggests that partial clustering may occur in $\text{Li}_{0.5}\text{Ga}_{0.5}$ though it is not clear what kind of clusters can be expected.

Some evidence that the local arrangement of atoms in the crystal structure of $\text{Li}_{0.5}\text{Ga}_{0.5}$ is preserved in the liquid state, comes from the first peak of the RDF of $\text{Li}_{0.5}\text{Ga}_{0.5}$. Figure 4 shows the crystal structure of $\text{Li}_{0.5}\text{Ga}_{0.5}$, which can be described as two interpenetrating diamond lattices, one for each component (B32 structure). Only a few alkali-group IIIb alloys crystallise in this structure, namely LiAl, LiGa, LiIn, LiTl and NaTl. As has been pointed out by Zintl and Brauer (1933) this is a consequence of the condition that the atoms in the alloy must be of the same size. For LiGa they found a lattice constant $a = 6.195 \text{ \AA}$ from which the interatomic distance $d = 2.68 \text{ \AA}$ follows. As can be seen in figure 4 the partial coordination numbers Z_{LiLi} , Z_{LiGa} and Z_{GaGa} are the same and equal to four. Turning now to the first peak in the RDF of $\text{Li}_{0.5}\text{Ga}_{0.5}$ we find that its position is 2.65 \AA and that the area under the peak yields a partial coordination number of 4.3, calculated under the assumption of equal partial coordination numbers. Comparing these data with those of the solid, we find that they agree satisfactorily.

Finally, we have used a simple model consisting of charged hard spheres for calculating the sfs making use of the mean spherical approximation (MSA). Details about MSA can be found among others in papers of Barker and Henderson (1976) and Parrinello and Tosi (1979). Waisman and Lebowitz (1970, 1972) have solved the problem for a binary mixture of equisized particles of opposite charge. Our method of solution is based on two papers of Hiroike (1969, 1977) that together deal with the more general case of a multicomponent system of particles of arbitrary size and charge. Figure 5(a) and 5(b) show the results of the total SF and the Bhatia–Thornton partial sfs. Table 6 shows the values of the various parameters involved: the particle diameter d , the partial density n and the charge z . The prepeak positions of the calculated curves are lower than the measured ones. The same holds for the position of the second peak in the SF of $\text{Li}_{0.50}\text{Ga}_{0.50}$. In addition its width is not so well reproduced. The high- q oscillations are slightly shifted to higher q -values compared with the experimental curves. From inspection of the partials follows that the prepeak is due to S_{CC} and that S_{NC} is almost zero in agreement with the supposition made before. Compared with $\text{Li}_{0.77}\text{Ga}_{0.23}$ the S_{NN} oscillations are strongly enhanced in $\text{Li}_{0.50}\text{Ga}_{0.50}$.

5. Conclusion

Neutron diffraction measurements for two samples of the Li–Ga system ($\text{Li}_{0.50}\text{Ga}_{0.50}$ and $\text{Li}_{0.77}\text{Ga}_{0.23}$, the latter being a zero alloy) indicate that there is strong ordering in the

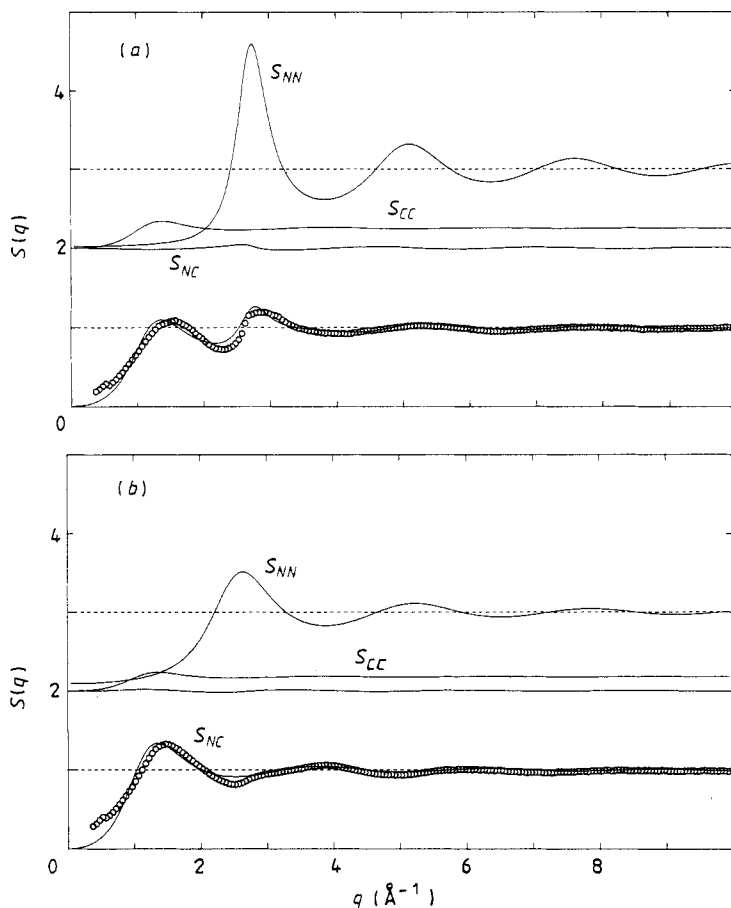


Figure 5. Results of the MSA calculations for (a) $\text{Li}_{0.50}\text{Ga}_{0.50}$ and (b) $\text{Li}_{0.77}\text{Ga}_{0.23}$. The upper three curves show the Bhatia–Thornton partial structure factors. The lower two curves are the measured structure factor (○) and the calculated total structure factor (full curve). For both sets of the Bhatia–Thornton partials the zero of the ordinate has been shifted by +2.

Table 6. Parameters used for the MSA calculations: diameter d_i , partial number density n_i and charge z_i . Here subscript 1 refers to Li and subscript 2 to Ga.

	d_1 (Å)	d_2 (Å)	n_1 (Å ⁻³)	n_2 (Å ⁻³)	z_1	z_2
$\text{Li}_{0.50}\text{Ga}_{0.50}$	2.55	2.45	0.028	0.028	0.145	-0.145
$\text{Li}_{0.77}\text{Ga}_{0.23}$	2.35	2.55	0.03214	0.00960	0.0747	-0.250

liquid which is induced by electron transfer from the Li towards the Ga atoms. The Warren CSRO parameter calculated for $\text{Li}_{0.77}\text{Ga}_{0.23}$ implies that there is a slight tendency towards hetero-coordination. For $\text{Li}_{0.50}\text{Ga}_{0.50}$ evidence has been found that the local coordination of both the Li and the Ga atoms is the same as in the solid. Simple MSA calculations reproduce the measured SFS qualitatively.

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