

The electronic and structural properties of liquid Mg - Bi near the stoichiometric composition

Mg₃Bi₂

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 10823

(<http://iopscience.iop.org/0953-8984/8/50/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 04:12

Please note that [terms and conditions apply](#).

The electronic and structural properties of liquid Mg–Bi near the stoichiometric composition Mg_3Bi_2

C Guo[†], A C Barnes[†] and W S Howells[‡]

[†] H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

[‡] Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

Received 31 July 1996

Abstract. The structure and electronic properties of liquid $\text{Mg}_{1-x}\text{Bi}_x$ alloys with compositions close to the stoichiometric composition Mg_3Bi_2 have been measured. The extremely deep minimum in the electronic conductivity observed previously at this composition is confirmed and shows a minimum value of $63 \pm 1 \Omega^{-1} \text{cm}$ which is characteristic of a good liquid semiconductor. In contrast, the thermopower of the samples never exceeds $10 \mu\text{V K}^{-1}$ for all the compositions studied and is more typical of that expected for a poor liquid metal. Measurements of the liquid structure at the total structure factor level for $x = 0.38, 0.4$ and 0.42 reveal broadly similar diffraction patterns despite a change in conductivity of two orders of magnitude over this composition range. However, a small enhancement of the intensity of the pre-peak in the total structure factor at 1.8 \AA^{-1} is observed at the stoichiometric composition and this may be indicative of stronger ordering in the Bi–Bi structure at stoichiometry. A detailed analysis of the total structure factors and a comparison with recent computer simulations confirm the ionic nature of the liquid. The electronic properties are discussed in terms of a charge-transfer-type density of electron states and it is concluded that the rapid change in conductivity and the low thermopowers are poorly understood using this framework. It is speculated that the unusual properties of this alloy are linked with an unusually high ionic mobility of Mg ions in the liquid.

1. Introduction

It has been known for many years that liquid Mg–Bi alloys show particularly unusual electronic properties around the stoichiometric composition Mg_3Bi_2 . This is most apparent in the electronic conductivity which shows a very deep and narrow minimum at Mg_3Bi_2 and yet becomes comparable with that of a poor liquid metal for compositions a few atomic per cent away from stoichiometry (Ilschner and Wagner 1958, Enderby and Collings 1970).

As simple elements, both magnesium and bismuth may be considered as good liquid metals whose conductivity σ , thermopower S and Hall coefficients show good agreement with the Ziman theory of liquid metals if their valences are assumed to be +2 and +5, respectively (Faber 1972). As a consequence, it might be expected that there would be relatively smooth variations in σ and S with concentration in a manner seen for many of the metal–metal liquid alloys studied in the 1970s. However, the results of Ilschner and Wagner (1958) and later Enderby and Collings (1970) show that at the composition Mg_3Bi_2 the material has a conductivity more typical of a narrow-definition liquid semiconductor (Enderby and Barnes 1990). An interpretation of this behaviour is to consider the liquid, at this composition, as more closely related to a molten salt than to a liquid metal such that the main species are Mg^{2+} and Bi^{3-} ions (in contrast with the +5 valence of pure Bi metal). As a consequence it is believed that there is a charge-transfer gap in the electronic

density of states at stoichiometry which is the origin of the poor electrical conductivity. The change in sign of the thermopower reported by Enderby and Collings (1970) as the composition passes through stoichiometry is fully consistent with this picture and agrees with principally hole-like transport for the Bi-rich side and electron-like transport for the Mg-rich side of Mg_3Bi_2 . Recently, however (Enderby and Barnes 1990), it was pointed out that the magnitude of the change in S on passing from p-type to n-type behaviour is an order of magnitude smaller than other liquid semiconductors of comparable conductivity (e.g. liquid Tl_2Se and Ag_2Se) and that the rate of change of S with composition is also very slow and inconsistent with a model based on a simple charge-transfer-type rigid-band picture of Mg–Bi (Barnes 1993). Unfortunately the only reported thermopower data for this system (Enderby and Collings 1970) covers a rather coarsely spaced composition range and it is possible to conceive that the large changes in S expected around stoichiometry were missed.

The aim of this paper is to present new, more detailed measurements of both the electronic properties (especially the thermopower) and the structure of this liquid close to the composition Mg_3Bi_2 in order to verify its ionic nature. We then discuss the electronic properties and compare them with those predicted for a charge-transfer-type liquid semiconductor. The structural results are also compared with recent *ab-initio* molecular dynamics calculations carried out by de Wijs *et al* (1996).

2. Experimental methods

2.1. Measurement of the electronic properties

The electronic properties of liquid $\text{Mg}_{1-x}\text{Bi}_x$ alloys were measured using modifications to basic techniques used previously (Barnes 1986, Ohno *et al* 1990). These were as follows.

(i) The measurements were made in cells of high-purity recrystallized alumina in order to avoid a reaction of the sample with the sample container.

(ii) The apparatus was adapted so that the sample composition could be modified during the course of the experiment by adding small quantities of either Mg or Bi to the sample already in the cell. This was achieved by using a small vacuum lock at the top of the apparatus. In this way the changes in σ and S with x could be followed continuously on the same sample. In order to ensure complete mixing of the added component the sample could be agitated and stirred using a thin tungsten rod.

At the beginning of the experiment a master sample of Mg_3Bi_2 was made by mixing appropriate, carefully weighed amounts of the pure elements, and reacting the mixture in a large-diameter alumina crucible.

2.2. Structural measurements

The neutron diffraction measurements were carried out using the LAD diffractometer at the ISIS facility at the Rutherford Appleton Laboratory, UK. Samples of Mg_3Bi_2 , $\text{Mg}_{58}\text{Bi}_{42}$ and $\text{Mg}_{62}\text{Bi}_{38}$ were prepared by directly mixing and reacting the pure elements in special vanadium containers of 8 mm diameter suitable for use in the LAD furnace. All the experiments on the liquid were carried out at 900 °C in these containers. We also measured the solid structure at several temperatures to confirm that the elements had fully reacted to form Mg_3Bi_2 . These measurements also allowed us to resolve the previously unreported structure of $\beta\text{-Mg}_3\text{Bi}_2$ (Barnes *et al* 1994). There was negligible reaction of the sample with

these containers over the time scale of the experiments (1 d). The raw data were corrected for self-attenuation, multiple scattering and inelasticity effects and reduced to give final total structure data $F(Q)$ using the ATLAS data analysis suite at RAL (Soper *et al* 1989).

3. Results

3.1. Electronic properties

The conductivity and thermopower of liquid $Mg_{1-x}Bi_x$ alloys were measured at nine equally spaced compositions between $Mg_{62}Bi_{38}$ and $Mg_{58}Bi_{42}$. The results for σ and S are shown in figures 1 and 2, together with the data of Enderby and Collings (1970). The minimum in the conductivity was found precisely at stoichiometry, in agreement with the previous work on this system. An interesting feature of the current data is the very rapid rise in σ on the magnesium-rich side of stoichiometry, followed by a much more gentle rise once σ reaches about $1500 \Omega^{-1} \text{ cm}^{-1}$. This is not clear in the data of Ilschner and Wagner or those of Enderby and Collings as they did not cover as many points close to the stoichiometric composition. It is also notable that the results for liquid Sr–Bi and Sr–Sb alloys (Xu *et al* 1993) show a similar sharp change in $d\sigma/dx$ at around this order of magnitude of the conductivity. At all the compositions studied, $d\sigma/dT$ was always greater than zero. The thermopower shows good agreement with the results of Enderby and Collings and does not rise above $\pm 10 \mu\text{V K}^{-1}$ over the composition range studied.

3.2. Structure

The total diffraction patterns measured over the range $0.5 \text{ \AA}^{-1} < Q < 20 \text{ \AA}^{-1}$ for all the compositions studied are shown in figure 3. The features of the three $F(Q)$ are broadly similar, with the same, slightly asymmetrical first peak appearing in each. This slight asymmetry gives a much smaller feature than the shoulder on the high- Q side of the first peak reported by Weber *et al* (1979). Similarly our results show a prominent feature at about 1.8 \AA^{-1} which is barely noticeable in their data. Intriguingly, this peak is strongest in Mg_3Bi_2 . The separately measured $F(Q)$ for the three samples from the LAD 35° and 60° detectors, which give the highest resolution for this area of Q -space, are shown for $0 \text{ \AA}^{-1} < Q < 2 \text{ \AA}^{-1}$ in figure 4. This indicates that the relative strength of this feature is not an artefact due to statistical fluctuations in the data. The corresponding total $g_{tot}(r)$ are shown in figure 5. The first peak in $g_{tot}(r)$ is relatively sharp and occurs at 2.95 \AA , which is consistent with the sum of the ionic radii of Mg^{2+} and Bi^{3-} , but, apart from this prominent first peak, the real space structure is relatively featureless, and no major differences were observed between the three compositions.

4. Discussion

The results presented in this work confirm the unusual behaviour of the electrical conductivity of this system reported by previous workers. We have also shown that the thermopower never rises above about $\pm 10 \mu\text{V K}^{-1}$ even for compositions very close to stoichiometry. This indicates, as suggested by Enderby and Barnes (1990), that this material cannot be understood using a rigid-band picture for the density $N(E)$ of states and energy-dependent conductivity $\sigma(E)$. The very deep minimum in σ suggests that $N(E)$ has a gap or deep pseudo-gap with a corresponding conductivity gap ΔE in $\sigma(E)$ at the composition Mg_3Bi_2 . For a rigid-band model this should give

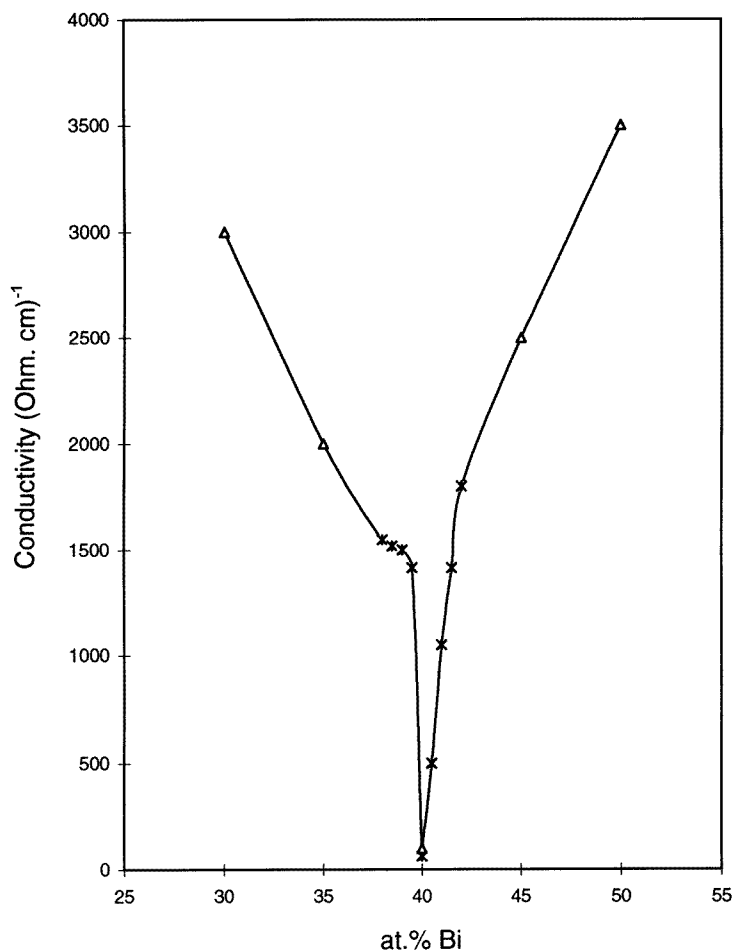


Figure 1. The electrical conductivity of liquid Mg–Bi as a function of Bi content: ×, current data; Δ, data of Enderby and Collings (1970).

rise to S -values of a few hundred microvolts per kelvin immediately away from the stoichiometric composition. The absence of such large values of S in our data suggests that a rapid collapse in ΔE takes place as the composition is moved slightly away from stoichiometry.

We shall now consider this departure from typical liquid semiconductor behaviour in a little more detail. Barnes (1993) described a scheme for calculating the electronic properties of a model charge-transfer-like liquid semiconductor using a simple quasi-ionic density $N(E)$ of states and showed how it could be used to interpret the behaviour of liquid Tl–Te. The reader is referred to this paper for the details of the model but the general form of the density of states used is shown in figure 6. The principle features of the model are the energy gap ΔE , and the bandwidths of the valence and conduction bands. These bands are

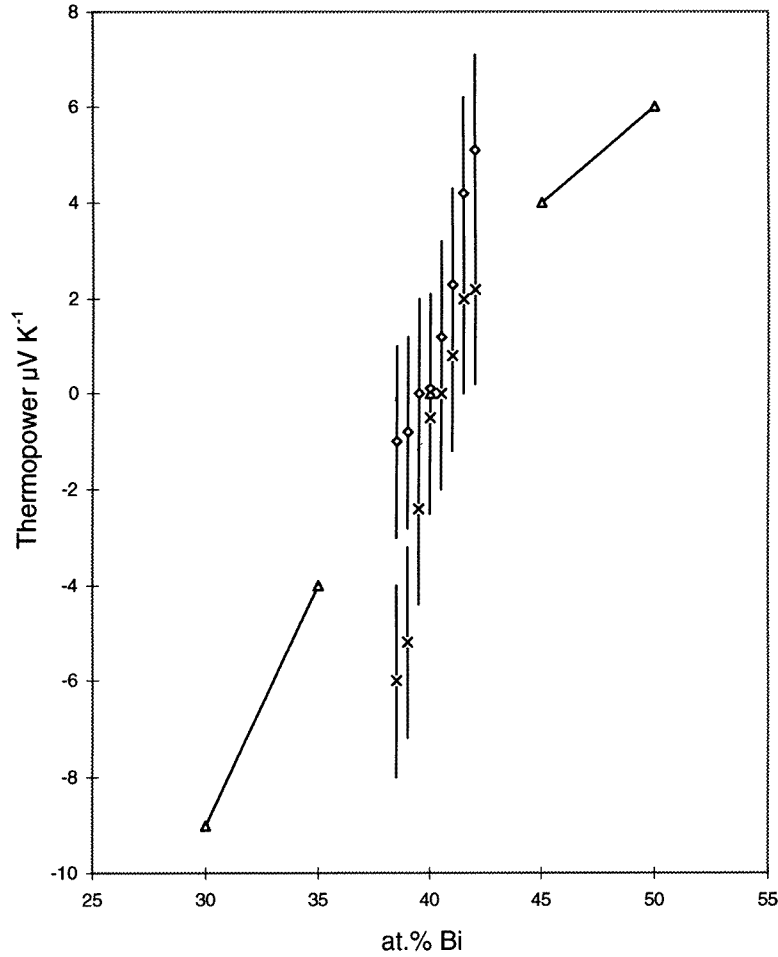


Figure 2. The thermopower of liquid Mg–Bi as a function of Bi content: ×, current data using a molybdenum reference; ◇, current data using a chromel reference; △, data of Enderby and Collings (1970).

fixed to have free-electron-like edges such that

$$N(E) = \begin{cases} k_v \sqrt{(E - E_{vl})} & E_{vl} \leq E \leq E_{vc} \\ k_v \sqrt{(E_{vh} - E)} & E_{vc} \leq E \leq E_{vh} \\ k_c \sqrt{(E - E_{cl})} & E_{cl} \leq E \leq E_{cc} \\ k_c \sqrt{(E_{ch} - E)} & E_{cc} \leq E \leq E_{ch} \end{cases}$$

where

$$k_{c,v} = 3\sqrt{2}n_b/2\Gamma^{3/2}$$

and n_b is the total number of electron states in the band of width Γ . It should be noted that in this model it is the values of k_c and k_v which are important in determining the properties of the system. Therefore the band widths should be considered as a means of adjusting k

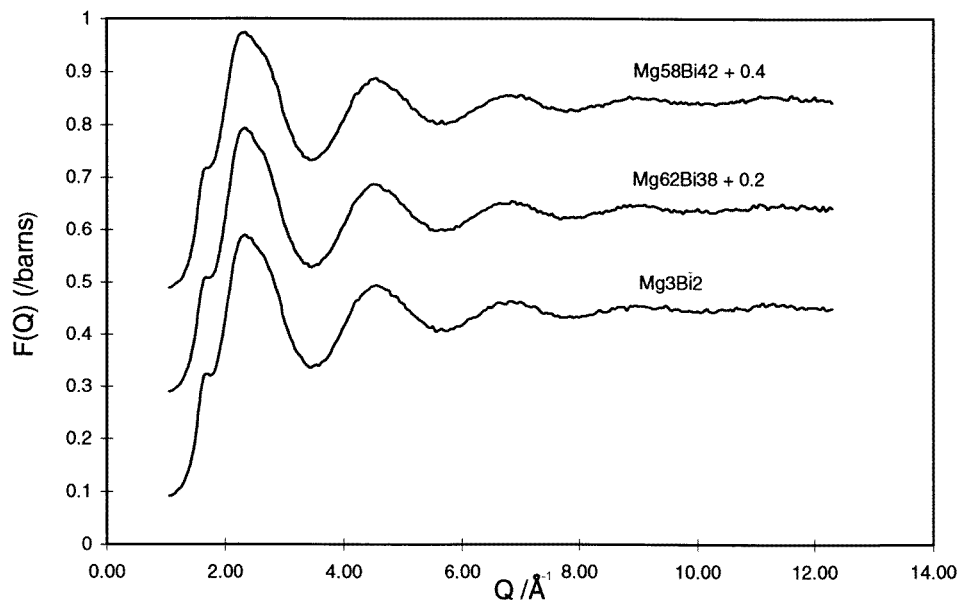


Figure 3. The total structure factors of liquid $\text{Mg}_{1-x}\text{Bi}_x$ for $x = 0.38, 0.4$ and 0.42 .

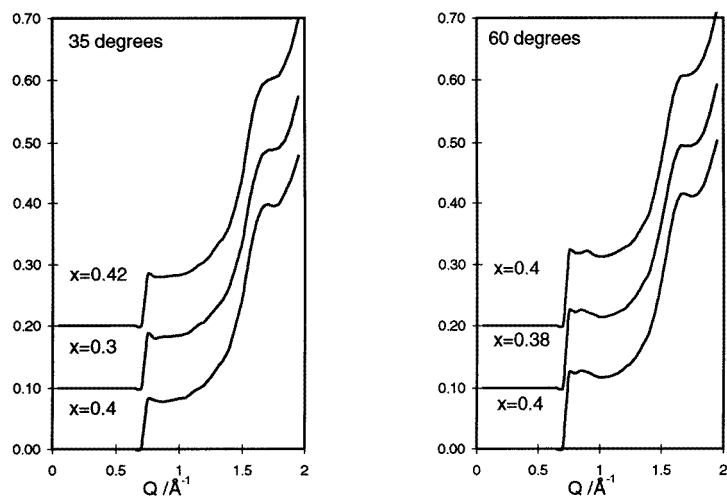


Figure 4. The total structure factors of liquid $\text{Mg}_{1-x}\text{Bi}_x$ of $0 < Q < 2 \text{ \AA}^{-1}$ for the LAD 35° and 60° detectors.

and not necessarily as a true reflection of the band widths of the material (in practice it is only the shape of $N(E)$ within a few $k_B T$ of the edge that determines the position of the chemical potential and hence the properties of the system). The important point about the model is that it makes firm predictions concerning the composition dependences of σ and S for a charge-transfer-type liquid semiconductor as the chemical potential is calculated for each composition and temperature from the model density of states. This method can be

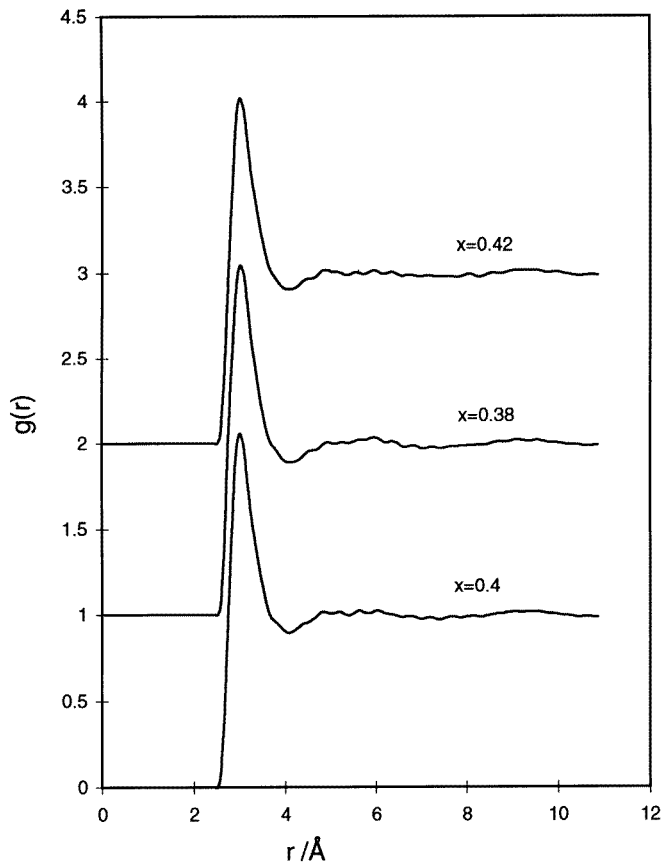


Figure 5. The total normalized $g(r)$ for liquid $Mg_{1-x}Bi_x$.

extended to any form of the density of states, if it is known.

To calculate the transport properties σ and S of the system, a relationship between $N(E)$ and $\sigma(E)$ (the energy-dependent conductivity in the Kubo–Greenwood equations) must be used. For simplicity in this work we have assumed that the relation

$$\sigma(E) = AN(E)^2$$

can be applied where the constant A can be determined empirically or estimated using the random-phase approximation (Cutler 1977). It should be noted that by making this assumption, $\sigma(E)$ decreases linearly towards the mobility edges in the same manner as the generic model of $\sigma(E)$ proposed by Enderby and Barnes (1990). The behaviour of Mg_3Bi_2 predicted from this model is shown in figures 7 and 8. The band widths ($\Gamma_v = 5$ eV and $\Gamma_c = 3$ eV) were taken directly from calculations of the crystalline density of states of Mg_3Bi_2 by Robertson (1979), and σ and S were determined for energy gaps $\Delta E = 0.0, 0.2$ and 0.4 eV. These should also apply to similar liquids such as Mg–Sb (Verbrugge and van Zytveld 1993), Sr–Bi and Sr–Sb (Xu *et al* 1993). It can be seen that in all cases a deep minimum in σ occurs at stoichiometry, and large changes in the thermopower are predicted on crossing stoichiometry. We have not found any parameters that can reproduce the very low thermopowers seen in the experimental data using this model.

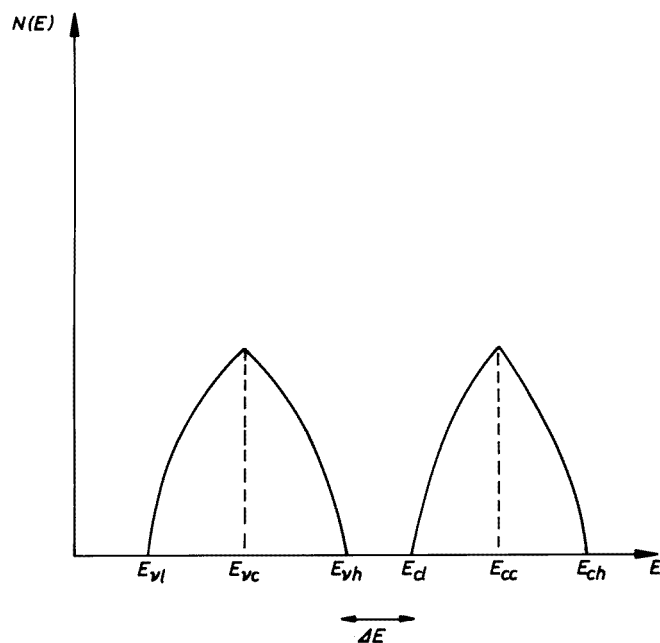


Figure 6. The model density of states used in the calculations of the conductivity and thermopower.

The possible effects of localization have not been discussed in the results so far. A very simple and harsh method of including them is to take the minimum metallic conductivity approach by setting $\sigma = 0$ for values of $N(E)$ below a given value (or equivalently $\sigma(E)$). This assumption is equivalent to saying that $\sigma(E)$ falls rapidly to zero from some minimum value σ_0 within much less than $k_B T$ of the mobility edge. The effect of including such a localization scheme has been tested and the results show that the minimum in the conductivity becomes slightly wider and less sharp, and the thermopower shows a slower transition from p to n type, although its magnitude remains broadly the same.

With the results of these calculations it is clear that the properties of Mg–Bi are rather unusual and pose severe problems when considering how the density of states changes as a function of composition and perhaps, more crucially, on the applicability of the Kubo–Greenwood equations for calculating the transport properties of these materials. In the calculations, the composition range over which the thermopower remains less than $\pm 10 \mu\text{V K}^{-1}$ is approximately 1 at.% or less which corresponds to a slope $d|S|/dx = 20 \mu\text{V K}^{-1} (\text{at.}\%)^{-1}$ at stoichiometry. The experimental results show that the thermopower never exceeds $\pm 10 \mu\text{V K}^{-1}$ and the slope is closer to $dS/dx = 2 \mu\text{V K}^{-1} (\text{at.}\%)^{-1}$. This behaviour is more typical of a liquid metal with a shallow minimum (or pseudo-gap) in the density of states near the chemical potential, which is in direct disagreement with the semiconductor behaviour inferred from the conductivity data. The composition dependence of the conductivity shows that the rise in σ for small deviations in composition away from stoichiometry is much more rapid in the experimental data than in the calculations. The implication of this observation is either that the slope of $\sigma(E)$ at the mobility edges is much larger than that used in the calculations or that $N(E)$ or $\sigma(E)$ (or both) changes rapidly with composition so that the material rapidly becomes metallic on either side of stoichiometry.

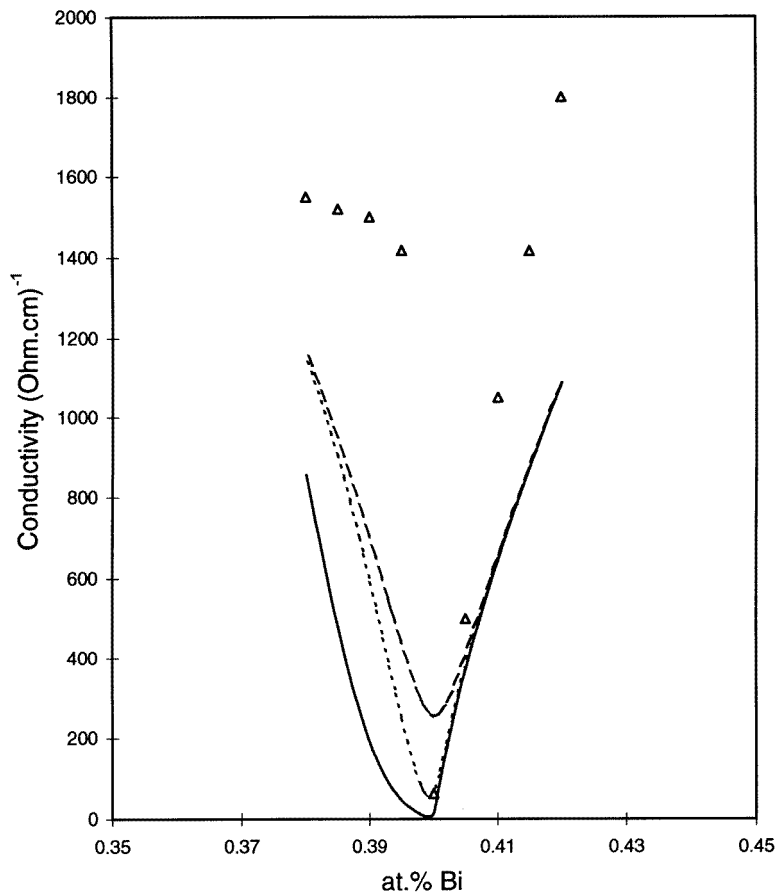


Figure 7. The experimental conductivity data (Δ) as a function of Bi content plotted against the model calculations for $\Delta E = 0.0$ eV (---), 0.2 eV (.....) and 0.4 eV (—).

In the experimental data it is noticeable that, within a few per cent of stoichiometry, there is a noticeable change in the gradient $d\sigma/dx$ and the conductivity rises much less rapidly. Closer examination shows that, if the data points within 1 at.% of stoichiometry are ignored, the experimental data (conductivity and thermopower) are fully consistent with a metallic alloy with a deep minimum in the density of states at the stoichiometric composition. This behaviour is also seen in other group II–group V alloys (Xu *et al* 1993) but is most severe in Mg–Bi.

In summary, the conductivity and thermopower of liquid Mg–Bi alloys show behaviour typical of metal–metal alloys with a deep pseudo-gap in the density of states, except for compositions very close to stoichiometry where the material develops an energy gap and behaviour typical of a good liquid semiconductor.

It might be expected that such a rapid change in the electronic properties around stoichiometry would be reflected in the atomic structure of the liquid. Weber *et al* (1979) examined the structure of liquid Mg–Bi over a broad range of compositions using neutron and x-ray diffraction, and through an analysis of the mean interatomic distance and coordination number \bar{n} they found strong evidence of the formation of a chemically

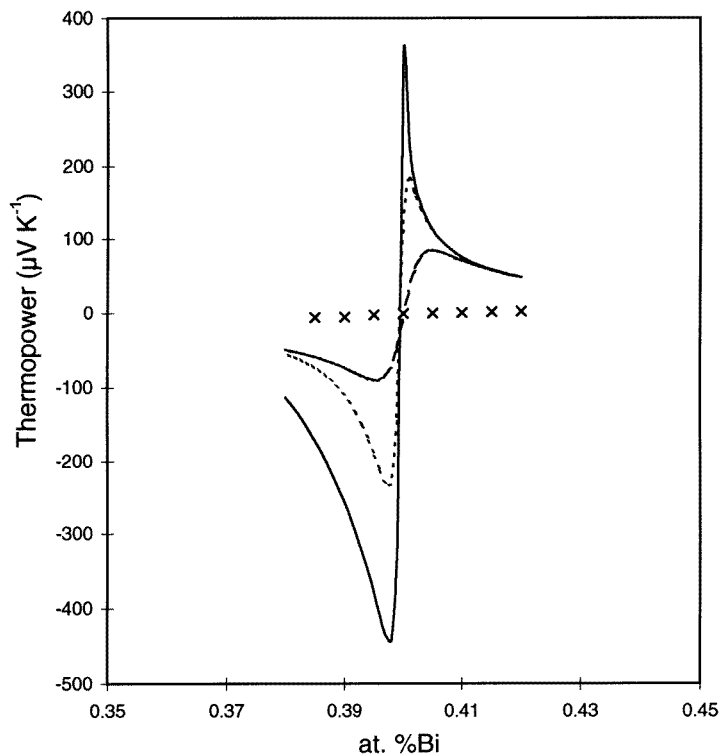


Figure 8. The experimental thermopower data as a function of Bi content (\times) plotted against the model calculations for $\Delta E = 0.0$ eV (---), 0.2 eV (.....) and 0.4 eV (—).

ordered state at the stoichiometric composition. In particular, \bar{n} decreased to less than 6 at stoichiometry, a value more closely associated with molten salts than metal alloys (which show values of the order 10). However, they did not measure the structure for small deviations away from stoichiometry. We therefore remeasured $F(Q)$ at stoichiometry and at 2 at.% either side of stoichiometry. The three total structure factors are shown in figure 3. It is immediately apparent that the $F(Q)$ are broadly similar even though the conductivity of the samples has changed by two orders of magnitude. Our $F(Q)$ at stoichiometry shows some significant differences from those reported by Weber *et al* (1979), notably the shoulder on the high- Q side of the main peak is not as pronounced in our data and, on the low- Q side, the shoulder at 1.8 \AA^{-1} is more pronounced. The latter observation may be due to the higher resolution of LAD at small Q -values. The feature on the low- Q side is of considerable interest as it appears to be more pronounced at stoichiometry than at the two neighbouring compositions. Figure 4. shows this region in more detail for the LAD detectors at 35° and 60° which have the highest resolution for this part of Q -space. The enhancement of this feature is clearly observed in both of these detectors, confirming that it is not a result of any statistical fluctuations in the data. Enderby and Barnes (1990) have discussed the origin of such pre-peaks in liquid semiconductors and have shown, by comparison of theory with experiment, that it is closely related to the effect of charge ordering (heterocoordination) in the molten phase. Barnes *et al* (1994) also showed that the structure of Mg_3Bi_2 immediately before melting ($\beta\text{-Mg}_3\text{Bi}_2$) is a superionic phase characterized as a body-centred cubic lattice

of Bi^{3-} in which Mg^{2+} ions are highly mobile. We therefore conclude that the $F(Q)$ of liquid Mg_3Bi_2 is consistent with charge ordering in agreement with the suggestion that its low electronic conductivity is due to the formation of a charge-transfer gap in the electronic density of states.

There are very few experimental results at the partial structure factor level for this type of material which can be used as benchmarks for discussing our total structure factor data. However, a complete decomposition to partial structure factors has recently been determined for liquid Ag_2Se which also melts from a fast ion phase (Barnes *et al* 1996). This reveals that the dominant contribution to the pre-peak is from $S_{AA}(Q)$ where A is the immobile ion in the superionic phase. The reason that it appears as a relatively weak feature in the total structure factor is because it is almost entirely cancelled out by the negative ‘charge ordering dip’ in $S_{AB}(Q)$ at exactly the same Q -value. In the paper of Weber *et al* (1979), x-ray data for compositions with up to 30 at.% Bi are also shown. In this case the weighting of the x-ray form factors means that $S_{BiBi}(Q)$ dominates the diffraction pattern, and the very strong peak observed at 1.8 \AA^{-1} in their data confirms the conclusion that the origin of the pre-peak in the neutron $F(Q)$ is predominantly from $S_{BiBi}(Q)$.

Unfortunately there are no favourable isotopes of either Mg or Bi which would make it possible to derive unambiguously the partial structure factors of the material using neutron diffraction. However, the relatively large difference between the neutron scattering lengths of magnesium and bismuth ($b_{Mg} = 5.37 \text{ fm}$ and $b_{Bi} = 8.52 \text{ fm}$) and the difference in sizes between the Mg^{2+} (0.75 \AA) and Bi^{3-} (2.13 \AA) ions suggest that it may be possible to obtain reasonable estimates of the partial structure factors of the liquid using a reverse Monte Carlo (RMC) analysis (McGreevy 1993). Therefore a RMC simulation of this liquid was carried out using a total number of 3645 atoms in a cubic simulation box corresponding to the liquid number density of 0.028 \AA^{-3} . A starting configuration corresponding to β - Mg_3Bi_2 was used. The partial $g(r)$ of the simulation data were constrained to limit the distance of closest approach to 2.4 \AA for Mg–Mg and Mg–Bi and 3.8 \AA for Bi–Bi in accordance with the distances observed in the superionic solid. It should be noted that without the constraint on the minimum Bi–Bi distance the simulation tended to give partial structure factors which all look very similar. Figure 9 shows the RMC fit to the total structure factor of liquid Mg_3Bi_2 and it can be seen that it gives a reasonable agreement with the data. Figure 10 shows the corresponding partial $S(Q)$ in the Faber–Ziman formalism obtained from the simulation. Figure 11 shows the partial $g(r)$ determined by Fourier transforming the $S(Q)$. These partial structure factors show close similarities to those of molten salts, most notably the ‘charge ordering dip’ characteristic of heterocoordination described above is observed in $S_{MgBi}(Q)$ at about 1.8 \AA^{-1} , and a strong peak is observed in $S_{BiBi}(Q)$ at the same position as predicted. It is also apparent that they are very similar to the partial structure factors obtained for other materials that melt from fast-ion solids (e.g. Ag_2Se (Barnes *et al* 1996), $SrCl_2$ (McGreevy 1993) and $CuBr$ (Allen and Howe 1992)) with $S_{MgMg}(Q)$ showing a relatively weak feature at the same Q -value as the ‘charge ordering dip’ followed by a stronger feature at slightly higher Q . It is also clear that $S_{BiBi}(Q)$ gives the dominant contribution to the pre-peak in the total structure factor as inferred above. In real space a strong penetration of $g_{MgMg}(r)$ into the first shell of $g_{MgBi}(r)$ is observed and a relatively shallow first minimum in $g_{MgMg}(r)$ is observed. This agrees with the conclusion that the Mg ions are highly mobile in this liquid. The observation of structure to large distances in $g_{BiBi}(r)$ is also consistent with a relatively well ordered Bi–Bi structure through which the Mg ions are free to move.

Recently de Wijs *et al* (1996) have carried out *ab-initio* molecular dynamics simulations

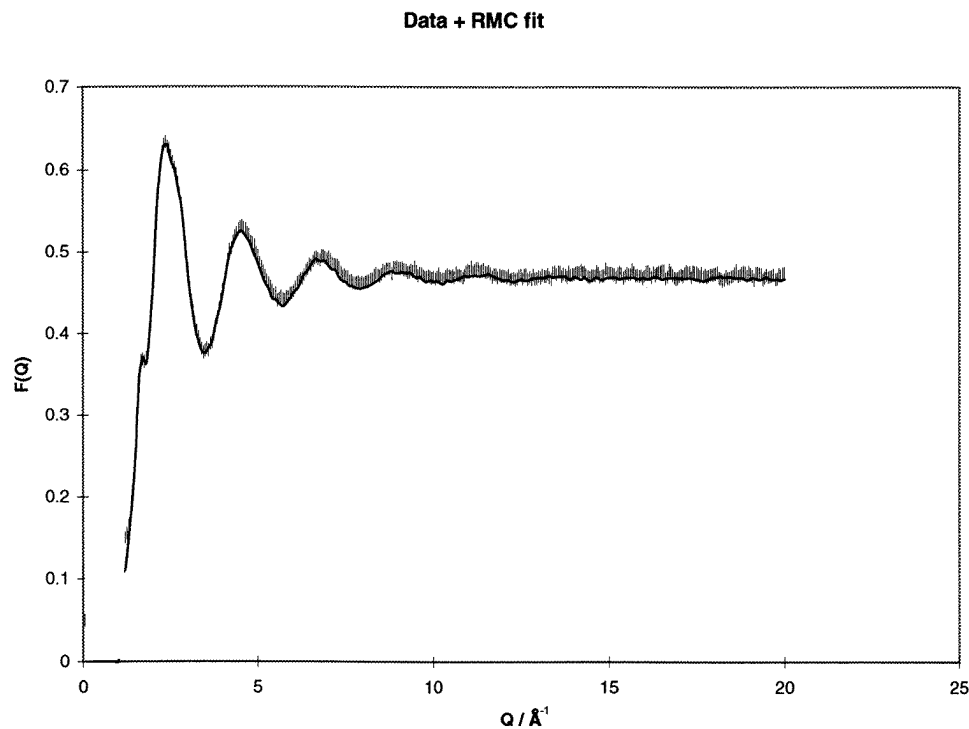


Figure 9. The experimental total structure factor of liquid Mg_3Bi_2 (||||) plotted against the RMC fit (—).

of liquid Mg_3Bi_2 and $\text{Mg}_{62}\text{Bi}_{38}$. These methods are extremely powerful for considering the electronic properties of liquid semiconductors as the forces on the ions are calculated from first-principles quantum methods with no adjustable parameters, and the atomic dynamics and electronic structure are calculated in a self-consistent manner. This is particularly important if off-stoichiometry liquids are to be simulated. It is this ability to obtain simultaneously the electronic structure and to deal with off-stoichiometric compositions that makes the method particularly powerful in the study of liquid semiconductors. Figure 10 shows our RMC partial structure factors in comparison with the *ab-initio* molecular dynamics simulations. The level of agreement between the experiment and the simulation is remarkably high, especially given the limitations of the RMC method in isolating partial structure factors from total structure factor data.

The density of electronic states determined from the *ab-initio* calculation confirms the ionic nature of the liquid although it is particularly interesting that it fails to find a deep minimum in the electronic density of states at stoichiometry which is suggested by the extremely low conductivity of the liquid. de Wijs *et al* discussed this problem and suggested one reason could be the possible problems with the experimentally known compositions when measuring the electronic properties. Our data fully support the results of Xu *et al* (1993) and suggest that the problem lies fundamentally with the simulation at the stoichiometric composition and is most probably due to problems with the local density approximation. The agreement between the electronic properties determined in the experiment and simulation away from stoichiometry suggests that the problems may be

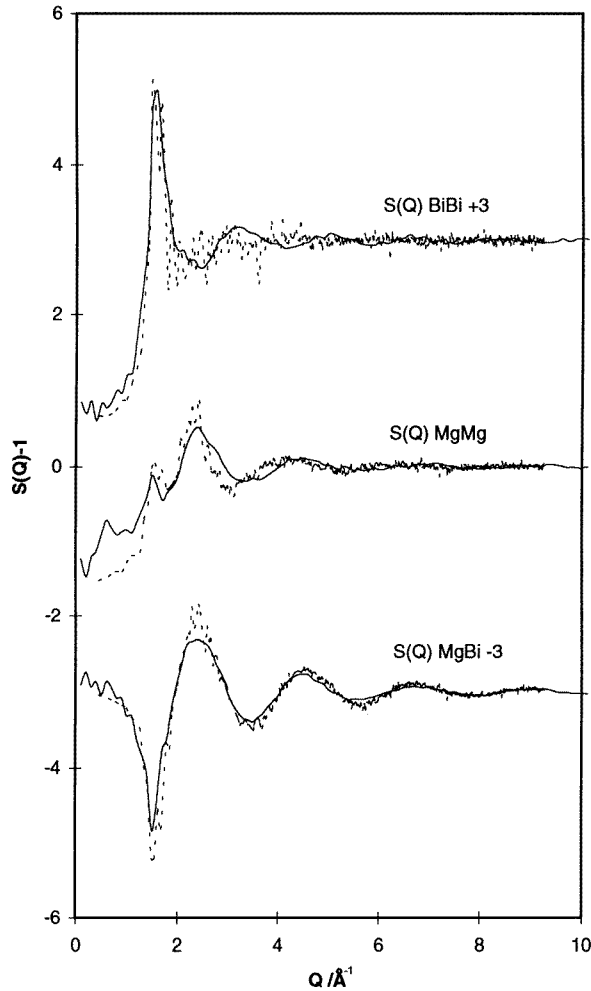


Figure 10. The partial structure factors of liquid Mg_3Bi_2 determined from the RMC fit (—) plotted against the partial structure factors from the *ab-initio* molecular dynamics simulations of deWijfs *et al* (1996).

uniquely associated with the stoichiometric composition. In this respect it should also be noted that liquid Ag_2S and liquid Ag_2Se also show extremely unusual properties at precisely the stoichiometric composition (Ohno *et al* 1990, 1994). An explanation for this behaviour has been suggested by Fortner *et al* (1995) who speculate that there is a coupling between the mobile ions and the electronic density of states in these materials in a manner suggested by Ramasesha (1982) and Huberman (1974).

5. Conclusions

We have carried out measurements of the structure and electronic properties of liquid Mg–Bi alloys with compositions at and in close proximity to the stoichiometric composition Mg_3Bi_2 . The measurements show that there is very little change in the basic structure of

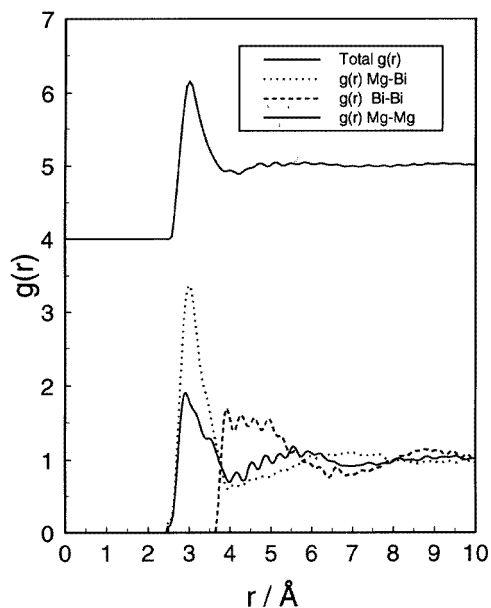


Figure 11. The $g_{MgMg}(r)$ (—), $g_{MgBi}(r)$ (·····) and $g_{BiBi}(r)$ (- - -) for Mg_3Bi_2 determined from the RMC fit to the data, plotted with the total $g(r)$ from the data.

the alloys even though the electrical conductivity changes by two order of magnitude for a 2 at.% variation in composition around stoichiometry. A comparison of the experimental data and *ab-initio* molecular dynamics simulations of de Wijs *et al* (1996) confirms the ionic nature of the liquid. However, apart from the region within 1 at.% of stoichiometry, the conductivity and thermopower are more characteristic of a poor liquid metal with a small dip in the electronic density of states. Although the poor conductivity at stoichiometry conforms well with the ionic picture of the liquid, the rapid change to metallic behaviour which takes place when moving off stoichiometry is not understood. It is speculated that the high mobility of the Mg ions in the liquid may be the origin of this behaviour in a similar manner to that predicted for other liquid semiconductors, but more experimental and theoretical work is needed to test these conclusions.

Acknowledgments

One of us (CG) would like to acknowledge the award of a scholarship from the British Council. We also acknowledge support from the Engineering and Physical Sciences Research Council and the ISIS spallation neutron source. We are also very grateful to Dr G A de Wijs for sending us his numerical results from his *ab-initio* molecular dynamics calculations.

References

- Allen D A and Howe R A 1992 *J. Phys.: Condens. Matter* **4** 6029
 Barnes A C 1986 *PhD Thesis* University of Bristol
 ——— 1993 *J. Non-Cryst. Solids* **156–8** 675

- Barnes A C, Guo C and Howells W S 1994 *J. Phys.: Condens. Matter* **6** L467
- Barnes A C, Lague S B, Salmon P S and Fischer H 1996 *J. Phys.: Condens. Matter* submitted
- Cutler M 1977 *Liquid Semiconductors* (New York: Academic)
- de Wijs G A, Pastore G, Selloni A and van der Lugt 1996 *J. Phys.: Condens. Matter* **8** 1879
- Enderby J E and Barnes A C 1990 *Rep. Prog. Phys.* **53** 85
- Enderby J E and Collings E W 1970 *J. Non-Cryst. Solids* **4** 161
- Faber T E 1972 *Introduction to the Theory of Liquid Metals* (Cambridge: Cambridge University Press)
- Fortner J, Saboungi M L and Enderby J E 1995 *Phys. Rev. Lett.* **74** 1415
- Huberman B A 1974 *Phys. Rev. Lett.* **32** 1000
- Ilschner B R and Wagner C 1958 *Acta Metall.* **6** 712
- McGreevy R L 1993 *J. Non-Cryst. Solids* **156–8** 949
- Ramasesha S 1982 *J. Solid State Chem.* **41** 333
- Robertson J 1979 *Phil. Mag. B* **39** 479
- Ohno S, Barnes A C and Enderby J E 1990 *J. Phys.: Condens. Matter* **2** 7707
- 1994 *J. Phys.: Condens. Matter* **6** 5335
- Soper A K, Howells W S and Hannon A C 1989 *Rutherford Appleton Laboratory Report* RAL-89-046
- Verbrugge D M and Zytveld J B 1993 *J. Non-Cryst. Solids* **156–8** 736
- Weber M, Steeb S and Lamparter P 1979 *Z. Naturf. a* **34** 1398
- Xu R, de Groot R A and Van der Lugt 1993 *J. Phys.: Condens. Matter* **5** 7551