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Abstract. We report on computer modelling studies of the structure of the equiatomic liquid alloy KPb over a temperature range from 873 K up to 1873 K. In the crystalline state, this semiconducting alloy contains tetrahedrally coordinated polyanions Pb_4^{4-}. Recent neutron diffraction results indicate the survival of polyanions in the expanded liquid alloy even up to the highest temperature measured, as indicated by the persistence of a prepeak in the static structure factor $S(Q)$ at a momentum transfer of $Q \approx 1$ Å^{-1} up to 1873 K. Applying the reverse Monte Carlo technique, we demonstrate that there is a structure consistent with the experimental data, which consists of small clusters with a partially tetrahedral arrangement or an open loose structural network of lead atoms, typically with three or fourfold coordination. The calculations show that the peak at approximately 1 Å^{-1} observed in the diffraction patterns occurs predominantly in the partial structure factor $S_{PbPb}(Q)$, which is related to correlations between Pb clusters, for all temperatures. The Pb–Pb bonds in the clusters are fluctuating. With increasing temperature the tendency of Pb atoms to form particular clusters becomes a more general tendency to microphase separation.

1. Introduction

Crystalline KPb contains tetrahedral arrangements of lead atoms. As a consequence of the large difference in electronegativity of the two components, an electron is transferred from the K atom to Pb. Zintl and Brauer [2] proposed that these so-called Zintl ions Pb_4^{4-} are stable, since Pb_4^{4-} is isoelectronic with P_4, which is known to form stable molecules. Each Pb atom has three nearest neighbours in the lead tetrahedron, and seven neighbouring K atoms (three and four at slightly different distances). Geertsma and Dijkstra [3] have pointed out that due to the relatively large size of the alkali metal atom, the formation of Pb_4^4 tetrahedra is energetically more favourable than a structure in which the Pb atoms are evenly distributed over the liquid.

Considerable evidence exists for the survival of these tetrahedral Zintl ions upon melting and a great deal of effort has been devoted to the experimental and theoretical investigation of the structure of the melt [4–18]. The thermodynamic and electrical transport properties of the molten potassium–lead alloy show drastic deviations from ideal mixing behaviour [4–7]. The electrical d.c. resistivity ρ_{el} shows a strong maximum ($\rho_{el} \approx 8.5 \times 10^{-4}$ Ω cm) at the equiatomic concentration of $K_x Pb_{1-x}$. The heat capacity $C_p(T)$ of liquid KPb drastically decreases from a very large value of 80 J mol^{-1} K^{-1} near the melting point to about 40 J mol^{-1} K^{-1} at $T = 1100$ K; this has been interpreted in terms of the dissociation of the polyanions [4, 5]. Neutron diffraction studies of the static structure factor $S(Q)$ of

the molten alloy at a temperature close to the melting point showed a distinct peak at a momentum transfer of about 1 Å^{-1}, which has been interpreted as an indication for the presence of polyatomic structural units [10–12].

Recently we have measured the static structure factor of liquid KPb up to much higher temperatures and correspondingly lower densities [1], in order to follow changes in the structure and arrangement of the polyanions in the expanded liquid state. The data clearly show indications of the persistence of polyanions even up to 1873 K. In order to gain information about the microscopic structure of the expanded liquid alloy, we have performed computer modelling studies based on a random packing of structural units model and the reverse Monte Carlo technique.

2. Methods

In the random packing of structural units (RPSU) model, the structural units are distributed according to a random packing of hard spheres. The structure factor is expressed as

$$S(Q) = f_1(Q) + f_2 [S_c(Q) - 1] \tag{1}$$

where $f_1(Q)$ is the form factor of the structural units, $f_2(Q)$ is a form factor expressing the orientational correlation between the units, and $S_c(Q)$ is the Percus–Yevick solution for the random packing of hard spheres [19–21]. In this study, the orientations of the structural units were taken to be random and uncorrelated.

In analogy to the solid structure, the structural unit was defined to be K_4Pb_4, which consists of a Pb_4 tetrahedron surrounded by a larger K_4 tetrahedron. The distances within the unit were chosen to be slightly larger than in the solid state. Only two parameters are involved in the calculation of the total structure factor: the hard-sphere diameter and the packing fraction $\eta = \pi \sigma_{HS}^3 \rho_0 / 6n$, where n is the number of atoms in the structural unit. A Debye–Waller factor, $\exp(-Q^2 \langle u^2 \rangle / 2)$, where $\langle u^2 \rangle$ is the mean square displacement in the bond distances within the structural unit, is applied to yield the correct damping of oscillations in $S(Q)$ at high Q values.

The reverse Monte Carlo method has been described in detail elsewhere [23–25]. Briefly, RMC is a variation of the standard Metropolis Monte Carlo method in which a sequence of configurations is systematically compared with experimental structure factor data until convergence is reached. One starts with an initial configuration of N particles in a periodic cubic box of side length L. The size of the box is chosen such that the density N/L^3 equals the experimental number density. The starting configurations may be a lattice, a random network or the results of another simulation. Normal periodic boundary conditions are applied, and $g(r)$ and $S(Q)$ are calculated from the configuration. Then, a new configuration is generated by random motion of one particle. The new pair correlation function $g'(r)$ and structure factor $S'(Q)$ are calculated, as are the mean squared differences χ^2 and χ'^2 between the experimental and calculated structure factors. If $\chi^2 > \chi'^2$, then the move is accepted. If $\chi^2 < \chi'^2$, then the move is accepted with probability $\exp(\chi^2 - \chi'^2)$, otherwise the move is rejected and the configuration is changed back to its previous state. These steps are repeated until χ^2 is sufficiently small and oscillates around an equilibrium value. At this point, it is possible to start collecting a set of independent configurations, which correspond to a structure factor that agrees with the experimentally determined one within the experimental error.

A closest distance of approach between pairs of particles was applied as a constraint in our RMC calculations. The smallest of the Pb–Pb distances can be determined from the total $g(r)$ obtained by direct Fourier transformation of $S(Q)$ as being 2.5 Å. For the minimal

K–K distances, a distance of 3.4 Å has been chosen, which is about the closest approach found for K atoms in the pure potassium melt [11, 26]. The K–Pb distance has been chosen to be 3.2 Å. Slightly different choices were also tried but no significant differences in the results were found.

Starting configurations were generated in different ways. The first method was to place atoms at random positions and then move them around. This was used to create starting configurations of 1728 atoms for KPb. A second calculation included the additional constraint that a threefold coordination of Pb is preserved and that the atoms within the lead tetrahedra of the simulation do not get further than 3.6 Å from one another.

We stress that the RMC solution is not unique, but the method has the advantage that the set of simulated functions is self-consistent and corresponds to a possible distribution of particles.

3. Results and discussion

Figure 1 depicts the structure factor $S(Q)$ of liquid KPb, which has recently been measured for various temperatures ranging from the melting point up to $T = 1873$ K [1]. These are Faber–Ziman averaged structure factors, where the partial structure factors $S_{ij}(Q)$ of the atoms i and j are weighted according to their atomic fraction x_i and the mean neutron coherent scattering length $\bar{b}_i$:

$$S(Q) = 1 + \sum_{ij} w_{ij} \left[S_{ij}(Q) - 1 \right]. \tag{2}$$

The weighting factors are given by

$$w_{ij} = \frac{\bar{b}_i \bar{b}_j x_i x_j}{\langle \bar{b} \rangle^2}. \tag{3}$$

The main contributions to the total $S(Q)$ derive from $S_{PbPb}(Q)$ and $S_{KPb}(Q)$, as $w_{PbPb} = 0.517$, $2w_{KPb} = 0.404$ and $w_{KK} = 0.079$. The data in figure 1 clearly show that the height of the peak around 1 Å^{-1} decreases and its width increases with increasing temperature. It has been suggested that this so-called prepeak is mainly caused by intermediate-range correlations between lead polyanions [11, 12]. A significant increase of $S(Q)$ at small Q values occurs at higher temperatures, indicating an enhancement in the composition fluctuations in the liquid under these conditions.

The total Faber–Ziman structure factor was Fourier transformed to give the pair distribution function $n(r) = 4\pi r^2 \rho_0 g(r)$ (see figure 2), where $g(r)$ is the pair correlation function and ρ_0 is the total number density. The first peak in $n(r)$ of liquid KPb is composed of a maximum around 3.2 Å, whose position does not change with temperature. Its height decreases, and a broad shoulder on the high-r side is seen, which shifts towards higher r values with temperature. Comparison with the KPb crystal data reveals that all three partials g_{PbPb}, g_{KPb} and g_{KK} probably contribute to the first peak in $n(r)$. The intratetrahedral Pb–Pb bond length in the crystalline solid state is 3.118 Å, while the average K–Pb and K–K bond lengths are 3.801 Å and 4.007 Å, respectively [11]. By analogy with these crystal structure data, the first peak in $n(r)$ of liquid KPb has been assigned to the Pb–Pb distance and thus gives evidence for the survival of these polyanions into the liquid state. The mean partial coordination number Z_{PbPb} of Pb atoms has been estimated by fitting a Gaussian function to the leading edge of the total correlation function $T(r) = 4\pi r \rho_0 g(r)$ [1]. It remains almost unchanged ($Z_{PbPb} \approx 3.2$–3.5) over the whole temperature range covered. If all Pb atoms were arranged in tetrahedra, the first maximum
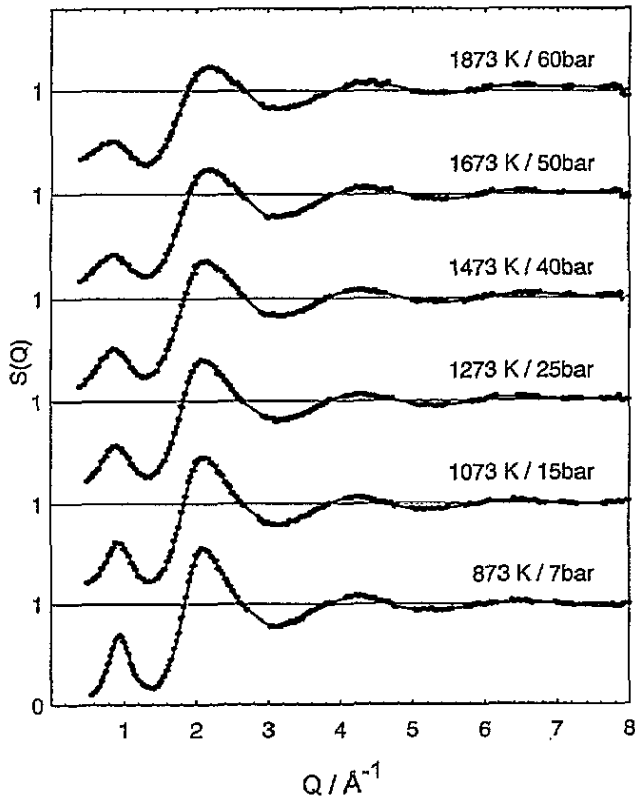
Figure 1. Structure factor $S(Q)$ of liquid KPb at different temperatures and pressures.

should give $Z_{PbPb} = 3$. The experimental results thus indicate that some of the Pb atoms have higher than threefold coordination and are arranged into larger clusters of lead atoms. With increasing temperature, the first coordination shell broadens and the shoulder of the first maximum of $n(r)$ shifts to larger r values. This might be taken as an indication that the mean K–Pb distances increase with increasing temperature while the Pb–Pb distances remain essentially unchanged. A more quantitative description of the microscopic structure requires computer simulation or modelling studies; a number of these have already been done for KPb at the melting point.

Reijers *et al* [10, 11] calculated the structure factor of liquid KPb at 870 K based on Pb_4^{4-} tetrahedra using both the reference interaction site model (RISM) and a model based on random packing of structural units (RPSU). These models reproduced the gross features of the experimental data. In detail, however, deviations are observed in the first peak of the structure factor, which is higher in the calculation, and at higher momentum transfers, where the models tended to overestimate the strength of the oscillations. Oscillations at high Q values are not observed experimentally for the molten KPb system indicating that the structural units are less rigid than stable molecules. This is supported by results obtained from inelastic neutron scattering experiments by Reijers *et al* [10], who find no evidence of distinct vibrational modes related to stable structural units.

Reijers *et al* [14] have also performed a molecular dynamics simulation of KPb. They used a Born–Mayer–Huggins-type potential to represent the interactions between alkali cations and tetrahedral Pb_4^{4-} anions. The Pb–Pb interactions within the Pb_4^{4-} tetrahedra
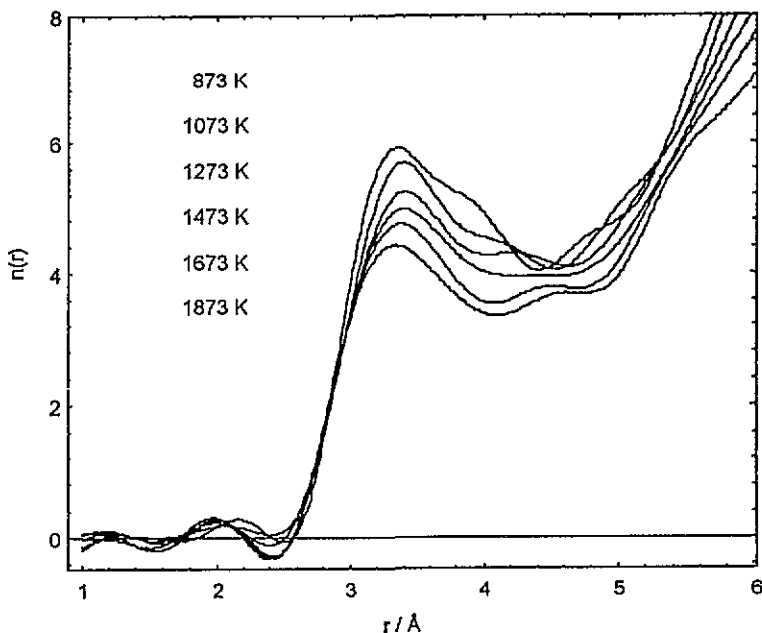
Figure 2. Pair distribution function $n(r)$ of liquid KPb at different temperatures and pressures.

were approximated by a simple harmonic potential. Polarization interactions were neglected. The position of the prepeak was correctly predicted by the simulation, but its height was overestimated, and the main peak of $S(Q)$ was shifted to the right with respect to the experimental $S(Q)$.

Hafner [16] has taken a different approach to simulation. He used first-principles pseudopotential theory and a modified linear screening model to calculate the effective interatomic interactions. He has found that large clusters of Pb atoms are formed with a rather broad distribution of coordination numbers indicating that the liquid does not comprise well defined lead tetrahedra. However, quantitative agreement of the calculated structure factor with the experimental data was poor.

In principle, partial correlation functions are essential for assessing the nature of chemical short-range order and the preferential coordination in a liquid. For the KPb alloy, such an approach is impossible using neutron diffraction as experimental tool, because there are no suitable isotopes available for the substitution method. In the absence of this possibility, the RMC method, which enables one to test three-dimensional structural models, is often applied. Fortunately, in the case of KPb, the neutron scattering length of Pb is significantly different from that of K (9.40×10^{-15} m against 3.67×10^{-15} m), so that a reasonable RMC calculation for this two-component system based on only one total structure factor is possible. Recently, the RMC method has been used to produce structural models of KPb in the melt at 870 K [15]. It has been shown that a range of structures is consistent with the experimental data, all of which have in common a tendency for the lead atoms to form clusters, and well defined tetrahedral structural units are not necessarily required to explain the prepeak.

In order to assess to what extent the chemical short-range order persists in the expanded liquid alloy, we have performed model calculations on the recently obtained structure factor data of liquid KPb between $T = 873$ K and $T = 1873$ K, applying the RPSU and RMC
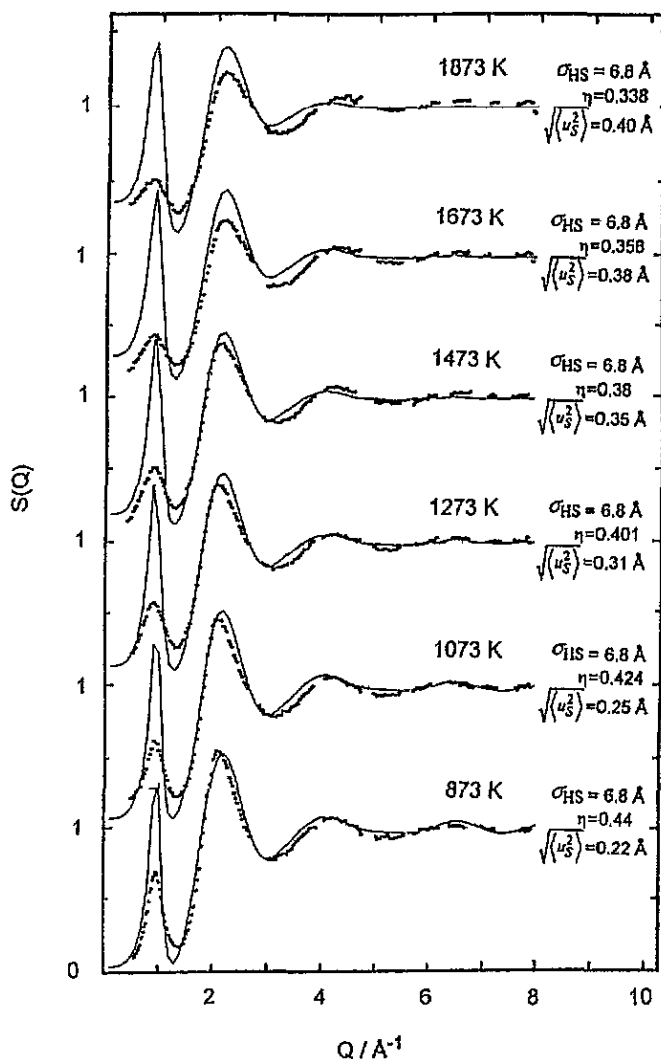
Figure 3. Comparison of the experimental structure factors of expanded liquid KPb (o) with the results obtained from RPSU calculations (full curve) (with $\sigma_{HS} = 6.8$ Å and the intramolecular distances $r_{PbPb} = 3.25$ Å, $r_{KPb} = 3.89$ Å and $r_{KK} = 6.65$ Å).

methods. The results obtained for the calculated structure factors within the RPSU model are plotted in figure 3 along with the measured ones. The numerical results obtained for the parameters of the RPSU calculation are also given in the figure. Whereas the overall features of the calculated and measured structure factor for KPb near the melting point at 873 K are in reasonable agreement, it can clearly be seen, that the agreement becomes worse with increasing temperature, thus showing that the picture of rigid K_4Pb_4 units is too simple to describe the nature of the chemical short-range order in the expanded liquid state.

In order to understand the deficiencies of this model, RMC calculations have been performed. In a first model, a starting configuration of 1728 particles at random positions was used. The shortest possible distances between atoms were chosen to be $r_{PbPb} = 2.5$ Å, $r_{KPb} = 3.2$ Å, and $r_{KK} = 3.4$ Å. A comparison of the RMC structure factors for $T = 873$ K
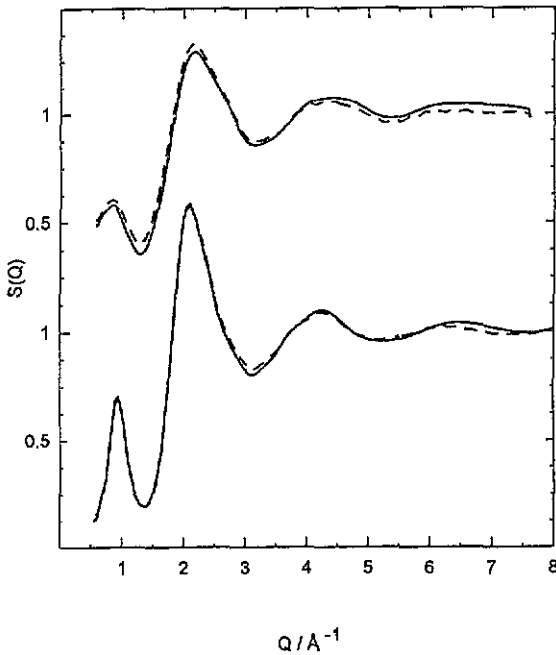
Figure 4. Comparison of the RMC structure factor (dashed curve) with the experimental $S(Q)$ data (full curve) for liquid KPb at $T = 873$ K (bottom) and $T = 1873$ K (top).
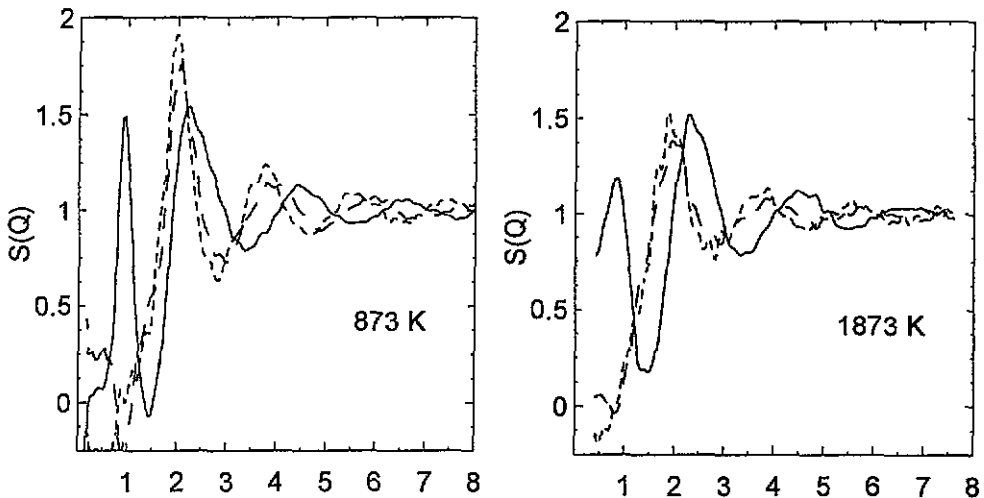

Figure 5. The partial structure factors $S_{KK}(Q)$ (– – –), $S_{KPb}(Q)$ (— — —) and $S_{PbPb}(Q)$ (——) of liquid KPb at $T = 873$ K and $T = 1873$ K as obtained from the RMC simulation.

and $T = 1873$ K after convergence is shown in figure 4. The agreement is very good, reproducing both the prepeak and the structure factor at higher momentum transfers within the experimental error. The calculated partial structure factors $S_{ij}(Q)$ and partial correlation
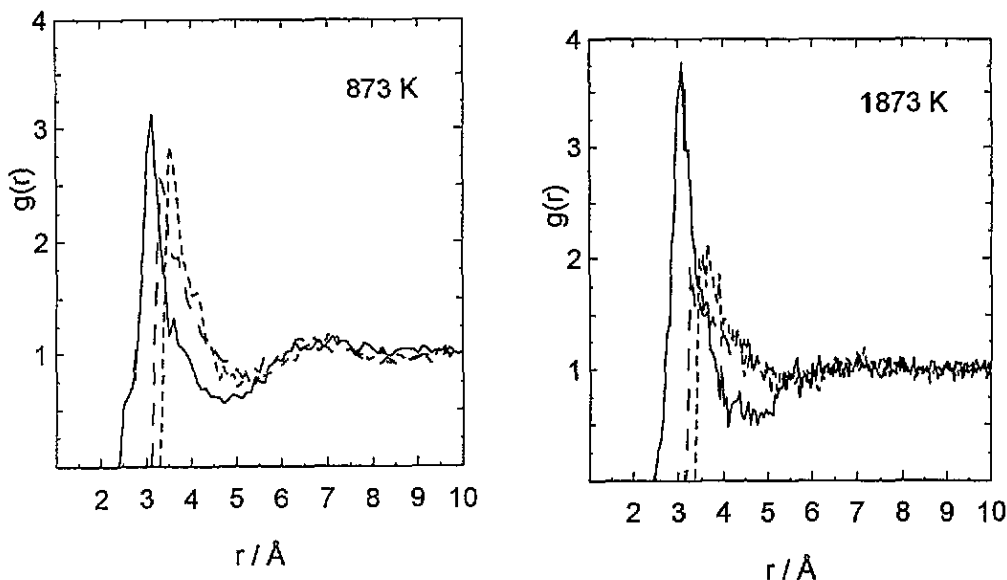
Figure 6. The partial pair correlation functions $g_{KK}(r)$ (– – –), $g_{KPb}(r)$ (— — —) and $g_{PbPb}(r)$ (——) of liquid KPb at $T = 873$ K and $T = 1873$ K as obtained from the RMC simulation.

functions $g_{ij}(r)$ ($i, j = $ K, Pb) for liquid KPb at the two temperatures are shown in figures 5 and 6, respectively. Inspection of the partials in figure 5 reveals that the prepeak in the experimental structure factor data at 1 Å^{-1} is reproduced predominantly in one of the partial structure factors, $S_{PbPb}(Q)$. This behaviour is found (independently) at all temperatures, which demonstrates that the cluster formation is dominated by the tetravalent metal not only at the melting point, but also at $T = 1873$ K. The first peak in $S_{PbPb}(Q)$ has become smaller and broader at the higher temperature, however.
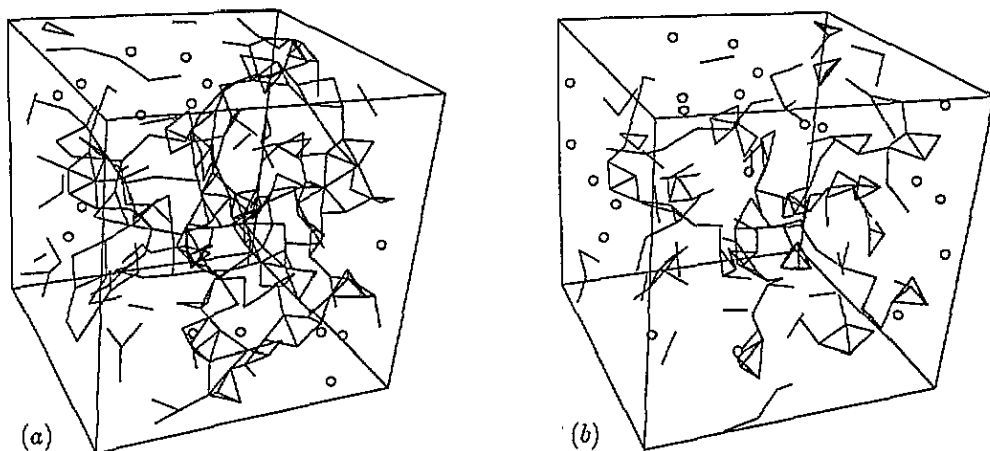

Figure 7. Configurations of Pb atoms after the RMC simulation: (a) liquid KPb at $T = 873$ K, (b) liquid KPb at $T = 1873$ K. Pb atoms within a distance of 3.6 Å are connected to visualize some kind of bonding (box size: 30 Å × 30 Å × 30 Å).

The three partial correlation functions (figure 6) peak at slightly different positions.
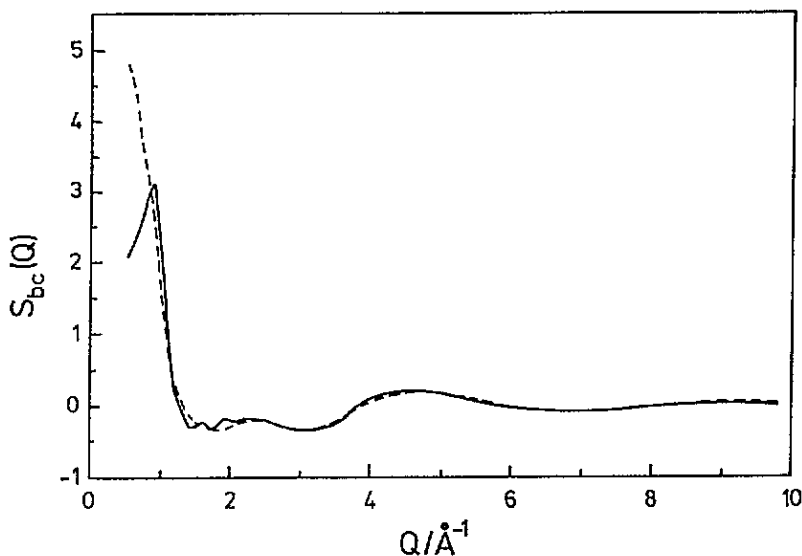
Figure 8. Bond centre structure factor $S_{bc}(Q)$ for Pb–Pb bonds in liquid KPb at $T = 873$ K (full line) and $T = 1873$ K (dashed line).

Their positions remain almost constant during the expansion of the liquid. Whereas the first maximum of $g_{PbPb}(r)$ remains sharp at 1873 K, the peaks in $g_{KPb}(r)$ and $g_{KK}(r)$ are drastically reduced and broadened at $T = 1873$ K. The slight increase in the height of $g_{PbPb}(r)$ is within the statistical fluctuations and has no significance. The bond angle distribution $P(\cos \theta)$ is similar at low and high temperatures. It exhibits a broad peak at $\cos \theta = 0.5$, corresponding to a Pb–Pb–Pb bond angle of 60°, but also indicates a significant number of larger angles. Figure 7 shows three-dimensional configurations of Pb atoms after the RMC calculations at $T = 873$ K and $T = 1873$ K. In these plots, the Pb atoms with distances smaller than $r = 3.6$ Å are connected to visualize some kind of bonding. Clearly, besides some Pb_4^{4-} tetrahedra, large clusters or an open network of lead atoms are observed, this network opens up at the higher temperature. The height of the first peak in $S_{PbPb}(Q)$ decreases rapidly with temperature up to approximately 1500 K and then less rapidly. The initial rapid decrease is similar to the decrease in $C_p(T)$ [4, 5] suggesting that both changes are due to break-up of the polyanions.

These configurations of lead atoms obtained in the RMC model for liquid KPb are similar to those found for molten NaSn and KSi by recent *ab-initio* molecular dynamics simulations. The *ab initio* MD simulation of liquid NaSn [17] revealed a clear tendency to network formation of threefold- and fourfold-coordinated Sn atoms in the liquid. Remnants of Sn_4 complexes were found in the melt, but always connected with other Sn atoms or groups of Sn atoms. Similar results were obtained for a related system, molten KSi, also using the *ab initio* MD scheme [18]. The theoretical results exhibit all the features normally associated with Zintl forming alloys, such as the prepeak. However, the underlying structure appears to be more complex than that predicted by the Zintl model valid for the crystalline state. The liquid contains extended networks of Si atoms, with two-, three- and fourfold-coordinated sites, the average coordination of Si being three. The subsystem of K atoms in the melt is much less structured.

In a further RMC model of expanded liquid KPb, we have constrained lead clusters to have approximately tetrahedral arrangements. This model also fits the experimental data

well. However the clusters have to approach each other almost to intramolecular distances to obtain agreement with the experimental data, much closer than would be expected for negatively charged clusters. In addition, the partial $g(r)$ show unphysical behaviour, which gets worse as the temperature increases, so we believe that this model is unreliable. On the other hand, as the intermolecular and intramolecular distances of lead atoms approach each other in this model, the situation obtained is not too different from that obtained for the unconstrained model, where larger clusters or an open network of lead atoms has been found.

Figure 8 shows the 'bond-centre' structure factor $S_{bc}(Q)$ for Pb–Pb bonds at 873 K and 1873 K. This is calculated by placing a point at the centre of each Pb–Pb bond (as defined earlier) and then calculating the structure factor for these points. If one considers in a simplistic way that excess electron density is located in the Pb–Pb bonds in the polyanion clusters then $S_{bc}(Q)$ gives some information about the distribution of this density. The main point to note is that at 873 K $S_{bc}(Q)$ has a sharp peak at the position of the first peak in $S_{PbPb}(Q)$, whereas at 1873 K it rises continuously as $Q \rightarrow 0$. This supports the idea that there is a general tendency to microphase separation between Pb and K at all temperatures. At lower temperatures Pb atoms prefer to form in specific types of cluster (Zintl ions or polyanions), but as temperature increases this becomes less specific and Pb simply prefer Pb neighbours. However even at 1873 K the existence of the first peak in $S_{PbPb}(Q)$, though now quite broad, still points to some remaining tendency to form polyanions.

4. Conclusions

In conclusion we can say that polyanions are present, to some extent, in liquid KPb over the entire liquid range from 873 K to 1873 K. The structure of the polyanions is partially related to the Zintl ions in the corresponding crystalline compound. The experimental data can be described by a loose network of the tetravalent metal, which can also account for the large heat capacity of the alloy compared to the pure metal. The Pb–Pb bonds in liquid KPb fluctuate strongly, as may be inferred from the absence of distinct oscillations at high values in $S(Q)$ or distinct vibrational bands in the inelastic neutron scattering spectrum. With increasing temperature polyanions do not simply break up and become a random K/Pb distribution. Rather there is a continuous evolution (most rapid between 873 K and 1473 K) from a structure with a strong tendency to form specific local Pb clusters to a structure with a more general tendency to microphase separation. This can explain the rapid decrease of the specific heat capacity.

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