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2007 J. Phys.: Condens. Matter 19 335202

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J. Phys.: Condens. Matter **19** (2007) 335202 (10pp) doi:10.1088/0953-8984/19/33/335202

Polyanions in molten KPb—a paradox explained?

T Arai[1], L Pusztai[2] and R L McGreevy[3]

[1] Department of Mathematics and Physics, National Defense Academy, Yokosuka 239, Japan
[2] Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, H-1525 Budapest, PO Box 49, Hungary
[3] ISIS, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot OX11 0QX, UK

Received 15 May 2007
Published 4 July 2007
Online at stacks.iop.org/JPhysCM/19/335202

Abstract
We have created new models of the structure of liquid KPb at 873, 1473 and 1873 K. These are used to illustrate specific points concerning the 'existence' of Pb_4^{4-} polyanions or 'Zintl' ions. We conclude that such groupings exist but are only transient, probably with a timescale of the order of 1 ps. All of the existing experimental data are consistent with such a model.

1. Introduction

There have been many papers published, and much discussion, concerning the structure of molten 'Zintl' alloys. These are typically alloys of an alkali metal and an element from groups 13–16 of the periodic table, such as K_xPb_{1-x}. A characteristic property of such alloys is that their resistivity shows a well defined maximum as a function of composition, often at or near the equiatomic composition [1]. Other parameters, such as the temperature derivative of the resistivity [1] or the Knight shift [2], also show maxima/minima at the same composition. These results have been interpreted following the ideas developed by Zintl and Brauer to explain features of the crystal structure of the same materials [3]. For example, K donates electrons to the more electronegative Pb. At the equiatomic composition Pb forms tetrahedral Pb_4^{4-} 'Zintl' ions which are iso-electronic with P_4; this is known to form stable tetrahedral molecules in the liquid and vapour phases. These ideas have been extended to other polyanions such as dimers (e.g. Te in KTe), chains (e.g. Sb in KSb) and networks (e.g. Al in LiAl). (The terms Zintl ion and polyanion seem now to be used in the literature in slightly different contexts, the former generally referring to a specific well defined geometrical unit while the latter refers to a less well defined, but similar, atomic cluster.)

Structural evidence for the existence of polyanions in the liquid state comes primarily from the presence of a so-called 'first sharp diffraction peak' (FSDP) in the neutron diffraction pattern [4] at values of momentum transfer, Q, around 1 $Å^{-1}$ (see figure 1). Such peaks signify some form of intermediate range ordering, which could clearly be consistent with an 'inter-molecular' correlation between Pb_4^{4-} ions. This is supported by MD simulations [5]

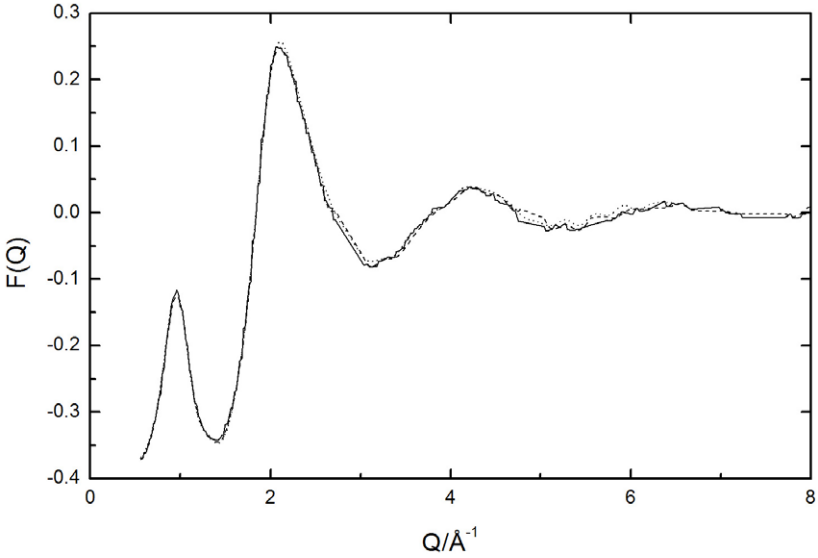

Figure 1. Total structure factor, $F(Q)$, for liquid KPb at 873 K (solid curve) and 'old' (dashed curve) and 'new' (dotted curve) RMC fits (see text for details).

(though these specifically include polyanions in the first place) and RISM modelling [4] (a technique which implicitly requires the presence of molecular units). However, reverse Monte Carlo (RMC) modelling has shown that the structural data can be quantitatively reproduced by models containing either relatively well defined Zintl ions or a more diffuse network type structure, though this still contains Pb atoms with predominantly three-fold coordination [6]. The network idea is supported by the results of *ab initio* (Car–Parinello) molecular dynamics simulations of similar compounds, e.g. CsPb [7, 8], NaSn [9] and KSi [10]. The specific heat of KPb is found to be rather high just above the melting point and then to decrease rapidly with increasing temperature [11], which is consistent with a relatively low initial number of polyanions which then decreases further. Inelastic neutron scattering measurements [12] have not shown any clear evidence of vibrational modes associated with well defined polyanions in the liquid state.

Most of the discussion has centred around the question of the degree of definition of the polyanions. In a review article [13] entitled 'Polyanions in liquid ionic alloys: a decade of research', van der Lugt concludes: 'there remains a paradox. Some sharp experimental features (superstructure peaks and maxima in the resistivities and stability functions) seem to indicate that the Zintl ions in the liquid are near perfect whereas specific heat results and *ab initio* computer simulations clearly show that the structure of the liquid is seriously blurred'. Certainly well defined polyanions exist in the low temperature crystalline state, and some form of predominantly tetrahedral bonding, i.e. the 'basic' Zintl ion idea, is correct in the liquid state. However, further discussion of their degree of definition is probably largely semantic. If Pb atoms show a preference for tetrahedral groupings then the same (instantaneous) structure may either be 'drawn' as a collection of identifiable tetrahedra, plus some 'extra' Pb atoms, or as a network. This problem is illustrated in this paper using a new RMC model of liquid KPb.

The central question would then be whether the 'identified' Pb tetrahedra keep the same Pb atoms as neighbours for a significant period of time (in comparison to the typical diffusion time in the liquid) or whether they exchange neighbours. Such information could be extracted

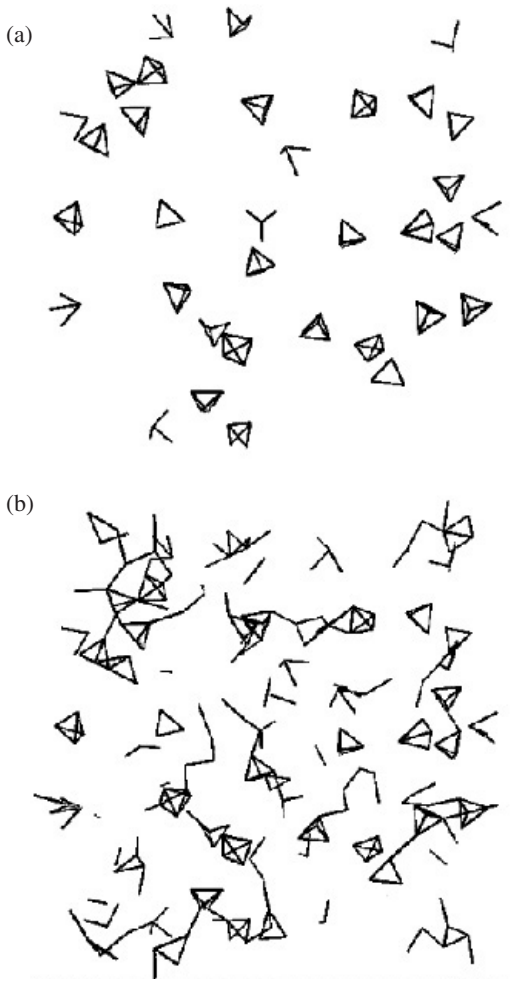

Figure 2. Pb–Pb bonds in the new RMC model for KPb at 873 K. (a) Bonds between Pb atoms in the 'original' Zintl ions are drawn (see text). (b) Bonds between all Pb atoms less than 3.6 Å apart are drawn.

from *ab initio* simulations. This has unfortunately not been done for the existing simulations of compounds most similar to KPb, but it has been done for Ag_xSe_{1-x} [14]. In these liquids Se are supposed to form covalently bonded 'chain' structures, but the simulations found that the lifetimes of the bonds were 'surprisingly short', of the order of 1 ps, and there were many relatively short 'cross-linked' chains. In KPb such a short lifetime would be consistent with the rapid break-up of polyanions as temperature increases.

Neutron diffraction measurements of the structure factor of liquid KPb at elevated temperature (and pressure) show that the FSDP in the structure factor remains, though it broadens and shifts to slightly lower Q [15]. One interpretation of this might be that significant numbers of polyanions remain at high T, which would contradict the specific heat data, and their average separation increases slightly. In this paper we show, using a new method for modelling the structure of expanded liquid metals, that the data are also explicable in terms of a simple break-up of polyanions, and there is no need to propose any increased local separation (though the average separation must of course increase due to the decrease in density). The

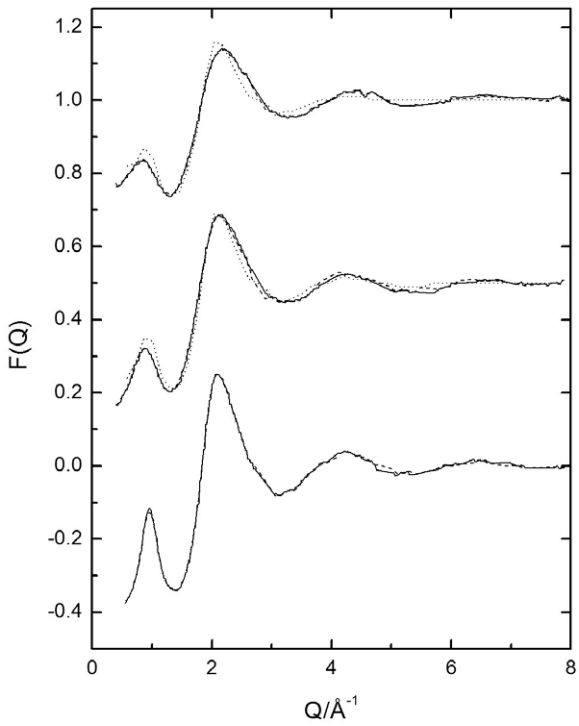

Figure 3. Total structure factors, $F(Q)$, for liquid KPb at 873 K (bottom), 1473 K (centre) and 1873 K (top). Solid line, experiment; dashed line, RMC model; dotted line, models obtained by atom removal as described in the text.

results presented will enable us to draw some general conclusions regarding the 'nature' of Zintl ions, or polyanions, in the liquid state.

2. RMC modelling

The data to be modelled have been obtained by neutron diffraction [4, 15]. The relative contributions to the scattering of the different partial structure factors KK:KPb:PbPb are in the ratios 0.079:0.404:0.507, i.e. Pb is the major contributor. Note that the equivalent ratios for x-ray diffraction are 0.035:0.306:0.659, so an x-ray measurement would not provide significantly different information. More distinct atom-specific information is provided by Pb edge EXAFS, where the effective ratios are then 0:0.188:0.812. Such a measurement has been performed, but this is not technically an easy experiment so the quality of the data was not high [16]. However it could be shown that the data were consistent with the RMC model (i) as defined below.

In order to illustrate a specific point concerning the confusion that can arise as a result of different 'perceptions' of a particular atomic structure, we have created a new RMC model of liquid KPb, slightly different from those of our previous study [6]. In that case two models were created:

(i) No constraints were applied, i.e. the structure consisted of individual K and Pb atoms. The result was a network type Pb structure with predominantly three-fold coordination. About 25% of the Pb atoms could be identified as being in distorted tetrahedral polyanions, but none in well defined Zintl ions.

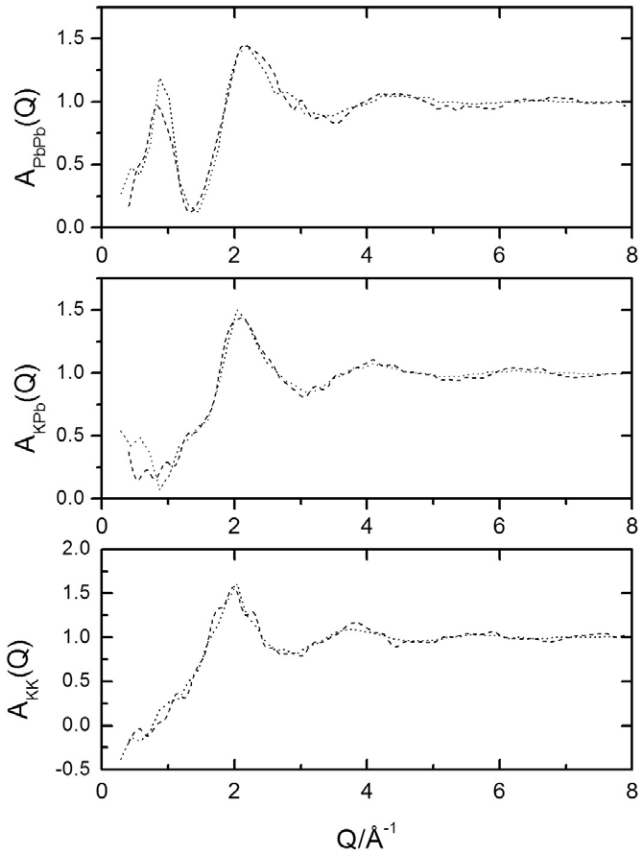

Figure 4. Partial structure factors, $A_{ij}(Q)$, for KPb at 1473 K. Symbols as in figure 3.

(ii) Modelling was started from a structure consisting of separated Pb_4 tetrahedra and K atoms. A constraint was applied such that each Pb atom had three Pb neighbours within 3.6 Å. Each Pb atom in the final model therefore had its original three neighbours, and only these neighbours, within the specified distance. Such a grouping was identified as a polyanion, even though there might be some significant distortions of the original tetrahedra. The experimental data were found to be inconsistent with a high proportion of undistorted Zintl ions.

Since model (i) may be considered as the least 'Zintl-like' that is consistent with the data, and model (ii) as the most 'Zintl like', we have here deliberately created an intermediate structure which may be rather more realistic. Starting from model (ii), where all Pb atoms have exactly three Pb neighbours within 3.6 Å, we have removed the coordination constraints on half of the tetrahedral groups, i.e. the model consists of 50% free atoms and 50% polyanions (there is no particular significance to the choice of 50%). We have then applied a new form of constraint where each Pb atom in a polyanion keeps its original three neighbours within 3.6 Å, but there is no constraint on its total number of Pb neighbours.

The first point to note is that when RMC modelling with the new constraint was started from the 'Zintl ion' model [6] (case (ii) above) the difference between the experimental and model structure factors decreased rapidly, by roughly a factor of two, even though the original

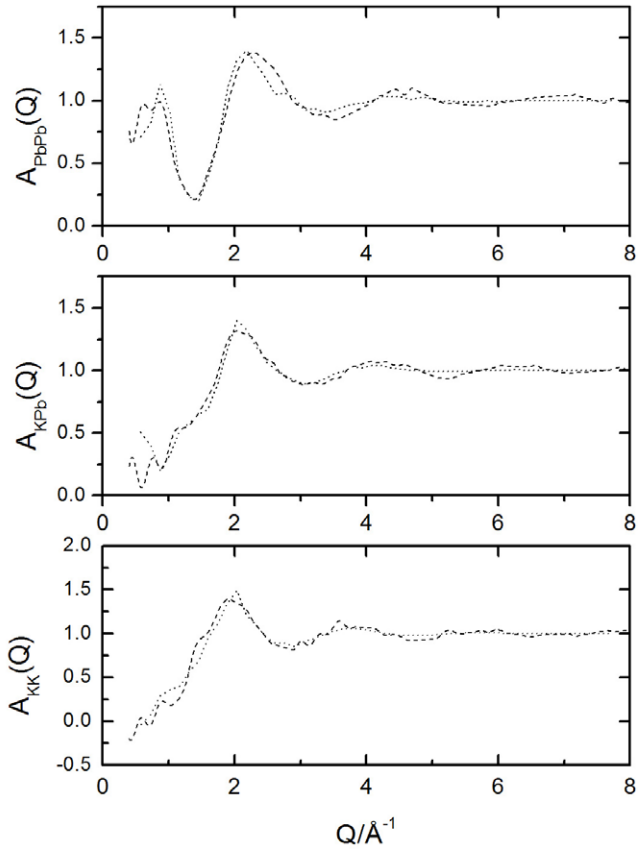

Figure 5. Partial structure factors, $A_{ij}(Q)$, for KPb at 1873 K. Symbols as in figure 3.

model was already considered to be a reasonable fit to the data. Figure 1 shows the experimental data and fits for the 'old' and 'new' models. The results suggest that the imposition of a constraint of exactly three-fold Pb–Pb coordination within 3.6 Å is too severe. In fact this is hardly surprising, since there is no experimental information that actually suggests that such a specific constraint should be applied.

In figure 2 we show two different views of the resulting RMC model. The atomic positions in both are identical. In figure 2(a) only bonds within the 'original' Zintl ions are drawn, whereas in figure 2(b) bonds are drawn between all Pb–Pb pairs separated by less than 3.6 Å. (We have not drawn the atoms themselves as 'balls' since this only obscures the bonding and provides no additional information.) Although the actual atomic structures are *identical* the perception in figure 2(a) is of a reasonably well defined 'molecular' liquid, whereas figure 2(b) seems quite clearly to be a network. This illustrates one of the major problems in structural studies of Zintl ions, or indeed of any form of complex ions, in the liquid state—what constitutes a complex ion?

3. High temperature modelling

For modelling of the high T structure of liquid KPb we have used a technique developed by Arai and McGreevy [17] in studies of the structure of expanded Cs. We start from the unconstrained

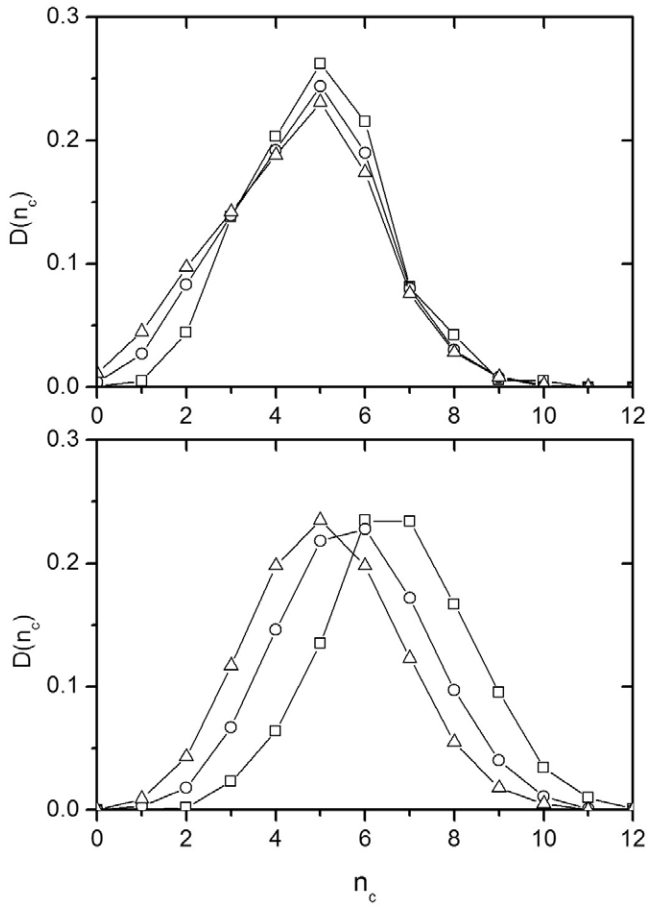

Figure 6. Coordination number distributions for KPb from 'atom removal' models at 873 K (squares), 1473 K (circles) and 1873 K (triangles). Bottom, K atoms within 5.5 Å of each other. Top, Pb atoms within 5.0 Å of each other.

RMC model for KPb at 873 K [6]. K and Pb atoms are removed from this model until the density decreases to that corresponding to the required high temperature and pressure; here we have made models for 1473 and 1873 K. In the Cs study it was found necessary to apply a criterion to atom removal, since random removal could not reproduce the experimental structure factor. In the present case we have found that random removal is satisfactory for K atoms, but a criterion has to be applied to Pb atoms such that the coordination number distributions of K and Pb become more similar at high T. In addition, in order to account for the increase in temperature, a random Gaussian displacement is added to the position of each remaining atom. For 1473 K the mean squared displacement is 0.3 $Å^2$ and for 1873 K it is 0.4 $Å^2$. In figure 3 we show the calculated structure factors for KPb, in comparison with the experimental data [15]—the agreement is remarkably good, particularly in view of the simplicity of the method. Figures 4 and 5 show the corresponding partial structure factors; figure 6 shows the coordination number distributions. It can be seen that the distributions for Pb and K become more similar at high T.

The main point to note here is that the FSDP in the models decreases in intensity and shifts to slightly lower Q as T increases. (The shift is not quite as large as in the experiment but we

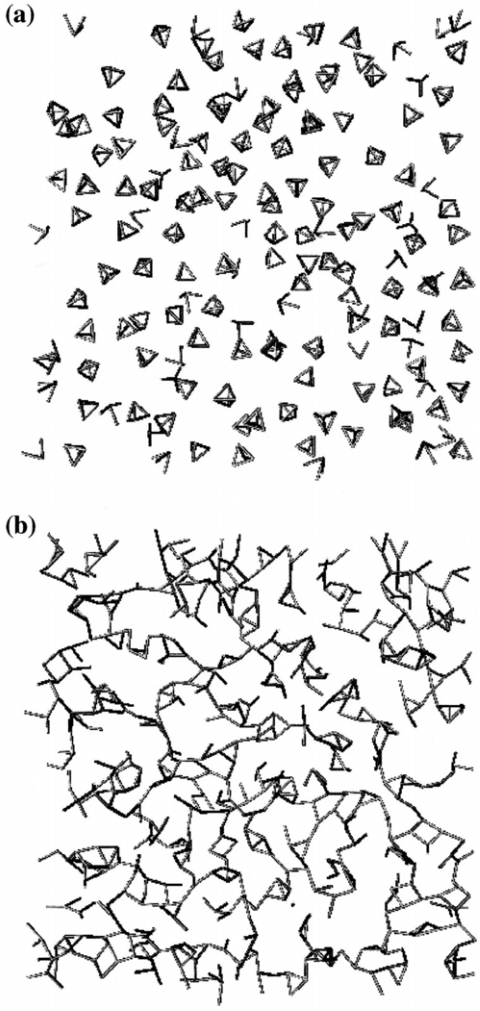

Figure 7. Models of two structures with the same density and with three-fold coordination within the same distance. (a) Tetrahedral clusters (100% three-fold coordination). (b) Network structure (94% three-fold coordination). In both cases a 10 Å slice is drawn. Bonds are not drawn in those cases where both atoms are outside the slice.

have not gone to great lengths to reproduce the data exactly.) However, the atomic positions *do not change* (apart from the small random Gaussian displacement). Atoms are simply removed. The shift to lower Q is therefore a natural consequence of two factors:

(i) polyanion break-up (atoms are removed so the number of such groupings naturally decreases) and
(ii) the distinction between K and Pb becomes less.

This is entirely consistent with the picture provided by specific heat measurements. A FSDP does not in itself indicate the presence of any particular type of structural unit, but simply of some form of intermediate range ordering. This type of ordering can change in nature, for example the 'units' may break up, without any dramatic change in the position

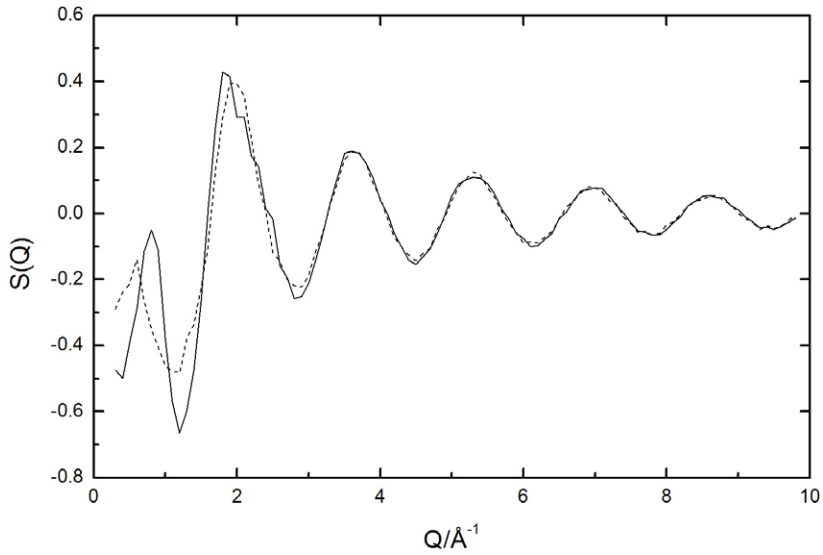

Figure 8. Structure factors corresponding to the structural models shown in figure 7 (a) solid curve and (b) dashed curve.

or intensity of the FSDP. To illustrate this we show in figure 7 two structures with the same density and with close to 100% three-fold coordination within the same distance. In figure 8 we show the corresponding structure factors. These are very similar, but one structure is a completely connected network containing no distinct three-fold coordinated clusters, and the other consists only of separated tetrahedral clusters. Note that the FSDP shifts to lower Q and becomes slightly less well defined for the network structure in comparison with the cluster structure. This is the type of change observed experimentally for KPb as temperature increases.

4. Discussion and conclusions

Here we have presented two very simple results from structural modelling of molten KPb, but they enable us to tie together many seemingly disparate views into a single coherent picture. The conclusions presented here are consistent with all of the available experimental data (electrical conductivity, specific heat capacity, diffraction) and models (RMC and *ab initio*)

Firstly we would stress the fundamental Zintl idea is confirmed by all results—Pb atoms in liquid KPb have a preference for forming approximately tetrahedral groupings which are associated with increased electron localization, i.e. they may be considered as polyanions. However, this is only a *preference*; such groupings are only *transient*. Here it is crucial to distinguish between the timescale for behaviour relating to electronic conduction and that relating to atomic diffusion. If the polyanion groupings last for times of order 1 ps then this is long on the electronic timescale, so the liquid appears ionic, but relatively short on the diffusive timescale, i.e. the polyanions cannot really be considered as stable complex ions in a structural context (see e.g. the simulation results for Ag_xSe_{1-x} [14]). Data from electronic measurements (resistivity, Knight shift) can therefore be perfectly consistent with those from atomic measurements (diffraction, inelastic neutron scattering, EXAFS) and macroscopic measurements (specific heat). The sharp peak in the resistivity occurs at the equiatomic composition because here the preference for tetrahedral groupings is optimized. The structure

factor provides an 'instantaneous' picture of the structure (i.e. short on a timescale compared to 1 ps), so the preference for tetrahedral clustering is clear and the FSDP is sharp. This would suggest that elastic scattering, corresponding to an average over a longer time period, would produce a smaller FSDP. This could be tested experimentally.

As the liquid cools and then crystallizes the preference for certain local groupings naturally combines with the presence of long-range order to make such groupings a dominant feature of the crystal structure. However, in the high temperature crystal it seems unlikely that the division between Zintl ions is structurally so distinct; even though the Pb remain in their original groupings the coordination number (using the same definition as for the liquid) is probably not exactly three and the instantaneous structure probably looks quite 'network-like'. As T increases in the liquid state the thermal vibrations naturally increase the variety of local structural groupings, so Zintl ions may be considered to 'break up'. There is a more rapid exchange of atoms which at any instant are considered to be 'in' Zintl ions with those which are 'out'. Note that Pb 'not' in Zintl ions may only be 0.1–0.2 Å away from positions where they 'are' in Zintl ions, so the structural changes are very small though the resulting conductivity changes may be significant.

So we can conclude that there is no 'paradox'. Polyanions exist in liquid KPb, and probably in many other similar alloys. Understanding the nature of such atomic groupings is crucial to understanding the physical properties of the system. However, they are not necessarily well defined, thermodynamically stable entities. Their apparent degree of definition depends on the timescale for observation, and to some extent on the semantic definition of a 'polyanion'.

References

[1] Meijer J A, Geertsma W and van der Lugt W 1985 *J. Phys. F: Met. Phys.* **15** 899
[2] van der Marel C, Stein P C and van der Lugt W 1985 *Phys. Lett.* A **95** 4512
[3] Zintl E and Brauer G 1933 *Phys. Chem.* B **20** 245
[4] Reijers H T J, Saboungi M-L, Price D L, Richardson J W Jr, Volin K J and van der Lugt W 1989 *Phys. Rev.* B **40** 6018
[5] Reijers H T J, van der Lugt W and Saboungi M-L 1990 *Phys. Rev.* B **42** 3395
[6] Howe M A and McGreevy R L 1991 *J. Phys.: Condens. Matter* **3** 577
[7] de Wijs G A, Pastore G, Selloni A and van der Lugt W 1994 *Europhys. Lett.* **77** 667
[8] de Wijs G A, Pastore G, Selloni A and van der Lugt W 1995 *J. Chem. Phys.* **103** 5031
[9] Seifert G, Pastore G and Car R 1992 *J. Phys.: Condens. Matter* **4** L179
[10] Galli G and Parrinello M 1991 *J. Chem. Phys.* **95** 7504
[11] Saboungi M-L, Reijers H T J, Blander M and Johnson G K 1988 *J. Chem. Phys.* **89** 5869
[12] Reijers H T J 1990 *PhD Thesis* University of Groningen
[13] van der Lugt W 1996 *J. Phys.: Condens. Matter* **8** 6115
[14] Kirchoff F, Holender J M and Gillan M J 1996 *Phys. Rev.* B **54** 190
[15] Stolz M, Winter R, Howells W S and McGreevy R L 1995 *J. Phys.: Condens. Matter* **7** 5733
[16] Bras W, Xu R, Wicks J D, van der Horst F, Oversluizen M, McGreevy R L and van der Lugt W 1994 *Nucl. Instrum. Methods* A **346** 394
[17] Arai T and McGreevy R L 1997 *Phys. Chem. Liq.* **33** 199