

The structure of molten K-Pb, Rb-Pb and Cs-Pb alloys

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

1991 J. Phys.: Condens. Matter 3 577

(<http://iopscience.iop.org/0953-8984/3/5/007>)

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

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:05

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

The structure of molten K-Pb, Rb-Pb and Cs-Pb alloys

M A Howe and R L McGreevy

Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK

Received 7 June 1990

Abstract. We have considered previously published neutron diffraction data, obtained at two different sources, on the molten alloys K_xPb_{1-x} , RbPb and CsPb. The difference between results for the same system obtained at the two sources has been shown to be attributable to instrumental resolution. The reverse Monte Carlo method has been used to produce structural models of all these melts. We have demonstrated that there is a range of structures consistent with the experimental data, all of which have in common a tendency for the lead to form clusters, typically of three or four atoms, with 60° Pb-Pb-Pb bond angles. The results appear to be generally consistent with the existence of some tetrahedral Pb_4^{4-} Zintl ions; however it seems unlikely that all Pb atoms occur in such well defined species since in this case the tetrahedra must approach each other too closely in order to accurately reproduce the experimental data. We have shown that for unconstrained (i.e. not completely tetrahedral) models the peak at a momentum transfer of approximately 1 \AA^{-1} observed in the diffraction patterns occurs in the partial structure factor $A_{PbPb}(Q)$ and is related to correlations between Pb clusters. The height of this peak varies with Pb concentration in K_xPb_{1-x} alloys in the same way as electrical resistivity, and we have postulated that this is due to electron localization associated with the cluster formation. For KPb the unconstrained model contains 25% tetrahedra, in good agreement with thermodynamic data.

1. Introduction

There have been a number of recent neutron diffraction experiments on the alloys K-Pb, Rb-Pb and Cs-Pb. Saboungi *et al* (1987) report an experiment on the equiatomic KPb alloy using the Special Environment Powder Diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory, Illinois, USA. The equiatomic alloys RbPb and CsPb have been studied by Reijers *et al* (1989a) again using SEPD. Compositions other than the equiatomic have been studied only for K-Pb alloys. Results are reported for mixtures containing mole fractions of 25%, 50%, 65% and 80% K (Reijers *et al* 1987, 1989b). These experiments were performed at the High Flux Reactor at Petten in the Netherlands.

The structure factors measured for all the equiatomic alloys show a sharp peak, known as the first sharp diffraction peak (FSDP) or prepeak, at a momentum transfer of approximately 1 \AA^{-1} although there is a significant difference in the height of this peak for KPb between the sets of data measured at Petten and at IPNS. This FSDP has been interpreted as indicating the presence of polyatomic structural units, specifically tetrahedral Pb_4^{4-} Zintl ions (Zintl and Brauer 1933) or double tetrahedral A_4Pb_4 (where $A = K, Rb$ or Cs) units. Reijers *et al* (1989a) calculated structure factors

based on such units using both the reference interaction site model (RISM) (Lowden and Chandler 1973) and a model based on random packing of structural units (RPSU) (Moss and Price 1985). They were able to obtain results that reproduced the gross features of the experimental data, particularly in the region of the first two peaks in the structure factors (at approximately 1 \AA^{-1} and 2 \AA^{-1} respectively) although the agreement was rather poorer at higher values of momentum transfer where the models tended to overestimate the strength of the oscillations. It should be pointed out that molecular liquids show strong oscillations at large momentum transfer which are a result of the well defined distances between atoms in the molecules. Such oscillations are not observed for the alkali-lead systems indicating that any structural units are rather less rigid than molecules. This is also supported by the inelastic scattering experiment of Reijers *et al* (1989a) who find no evidence of modes related to the structural units. In their models Reijers *et al* (1989a) used an RMS variation in the Pb-Pb distance within units of 0.2 \AA .

Reijers *et al* (1990) have done molecular dynamics simulations on the equiatomic systems using an *ad hoc* Born-Meyer-Huggins type potential to represent interactions between alkali cations and tetrahedral Pb_4^{4-} anions and again are able to obtain qualitative agreement with the data. Hafner (1989) has taken a different approach to simulation. He has calculated effective interatomic interactions from pseudopotentials and considered the effect of a limited electronic free path. He finds a tendency to form the 60° Pb-Pb-Pb angles found in tetrahedra but also a rather broad distribution in coordination numbers indicating that the liquid does not comprise well defined Pb_4 tetrahedra. However his calculated structure factor does not reproduce the FSDP well although it is in fairly good agreement with the experimental data elsewhere. It seems that molecular models overestimate, and the MD pseudopotential underestimates, the degree of ordering.

In order to investigate this matter further and to assess to what extent the neutron diffraction data do imply the formation of structural units in these melts we have applied the reverse Monte Carlo (RMC) method (McGreevy and Pusztai 1988) which enables us to produce three dimensional structural models that accurately reproduce the experimental data. Before we do this, however, we consider the difference between the results obtained for KPb at IPNS and Petten and show that it can be accounted for in terms of instrumental resolution.

2. Instrumental resolution

The two sets of data for KPb were measured at approximately the same temperature (858 K and 870 K) and are in good agreement at all points except in the vicinity of the FSDP. Although the height of this peak is known to vary with temperature (Saboungi *et al* 1987) the difference here seems too large for a relatively small change in temperature, and is also in the wrong direction, so we wish to consider whether it is genuine.

The effect of instrumental resolution is usually neglected in diffraction studies of liquids because the peaks in the structure factors are generally rather broad compared with the resolution function. However, in certain cases peaks can be fairly sharp, as is the case here with the FSDP, and the effect ought to be considered. As we do not know the exact resolution functions of the two instruments used we have simply tried to determine whether it is feasible that the difference is due to resolution. The resolution

of SEPD is better than that of the Petten spectrometer because it uses mainly higher energy neutrons. For this reason we have made the approximation that the effect of resolution is relatively unimportant for the IPNS data and then attempted to find a reasonable resolution function for the Petten spectrometer with which to convolute the IPNS data so as to reproduce the Petten data. This was done by assuming the simple functional form of a Gaussian in θ , the scattering angle, with a constant width $\Delta\theta$, and finding the best value of $\Delta\theta$ by a least squares method. The value obtained was $\Delta\theta = 0.0035$ ($\approx 0.2^\circ$) which gives the results shown in figure 1. This is a perfectly reasonable value and so we conclude that the difference between the two sets of data is almost certainly due to instrumental resolution.

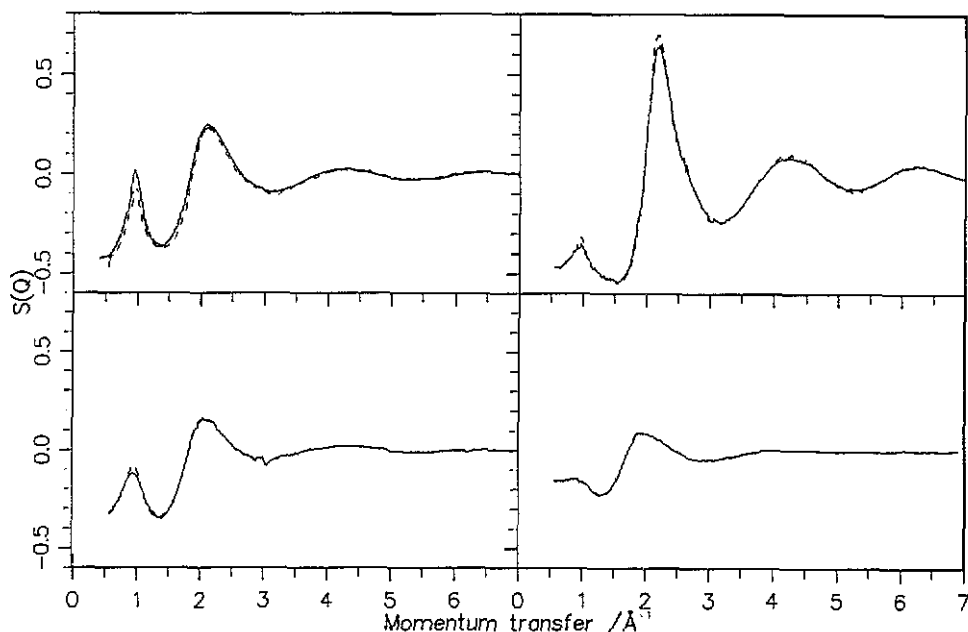


Figure 1. The experimental structure factors for the molten potassium-lead alloys $K_{0.5}Pb_{0.5}$ (top left), $K_{0.25}Pb_{0.75}$ (top right), $K_{0.65}Pb_{0.35}$ (bottom left) and $K_{0.8}Pb_{0.2}$ (bottom right). For $K_{0.5}Pb_{0.5}$ the full curve is the Argonne data, the broken curve the Petten data and the broken and dotted curve is the Argonne data after convolution with our resolution function. For the other compositions the full curve is the experimental data and the broken curve is our deconvolution.

Although this will not be exactly the resolution function of the instrument it should be a good approximation to it. We have therefore attempted to correct the Petten data sets, for different compositions of K-Pb alloy, for resolution. This is not a trivial task as there is, in general, a range of solutions that reproduce the experimental data when convoluted with the resolution function so it is necessary to choose a method that produces a solution with desirable properties. We tried a number of methods including maximum entropy and minimization methods but the most successful was the following. We took an estimate of the structure factor, which in the first instance was the experimental data itself, and convoluted this with the instrumental resolution function and compared the result with the experimental data. We then made a small change in the structure factor by making a random change in

its value at one point, convoluted with the resolution function and compared with the experimental data. If the agreement had improved we accepted this change but if it had not we reverted to the previous estimate. The process was then repeated. This quite rapidly produced a solution that, after convolution, reproduced the experimental data very well. However because of the randomness involved in generating it the solution contained a lot of statistical noise. This can be removed if at the same time as maximizing agreement of the convoluted function with the experimental data, the difference between neighbouring points of the solution, i.e. the first derivative of the structure factor, is minimized. This produced a fairly smooth solution but it showed small scale oscillations which were undesirable. To reduce these a further constraint was added: the deviation between the unconvoluted structure factor and the experimental data was minimized except in the region of 1 \AA^{-1} where the difference was expected to be large. These additional constraints were achieved by accepting only those changes in the estimated structure factor that decreased a function that was the sum of three terms: the mean square deviation of the convoluted structure factor from the data, the mean square derivative of the structure factor and the mean square deviation of the structure factor from the experimental data except in the region of 1 \AA^{-1} . The relative weighting of these terms was chosen so as to gain the beneficial effects of the latter two terms whilst still getting excellent agreement with the experimental data.

The results are shown in figure 1 where it can be seen that they do not exhibit spurious small scale oscillations or excessive noise. They are however not totally smooth as might be expected from some methods of deconvolution but tend to reproduce the errors in the data. For our purposes we consider this desirable. It is clear, though, that the effect of resolution is relatively unimportant for most of these samples because they do not have such a sharp FSDP as is seen for equiatomic KPb. The FSDP in the Petten data and the convoluted Argonne data have approximately the same height and width, but differ by a small constant. This remaining deviation between the data sets disappears as Q increases; its origin is unknown but could have many causes such as inadequate absorption or inelasticity corrections.

3. The reverse Monte Carlo calculation

The reverse Monte Carlo method has been described in detail by McGreevy and Pusztai (1988) and by McGreevy *et al* (1990). It is similar in operation to the standard Metropolis method of Monte Carlo simulation in that one represents in a computer a box containing a number of atoms and applies the usual periodic boundary conditions to calculate the pair correlation function $g(r)$ and structure factor $S(Q)$. A particle is then moved at random; this move is accepted or rejected according to some criterion and another move is tried. This process is repeated many times. In Monte Carlo simulation the acceptance criterion is based on the energy of the configuration calculated using some interatomic potential and thus one eventually obtains, after the simulation has equilibrated, a system with a structure determined by the given interaction potential. RMC, on the other hand, is a method of modelling based on the experimental data: no interaction potential is used and the acceptance criterion is based solely on the agreement of the calculated structure factor with the experimental data. After convergence one has obtained a model structure that reproduces, within the experimental errors, whatever experimental data was available for the calculation.

McGreevy and Pusztai (1990) have used this method to obtain model structures of molten alkali and alkaline earth halides. For these salts the neutron diffraction method of isotopic substitution had been used so that three different total structure factors, comprising three different combinations of the three partial structure factors that together completely describe the pair correlations in the liquid, had been obtained. Their models, which agreed with all three total structure factors, could therefore be considered to be good representations of the liquids in question. In the present case, however, there are no suitable isotopes to do an isotopic substitution experiment. The same is true for silica in which case Keen and McGreevy (1990) were able to combine neutron and x-ray diffraction data to obtain a model of the glass. However, because of the high absorption of lead, the alloys we are considering here are not suited for x-ray studies. It seems, then, that we must obtain what information we can solely from the single neutron diffraction pattern we have for each system.

There is no reason why we cannot do an RMC calculation for a many component system based on only one structure factor: the algorithm will accept as little or as much constraint from experimental data as can be provided. With only a single structure factor, however, one must be a little cautious. For example, if the scattering lengths of two components were the same then they would be indistinguishable by neutron diffraction and one could hardly expect to obtain a model in which they were differentiated, at least not without some additional constraint. Fortunately in this case the scattering length of lead is significantly different from those of the alkali metals (the values, in units of 10^{-12} cm, are 0.367, 0.708, 0.542 and 0.9401 for K, Rb, Cs and Pb respectively).

One additional constraint was applied, namely a restriction on the closest distance of approach allowed between pairs of particles. Such a constraint is normally applied in RMC calculations but is often not a particularly strong constraint. That is, the closest distances of approach are actually implied by the data and the use of the constraint is to ensure that $g(r)$ is exactly zero at closer distances, rather than just approximately zero. In the present case the choice of different closest distances of approach for the three different pairings of particles provided a distinction between the two types of atom additional to their different scattering lengths. The smallest of these distances can be determined from the total $g(r)$ obtained by direct Fourier transformation as being 2.7 Å which is the closest distance of approach for two lead atoms. This same value was used for all the systems modelled. It is not so clear what the distances should be for the other two pairings of atoms. One choice for the alkali-alkali closest approach would be that found in the pure alkali melts. However because of partial charge transfer the alkali atoms are expected to be slightly smaller in these alloys than in the pure melts (although this might be slightly less true for the potassium rich alloy $K_{0.8}Pb_{0.2}$) so we chose values some 0.1 Å or 0.2 Å smaller giving 3.3 Å for the K-K closest distance of approach, 3.5 Å for Rb-Rb and 3.6 Å for Cs-Cs. The alkali-lead distances were then chosen to be the mean of the lead-lead and alkali-alkali in the system under consideration. Slightly different choices were also tried but were found to make no significant difference.

Our starting configurations were generated in two different ways chosen so as not to bias the results towards a preconception of the structure. One method was to place atoms at random positions and then move them around until the restrictions on closest distance of approach were satisfied. This was used to create starting configurations of 1000 atoms for each of CsPb, RbPb and KPb. The other method was to start from a configuration of 1728 atoms that had previously been obtained in a calculation for

molten CsCl (chosen because Cs and Cl have similar ionic radii, as do K and Pb, but CsCl is strongly chemically ordered while KPb is not). This was used for all the K-Pb alloys. The calculation for KPb was thus run from two completely different starting configurations. The final results from the two were found to be the same (i.e. not with identical atomic coordinates but with identical correlation functions, within statistical error). After convergence the calculation continued saving one configuration every N accepted moves (where N is the number of atoms used in the model) in order to obtain better statistics on the correlation functions calculated. The numbers of configurations saved were 10 for KPb and 20 for all the other systems.

The procedure just described would be expected to produce the least ordered structure that is both physically self-consistent and consistent with the data and constraints. To see whether it is possible to find a more ordered structure we have done two calculations for KPb starting with a configuration produced by the MD simulation of Reijers *et al* (1990). In the first of these we accepted only moves that improved the fit (the usual procedure, see McGreevy and Pusztai (1988), is to allow some moves that worsen the fit to avoid the possibility of getting trapped in local minima) and ran the calculation until agreement with the data was obtained; i.e. the initial configuration was changed only as much as was necessary to obtain agreement with the data. In this way we hoped that the Pb_4 tetrahedra that exist in the simulated configuration would be retained by the RMC calculation if they were actually consistent with the experimental data. The second calculation was slightly different because it included an additional constraint concerning the coordination of Pb atoms. The atoms within the Pb_4 tetrahedra of the MD simulation do not get further than 3.6 Å from one another. This means that all the Pb atoms have exactly three Pb neighbours within this distance. We retained this condition in our RMC calculation by rejecting any move that would change this coordination number. In what follows we will refer to these calculations as RMC-II and RMC-III respectively and to that described in the previous paragraph as RMC-I.

4. Results

A comparison of some of the RMC structure factors after convergence are shown in figure 2. In the case of the equiatomic alloys the agreement, although not perfect, is very good, reproducing both the peak at approximately 1 \AA^{-1} and the structure at higher momentum transfer, and can be considered to be within the experimental error. This is also true for the RMC-I, II and III calculations for $\text{K}_{0.5}\text{Pb}_{0.5}$ although for clarity they are not all shown. The agreement in the case of the other K-Pb alloys does not appear so good but in these cases the quality of the data is apparently less good too. The resolution is rather poorer and may not have been entirely corrected for by our correction procedure (it was not possible to get any better agreement with the uncorrected data). We believe, therefore, that even in these cases the agreement is reasonable.

The partial pair correlation functions $g(r)$ for $\text{K}_{0.5}\text{Pb}_{0.5}$ and CsPb are shown in figure 3. Considering first those for $\text{K}_{0.5}\text{Pb}_{0.5}$ we see that for RMC-I the three functions $g_{\text{KK}}(r)$, $g_{\text{KPb}}(r)$ and $g_{\text{PbPb}}(r)$, although they do show small differences and peak at slightly different positions, are on the whole fairly similar to one another. In CsPb there is more difference, with a much taller and sharper peak in $g_{\text{PbPb}}(r)$. This can be understood as being due to the larger size constraint imposed for Cs than for K

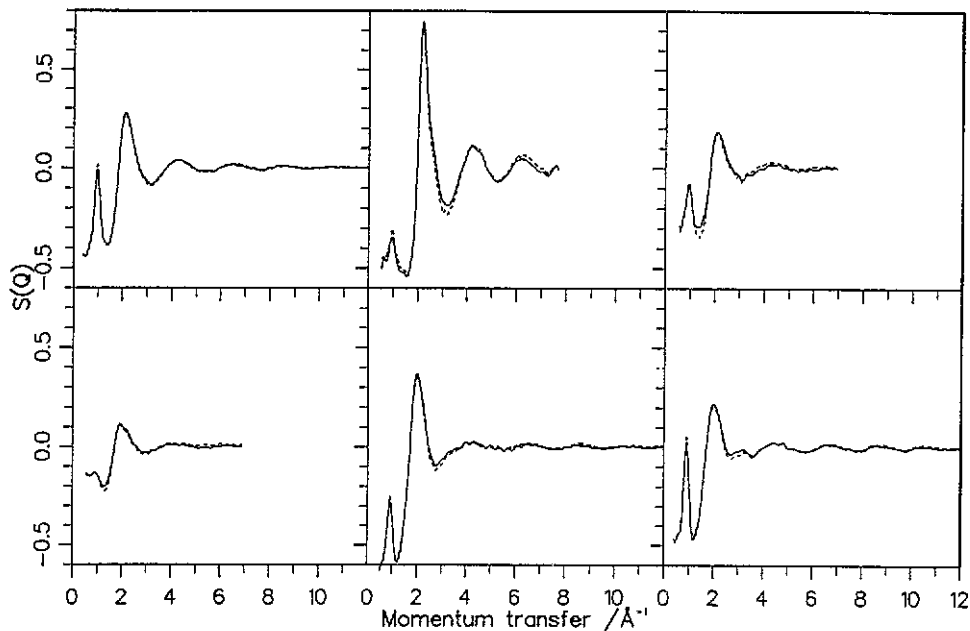


Figure 2. Comparison of RMC (full curve) with experimental data (broken curve) for $K_{0.5}Pb_{0.5}$ (top left), $K_{0.25}Pb_{0.75}$ (top centre), $K_{0.85}Pb_{0.35}$ (top right), $K_{0.8}Pb_{0.2}$ (bottom left), RbPb (bottom centre) and CsPb (bottom right). For $K_{0.5}Pb_{0.5}$ the experimental data is the Argonne data and the RMC result is from RMC-I, for the other compositions of K_xPb_{1-x} we have used our deconvolution.

in the calculations and it may be that such a larger peak would be a more realistic description for KPb. The result of RMC-II, equally consistent with the experimental data, indeed has a slightly more sharply peaked $g_{PbPb}(r)$ although the main difference is a rather broader $g_{KK}(r)$. RMC-III again produces a broader $g_{KK}(r)$ with a slightly narrower $g_{PbPb}(r)$. However it is clear that in RMC-III the Pb_4 tetrahedra are not as well separated as they are in the MD configuration, since the first minimum is non-zero.

The corresponding partial structure factors are shown in figure 4. Despite the apparent similarity of the three partial $g(r)$'s for RMC-I, the structure factors are not similar as it is quite clear that the FSDP seen in the experimental data at $Q \approx 1 \text{ \AA}^{-1}$ is reproduced predominantly in one of the partial structure factors: $A_{PbPb}(Q)$. This is also true for RbPb and CsPb and for all the other compositions of K_xPb_{1-x} and indicates that this feature is due to lead-lead correlations, presumably between neighbouring lead clusters. RMC-II and III, however, produce a different result: although the structure factors are similar to those of RMC-I at higher Q the FSDP is distributed differently being seen in both $A_{KK}(Q)$ and $A_{PbPb}(Q)$ with a corresponding negative peak in $A_{KPb}(Q)$. This is a feature typically found in ionic systems, indicating charge ordering, and can be considered to be due to the ionic potentials used in the MD simulation.

To consider whether the clusters indicated in RMC-I are the Pb_4 tetrahedra that have been hypothesized we have calculated bond angle correlations and nearest neighbour distributions, some of which are shown in figures 5 and 6 respectively. Neighbours are defined as those within 3.6 \AA of a Pb (chosen from the maximum separation of tetrahedral Pb in the MD simulation) or 4.0 \AA of a K (because of the slightly larger

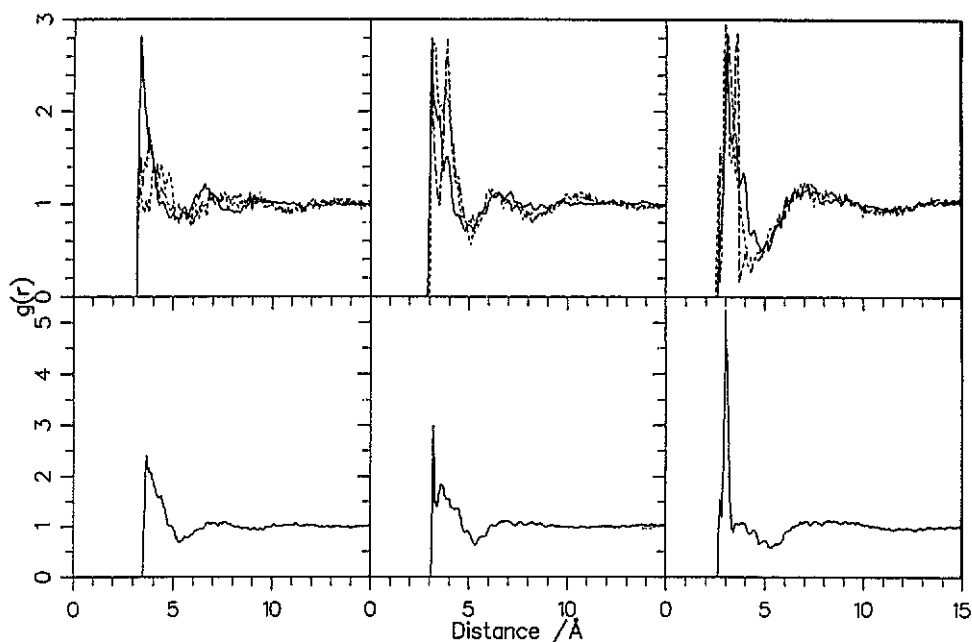


Figure 3. The partial pair correlation functions $g_{AA}(\tau)$ (left), $g_{APb}(\tau)$ (centre), and $g_{PbPb}(\tau)$ (right) for $K_{0.5}Pb_{0.5}$ (top) and $CsPb$ (bottom). For $K_{0.5}Pb_{0.5}$ the full curve is the result of RMC-I, the broken of RMC-II, and the broken and dotted of RMC-III.

K-K cut-off). The bond angle distributions calculated were similar for all the systems and we show only those for $K_{0.5}Pb_{0.5}$. For RMC-II and III, which both started with well separated Pb_4 tetrahedra, the Pb-Pb-Pb distribution is almost entirely a peak about $\cos\theta = 0.5$ as would be expected for tetrahedra. However the distribution of number of near neighbours in RMC-II shows that a majority of the leads have zero, one or two lead neighbours within 3.6 \AA rather than the three that would be obtained from the starting configuration of tetrahedra. This indicates that in order to obtain a good fit to the experimental data, starting from the MD configuration, RMC-II has broken up the tetrahedra into fragments which have retained their internal angles of approximately 60° ; these fragments have not yet come close enough to one another to either produce any neighbour numbers greater than three or introduce any 'bond angles' significantly different from 60° . The neighbour distribution obtained from RMC-I is really rather similar, the difference being that there are slightly fewer three coordinated leads and there are some four and five coordinated ones. The bond angle distribution is peaked at $\cos\theta \approx 0.5$ but also indicates a significant number of larger angles. This suggests a similar structure to that found from RMC-II but slightly more disordered. (Note that if RMC is run on from the RMC-II structure then the RMC-I structure is eventually obtained.) For $CsPb$ we find a slightly greater tendency to tetrahedra formation than KPb (RMC-I), i.e. a sharper 60° peak and a larger degree of three-fold Pb-Pb coordination, and for $RbPb$ a slightly smaller tendency (see later discussion).

Turning our attention to the results for the non-equiatomic K-Pb alloys we see that the partial $g(r)$'s (figure 7) slope gradually towards their limiting values of 1 at large r , $g_{KPb}(r)$ sloping upwards and $g_{KK}(r)$, in the case of the lead-rich alloy, or

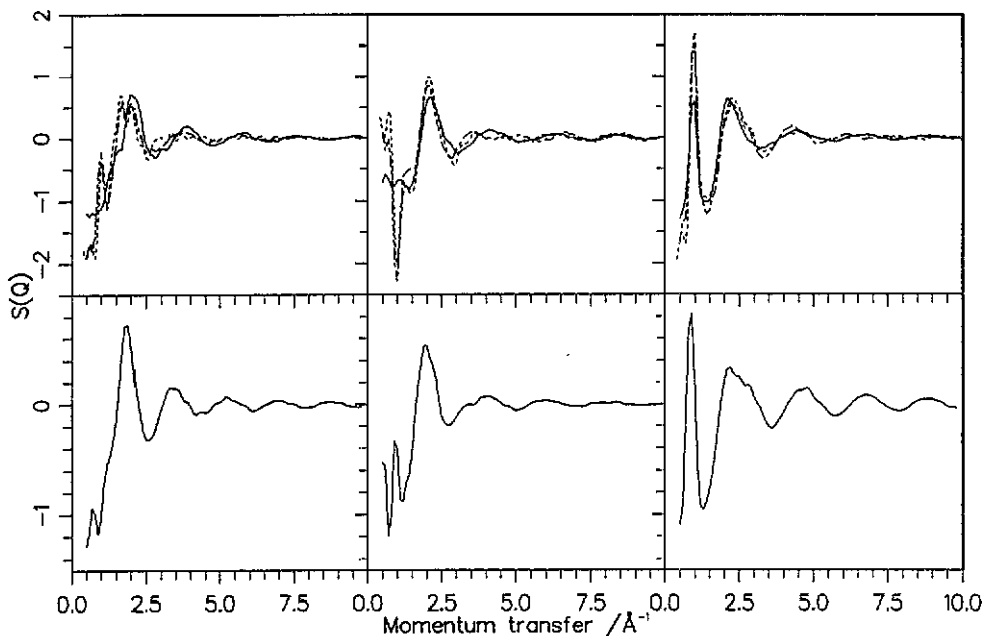


Figure 4. The partial structure factors $A_{AA}(Q)$ (left), $A_{APb}(Q)$ (centre), and $A_{PbPb}(Q)$ (right) for $K_{0.5}Pb_{0.5}$ (top) and $CsPb$ (bottom). For $K_{0.5}Pb_{0.5}$ the full curve is the result of RMC-I, the broken of RMC-II, and the broken and dotted of RMC-III.

$g_{PbPb}(r)$, in the case of the potassium-rich alloys, sloping downwards. This indicates a degree of phase separation, or clustering, in these alloys. The fact that the limiting value of 1 is reached only at the largest distance for which $g(r)$ is calculated, which is half the box size, suggests that the box used was not quite large enough to provide an entirely accurate description of this phase separation and may partly explain why the agreement with the experimental data in these cases is not as good as it might be. The partial structure factors (figure 8) show an FSDP only in $A_{PbPb}(Q)$, with the peak height being small for $K_{0.8}Pb_{0.2}$ and $K_{0.25}Pb_{0.75}$. $K_{0.8}Pb_{0.2}$ and $K_{0.65}Pb_{0.35}$ also show steep rise at the lowest Q value, indicative of phase separation; this rise is probably larger than it should be since to adequately model this effect would require additional data below 0.5 \AA^{-1} .

Considering now the neighbour distributions for the K-Pb alloys as a function of composition we find that increasing the lead concentration causes a shift in the distribution of number of lead and potassium neighbours of a lead atom towards higher and lower numbers respectively, as might be expected. However decreasing the lead concentration does not have the opposite effect. Although there is a slight increase in the number of leads with no lead neighbours the distribution for $K_{0.8}Pb_{0.2}$ is really remarkably similar to that for the equiatomic alloy. This indicates that the lead atoms are still tending to cluster when they are present in relatively low concentrations. The distribution of numbers of neighbours around potassium shows similar behaviour when the concentration of potassium is increased beyond the equiatomic: the distribution of potassium neighbours shifts to higher numbers while that of leads shifts to lower numbers. However when the concentration of potassium is reduced the distribution of potassium neighbours stays much the same while that of lead neighbours is shifted

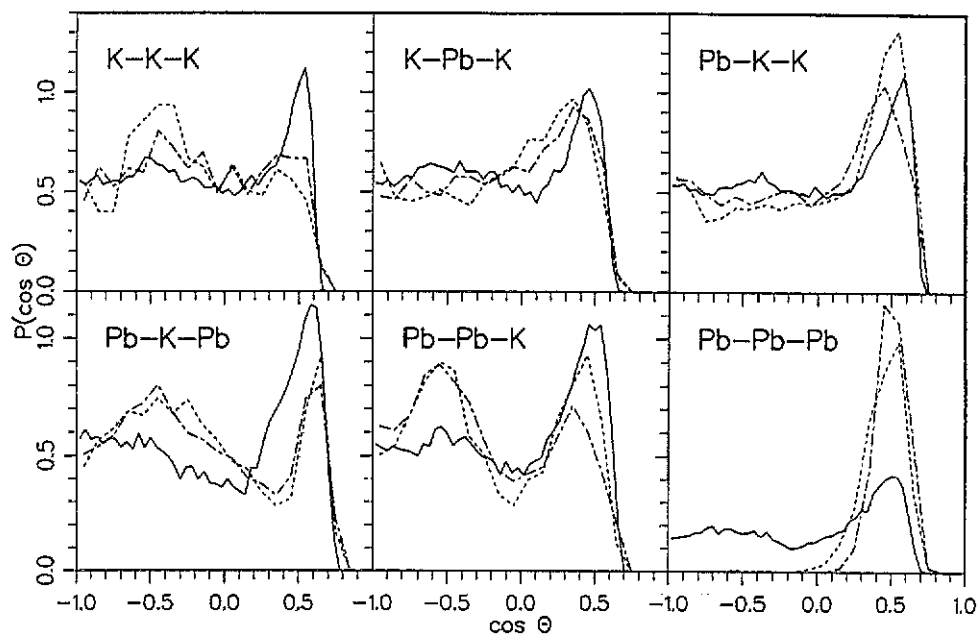


Figure 5. Distributions of number of K (white bars) and Pb (black bars) within 4.0 Å of K atoms (top) and 3.6 Å of Pb atoms (bottom) for $K_{0.25}Pb_{0.75}$ (left), $K_{0.5}Pb_{0.5}$ (centre) and $K_{0.8}Pb_{0.2}$ (right).

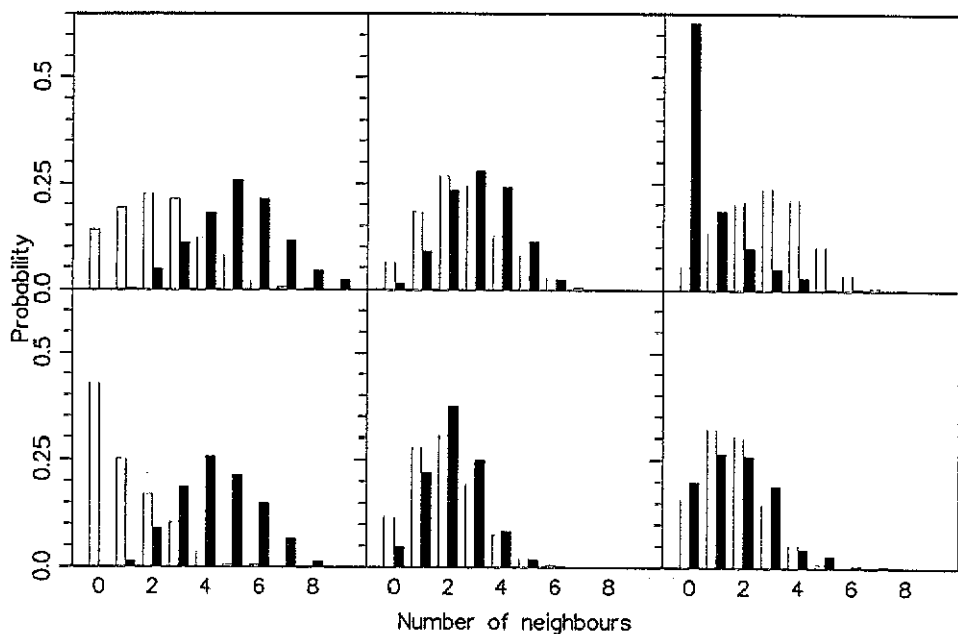


Figure 6. Bond angle distributions for molten $K_{0.5}Pb_{0.5}$. The full curve is for RMC-I, the broken for RMC-II, and the broken and dotted for RMC-III. The Pb-Pb-Pb distributions have been divided by 3.

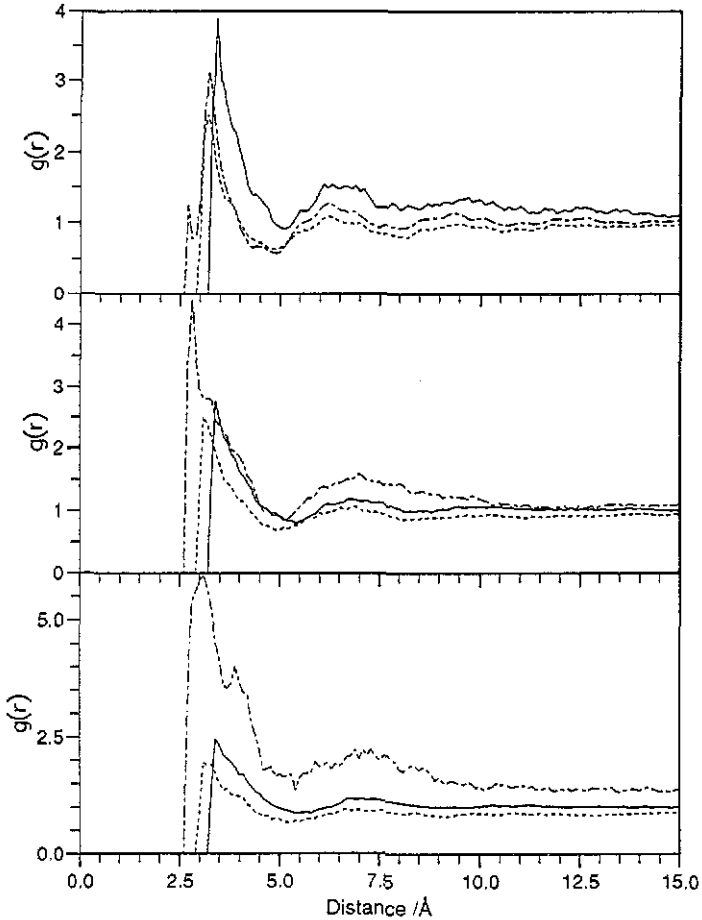


Figure 7. The partial pair correlation functions $g_{KK}(r)$ (full curve), $g_{KPb}(r)$ (broken curve), and $g_{PbPb}(r)$ (chain curve) for $K_{0.25}Pb_{0.75}$ (top), $K_{0.65}Pb_{0.35}$ (centre) and $K_{0.8}Pb_{0.2}$ (bottom).

towards higher numbers. This indicates that while there must be some degree of phase separation in order to maintain the same distribution of potassium neighbours the increased number of smaller lead atoms increases the total number of neighbours.

5. Discussion

The crystalline phases of (K,Rb,Cs)(Sn,Pb) alloys contain tetrahedral arrangements of Pb or Sn atoms. Zintl and Brauer (1933) proposed that such 'polyanions' were stable since Pb_4^{4-} is isoelectronic with the P_4 molecule, which is known to be stable in the gas phase. Geertsma *et al* (1984) extended this idea to propose that the persistence of 'Zintl' ions into the liquid phase would account for the unexpected resistivity behaviour of Na_xSn_{1-x} and Na_xPb_{1-x} alloys (van der Marel *et al* 1982). The idea was further supported by resistivity measurements on $(K,Rb,Cs)_xPb_{1-x}$ alloys (Meijer *et al* 1985, Meijer *et al* 1986, Meijer 1988) which show strong maxima at the

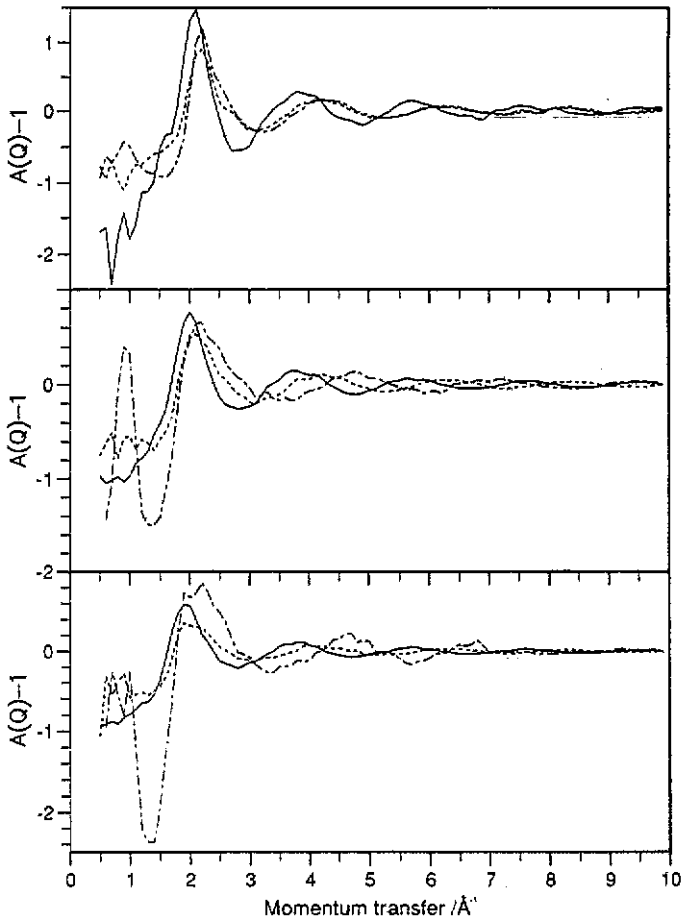


Figure 8. The partial structure factors $A_{KK}(Q)$ (full curve), $A_{KPb}(Q)$ (broken curve), and $A_{PbPb}(Q)$ (chain curve) for $K_{0.25}Pb_{0.75}$ (top), $K_{0.65}Pb_{0.35}$ (centre) and $K_{0.8}Pb_{0.2}$ (bottom).

equiatomic composition. The rapid decrease in specific heats as a function of temperature of (K,Rb,Cs)(Pb,Sn) alloys (Johnson and Saboungi 1987; Saboungi *et al* 1988; Reijers 1990) is indicative of a tendency for some structural unit, presumably the Zintl ion, to dissociate as temperature increases. Reijers (1990) has developed a thermodynamic model which suggests that in KPb 78% of the tetrahedra are in fact dissociated just above the melting point. This would be consistent with inelastic neutron scattering data which show no evidence of vibrational modes of well defined tetrahedral species, but inconsistent with RPSU, RISM or MD structural models which assume 100% tetrahedra.

In the discussion that follows we shall concentrate on K_xPb_{1-x} . It has been noted earlier that the results for CsPb are similar to those for KPb but with a greater tendency to tetrahedra formation, while RbPb has a smaller tendency. This can of course be directly correlated with the FSDP height. The result for CsPb is not surprising since here the resistivity maximum at the equiatomic composition (Meijer *et al* 1986) is much sharper than for KPb (Meijer *et al* 1985). However for RbPb, which has a

resistivity behaviour intermediate between KPb and CsPb (Meijer *et al* 1986) one would have expected an intermediate FSDP; the observed height is not explicable in terms of the scattering length differences between the alkali atoms so we would suggest that for this sample the composition may have been incorrect by a few per cent. A temperature error is also possible though this would have to be 100–200 K.

RMC has produced a number of structural models that are consistent with the data for KPb, which is not particularly surprising for such an ill-conditioned problem. However these models have three features in common: (a) a degree of clustering of the Pb atoms, (b) intermediate range order between Pb clusters leading to a FSDP predominantly in $A_{\text{PbPb}}(Q)$ and (c) 60° Pb–Pb–Pb bond angles. All of these features are indicative of a *tendency* to form Pb_4 tetrahedra and so are consistent with the underlying picture of Zintl ion stability. We believe that this in itself is a remarkable result and demonstrates the strength of the RMC technique. This information is inherent in the data and yet it could not be extracted (i.e. one could not tell, for instance, whether K or Pb atoms were clustering) simply by observation of the structure factor or radial distribution function. However the range of RMC structures also shows that well defined (tetrahedral) structural units are not *required* to explain the FSDP (this has also been found for molten salts (McGreevy and Pusztai 1990)).

The RMC-III model contains 100% Pb_4 tetrahedra which would appear to be inconsistent with thermodynamics; in addition the tetrahedra approach each other more closely than would be expected for a (4–) charge so we believe that this model is unreliable. In any case a completely tetrahedral model would be inapplicable for non-equiatomic compositions. We could easily construct a whole range of models intermediate between RMC-III and RMC-I, so how should we choose the one that is consistent with the other data? In figure 9 we plot the resistivity as a function of Pb concentration (Meijer 1988) and the height of the FSDP in $A_{\text{PbPb}}(Q)$ (RMC-I model for KPb); they are highly correlated. This can be qualitatively understood since the FSDP height is related to the degree of Pb clustering which is in turn related to the degree of electron localization. Further support for a simple relationship comes from the temperature dependence of the structure of KPb (Reijers *et al* 1989a); the FSDP height in the total structure factor decreases by $\approx 20\%$ as the temperature increases by 60K, which is approximately the same as the decrease in resistivity. Such a relationship would not be so clear in the more strongly tetrahedral models (e.g. RMC-II and III) where the FSDP also occurs in $A_{\text{KK}}(Q)$. Finally we would note that the RMC-I model contains 25% tetrahedra, very close to the 22% predicted by the thermodynamic model of Reijers (1990).

At non-equiatomic compositions of the K–Pb alloy there seems to be a degree of phase separation, although this appears to be not into separate regions of K and Pb but into regions in which K and Pb are mixed in roughly equal proportions and regions composed almost entirely of the predominant component. In the potassium-rich alloys the lead clusters and the arrangement of potassiums around the leads are much the same as they are in the equiatomic alloy; however in the lead-rich alloys the environment of the potassium ions differs from that in the equiatomic alloy, containing more lead atoms. These results are completely consistent with the high excess stability of the equiatomic composition (Saboungi *et al* 1987). As clustering is observed when K is present only in fairly small amounts one might also expect a slight tendency to cluster in pure molten lead. In this context it is interesting to note that Dzугutov *et al* (1988) have fitted a pair potential to the structure factor for liquid lead using MD simulation; they can reproduce the experimental data to a high degree of accuracy

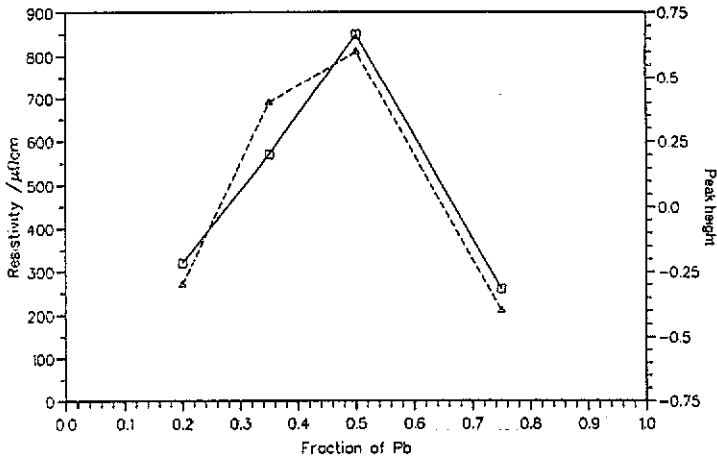


Figure 9. Electrical resistivity (squares and full curve) and height of the FSDP (triangles and broken curve) in $A_{Pb}B_{1-Pb}(Q)$ as a function of composition of molten KPb alloys.

except in the region of $Q \approx 1 \text{ \AA}^{-1}$ where the data has a slight shoulder which might be indicative of such a clustering tendency. Presumably to reproduce this feature would require three body terms in the potential.

6. Conclusions

Although the bad conditioning of this problem means that we must be careful it is nevertheless possible to come to some conclusions. The diffraction data are not consistent with all the Pb atoms in KPb being in tetrahedral Pb_4^{4-} Zintl ions, since these must approach each other too closely to reproduce the data accurately. However unconstrained RMC models, which are found to contain 25% tetrahedra at the equiatomic composition, would appear to be in remarkably good agreement with diffraction, thermodynamic and resistivity data over a range of compositions. We have stressed that the RMC solution is not unique and, given the tendency of RMC to produce the most disordered structure consistent with data and constraints, this is likely to represent a lower bound to the degree of Zintl ion formation. What is now required is a more sophisticated method of quantitatively combining thermodynamic and resistivity data with structural modelling.

Acknowledgments

We wish to thank Professor W van der Lugt and Dr H T J Reijers for many useful discussions and for the provision of their data. We also acknowledge the continued support of the Science and Engineering Research Council and of the Royal Society.

References

- Dzugutov M, Larsson K-E and Ebbsjö I 1988 *Phys. Rev. A* **38** 3609-17
- Hafner J 1989 *J. Phys.: Condens. Matter* **1** 1133-40
- Geertsma W, Dijkstra J and van der Lugt W 1984 *J. Phys. F: Met. Phys.* **14** 1833-45

- Keen D A and McGreevy R L 1990 *Nature* **344** 423-4
- Lowden L J and Chandler D 1973 *J. Chem. Phys.* **59** 6587-95
- McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
- 1990 *Proc. R. Soc. A* **430** 241-61
- McGreevy R L, Howe M A, Keen D A and Clausen K 1990 *Neutron Scattering Data Analysis 1990: IOP Conf. Ser. 107* pp 165-84
- Meijer J A 1988 *Thesis* University of Groningen
- Meijer J A, Geertsma W and van der Lugt W 1985 *J. Phys. F: Met. Phys.* **15** 899-910
- Meijer J A, Vinke G J B and van der Lugt W 1986 *J. Phys. F: Met. Phys.* **16** 845-51
- Moss S C and Price D L 1985 *Physics of Disordered Materials* ed D Adler *et al* (Plenum: New York) p 77
- Reijers H T J 1990 *PhD Thesis* University of Groningen
- Reijers H T J, Saboungi M-L, Price D L, Richardson J W, Volin K J and van der Lugt W 1989a *Phys. Rev. B* **40** 6018-29
- Reijers H T J, van der Lugt W and van Dijk C 1987 *Physica B* **144** 404-6
- Reijers H T J, van der Lugt W and Saboungi M-L 1990 *Phys. Rev. B* **42** 3395-405
- Reijers H T J, van der Lugt W, van Dijk C and M-L Saboungi 1989b *J. Phys.: Condens. Matter* **1** 5229-41
- Saboungi M-L, Blomquist R, Volin K J and Price D L 1987 *J. Chem. Phys.* **87** 2278-81
- Saboungi M-L, Leonard S R and Ellefson J 1986 *J. Chem. Phys.* **85** 6072-81
- Saboungi M-L, Reijers H T J, Blander M and Johnson G K 1988 *J. Chem. Phys.* **89** 5869-75
- van der Marel C, van Oosten A B, Geertsma W and van der Lugt W 1982 *J. Phys. F: Met. Phys.* **12** 2349-61
- Zintl E and Brauer G 1933 *Phys. Chem.* **20** 245