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LETTER TO THE EDITOR

Formation of polyanionic clusters in liquid potassium–lead alloys: a molecular-dynamics study

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Abstract. We show that alloying effects in the effective interatomic potentials lead to a strong preferential interaction between the Pb ions in K–Pb alloys and to the formation of polyanionic clusters not only in the crystal, but also in the liquid alloy. For the first time it is demonstrated that the limitation of the electronic mean free path arising from the strong disorder scattering has a pronounced influence on the interatomic forces and hence on the structure of the liquid alloy.

The physics and chemistry of solid and liquid alkali–lead compounds present many interesting facets [1, 2]. In the lithium–lead and sodium–lead systems the most stable intermetallic compounds are formed close to the ‘octet composition’ A_4Pb (Li_7Pb_2 , $Na_{15}Pb_4$, respectively see [3, 4]). In these crystal structures each Pb atom is surrounded by alkali atoms only. In the alloy systems of the heavy alkali metals K, Rb and Cs with Pb, the most stable intermetallic compounds are formed at the equiatomic composition. KPb, RbPb and CsPb have the NaPb crystal structure [5, 6]. The unit cell contains eight nearly regular Pb_4 tetrahedra. Neighbouring Pb_4 tetrahedra are separated by sodium atoms in such a way that each sodium is tetrahedrally coordinated by Pb_4 tetrahedra. Diffraction experiments have shown that the short-range order is preserved upon melting. In liquid Li–Pb and Na–Pb alloys a pronounced chemical short-range order (CSRO) is observed [2, 7] which is strongest at the ‘octet composition’. The CSRO is well understood in terms of charge ordering effects [8, 9]. In liquid KPb, RbPb and CsPb a sharp first diffraction peak (‘prepeak’) is observed at $q \approx 1 \text{ \AA}^{-1}$. It is strongest at the equiatomic composition [10–12]. A molecular model based on a random arrangement of tetrahedral Pb_4 units in a matrix of alkali atoms has been proposed [11]. The assumption is that the valence electrons of the alkali atoms are transferred to the lead clusters. The polyanionic Pb_4^{4-} tetrahedra are then isoelectronic to the tetrahedral molecules of the group V elements (P_4 , As_4 , . . .). The model gets some support from electronic structure calculations in a cluster-Bethe-lattice approximation [13], but an actual calculation of the structure of the liquid alloys of the heavy alkali metals with lead is still missing.

In this Letter we present the first molecular dynamics calculation for a liquid alloy with a strong tendency to a formation of polyanionic clusters. Our approach is based on effective interatomic interactions derived from first-principles pseudopotentials and a modified linear screening approach. It is clear that a proper description of such crystalline and liquid cluster compounds will be possible only if the effective interatomic potentials

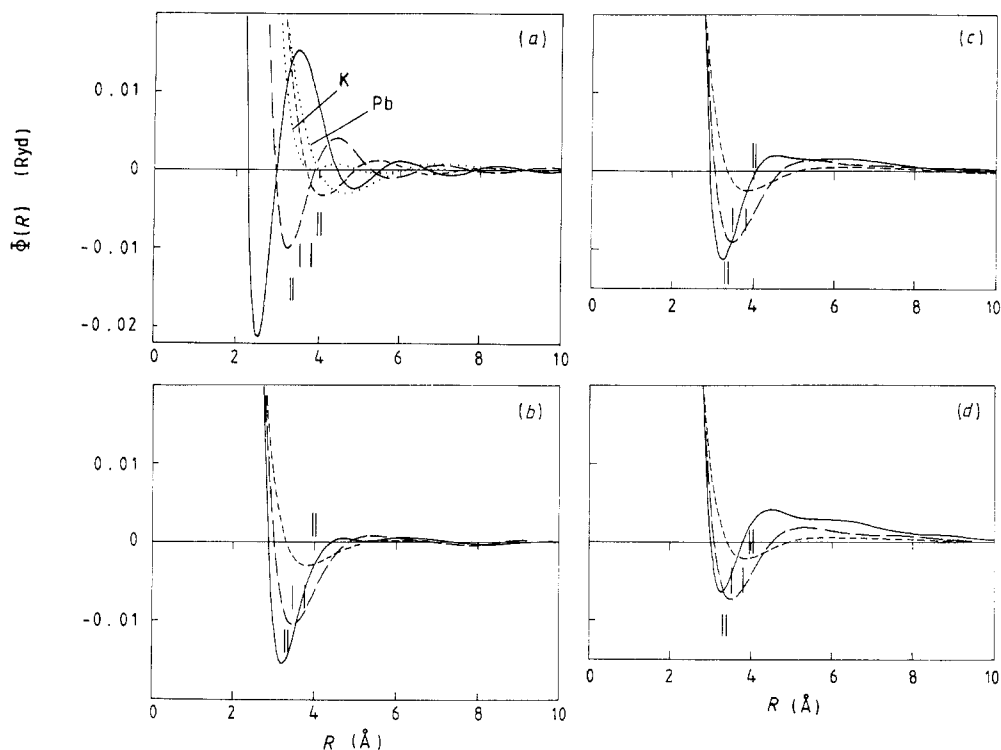


Figure 1. Effective interatomic potentials $\Phi_{ij}(R)$ in KPb alloys. (a) Calculated using concentration-independent ionic model potentials. (b–d) Calculated using optimised first-principles pseudopotentials, assuming different values for the electronic mean free path l : (b) $l = \infty$, (c) $l = 32$ Å and (d) $l = 21$ Å. Full curves, $\Phi_{\text{Pb-Pb}}$; long broken curves, $\Phi_{\text{K-Pb}}$; short broken curves, $\Phi_{\text{K-K}}$. Dotted curve, pair interactions in the pure liquid metals. The vertical bars indicate the nearest-neighbour distances in the crystal.

in the alloy are substantially different from those in the pure metals. Variations in the interatomic interactions may be caused by:

- (i) changes in the electron density and in the Fermi-momentum;
- (ii) changes in the ionic pseudopotentials; and
- (iii) changes in the mean free path of the electrons caused by strong disorder scattering.

Changes in the electron density alter the screening function, a change in the Fermi momentum affects first of all the on-Fermi-sphere matrix element $w(2k_F)$ setting the amplitude of the oscillations in the pair potential [14]. If the pseudopotential does not change on alloying (for example if we use empty-core model potentials with fixed core radii, $R_c(\text{Pb}) = 0.508$ Å, $R_c(\text{K}) = 1.207$ Å) this results in a very strongly enhanced Pb–Pb interaction in KPb compared with pure lead (see figure 1(a)). This is a consequence of the strong increase to the on-Fermi-sphere pseudopotential matrix element $w(2k_F)$ with the reduction of the Fermi momentum and leads to a completely unrealistic form of the pair potentials.

Changes in the ionic pseudopotentials on alloying are related very intimately to the quantum mechanical nature of the pseudopotential. In most cases the ionic pseudopotentials are considered as transferable, i.e., the pseudopotentials calculated for a

free-atom or free-ion reference configuration are considered as a valid approximation to the pseudopotential in the metal or alloy. The modern 'normconserving' pseudopotentials represent an attempt to optimise the transferability of the pseudopotential. However, within the framework of pseudopotential perturbation calculations it was found to be advantageous to drop the requirement of transferability altogether and to construct pseudopotentials which are optimised specifically for each composition and electron density of the alloy. The aim of the optimisation is to improve the convergence of the perturbation series by folding down higher-order perturbation corrections into lower order. A detailed description of these composition-dependent changes in the pseudopotential and further in the effective interatomic interactions has already been given for alloys with moderate (Ca–Al [14]) to strong (Li–Pb, Na–Pb [8, 9]) chemical bonding effects. For K–Pb we find that the weaker orthogonalisation effect in the alloy than in pure lead yields a more attractive ionic pseudopotential for Pb, partially compensating for the reduced screening. The resulting pair potentials (figure 1(b)) are now much more realistic: the nearest-neighbour distances in the stable KPb structure fall exactly into the minima of the corresponding pair potential. However, if we use these potentials in a simulation of liquid KPb we find a strong tendency to a formation of large Pb clusters containing more than just four lead atoms. This suggests that the Pb–Pb interactions are still too strong.

A problem to which hardly any attention has been devoted up to now is the influence of an eventually finite mean free path of the conduction electrons on the screening function and hence on the effective interatomic interactions. The well known Lindhard formula for the electronic susceptibility is based on the assumption of an infinite mean free path of the electrons. For the liquid alkali–lead alloys the available electronic transport data [15] point to an electronic mean free path of the order of a few interatomic distances at the compound-forming composition. The effect of an impurity- or disorder-limited electronic mean free path on the susceptibility has been discussed by de Gennes [16]. The complex self-energy of the electrons scattered by the disorder is calculated in a very simple approximation, assuming a scattering matrix element independent of the momentum transfer. This leads in particular to a mean free path independent of the energy of the electrons. De Gennes showed that with a decreasing mean free path the logarithmic singularity in the susceptibility disappears, and that this yields a strong damping and a slight phase shift of the Friedel oscillations in the induced screening charges. The result is however quite different from the 'intuitive' approximation of a damping by a factor $\exp(-R/l)$ (where l is the mean free path). We have applied de Gennes' method to the calculation of the effective interatomic interactions. In principle the atomic structure of the liquid and the electronic mean free path l should be calculated self-consistently. Here we take the freedom to treat l as an adjustable parameter. The effect on the interatomic potentials $\Phi_{ij}(R)$ is illustrated in figures 1((b)–(d)): with a decreasing mean free path the Friedel oscillations are damped and the repulsive part of $\Phi_{ij}(R)$ cuts off less sharply so that the first few wiggles are superposed to an essentially exponentially decaying repulsive tail. As expected the interactions between the small polyvalent lead pseudoatoms are much more strongly affected than those between the large alkali pseudoatoms. There is no room here for mathematical details which will be given in a forthcoming paper, but the reader might find it helpful to consult the paper by Hafner and Heine [17] on the general theory of interatomic interactions in s,p-bonded materials.

These interatomic potentials serve as the basis for a molecular dynamics simulation of liquid KPb. We have used a classical constant-energy molecular dynamics method

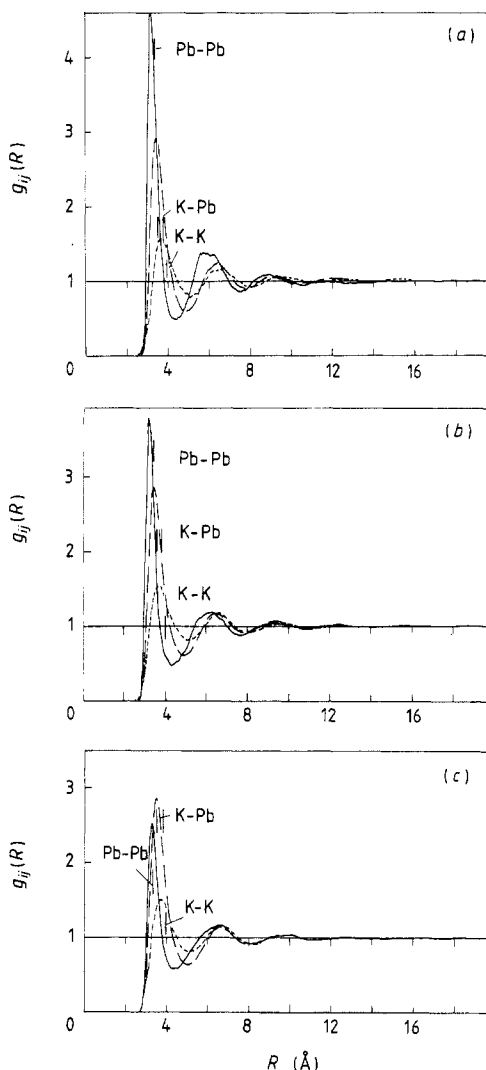


Figure 2. Partial pair correlation functions $g_{ij}(R)$ in liquid KPb at $T = 880$ K calculated using molecular dynamics and different values of the electronic mean free path l : (a) $l = \infty$, (b) $l = 32$ Å, (c) $l = 16$ Å. Full curves, $g_{\text{Pb-Pb}}(R)$, long broken curves $g_{\text{K-Pb}}(R)$, short broken curves $g_{\text{K-K}}(R)$. The vertical bars indicate nearest-neighbour distances in crystalline KPb.

with a fifth-order predictor-corrector algorithm for the integration of the Newtonian equations of motion and an efficient network-cube approximation for nearest-neighbour book-keeping [18]. The simulations were performed for an ensemble of 1372 particles (686 K at 686 Pb atoms) in a cubic cell at a number density of $n = 0.0217$ Å⁻³ at $T = 880$ K [19] (the large negative excess volume of the alkali-lead alloys is rather well understood even in lowest-order pseudopotential theory (see Ch. 6.1 in [14], and [20]). The time increment was $t = 0.3 \times 10^{-14}$ s. The interatomic potentials were cut at $R_{\text{max}} = 12$ Å, corresponding to about 30% of the length of the edge of the MD cell. At this distance the amplitude of the pair potential is smaller than 0.0001 Ryd. With this cut-off each particle interacts with about 160 neighbours on average.

The particle pair correlation functions $g_{ij}(R)$ calculated for various values of the electronic mean free path l are shown in figure 2. Independently of l the peaks in the

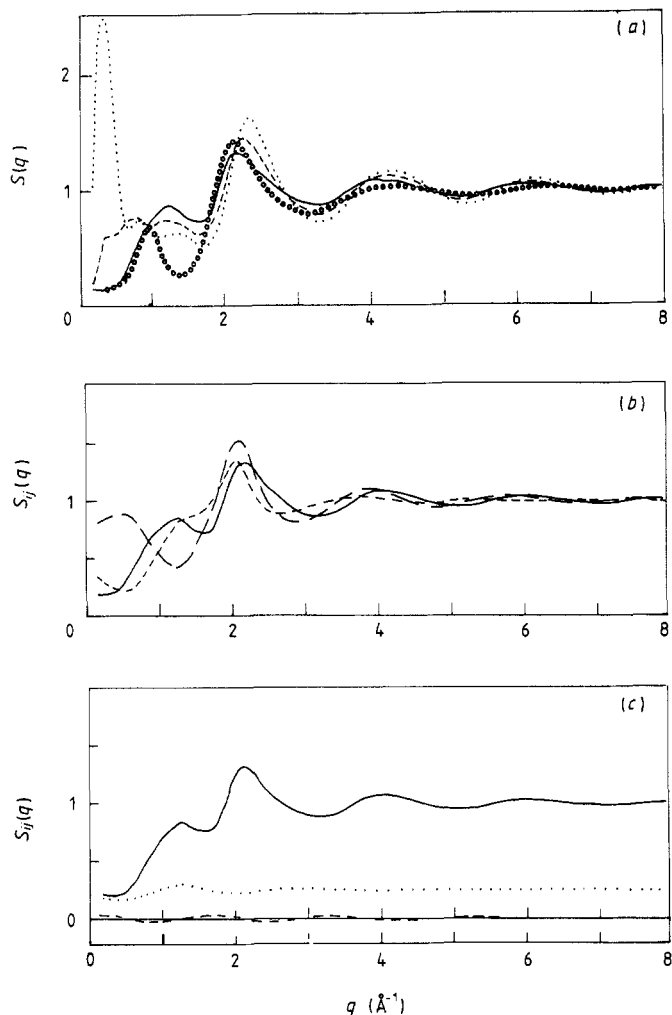


Figure 3. (a) Neutron-weighted composite structure factor $S(q)$ for liquid KPb at $T = 880$ K. Dotted curve calculated with $l = \infty$, broken curve, calculated with $l = 32$ Å, full curve, $l = 21$ Å. The open circles give the neutron diffraction results of Reijers *et al* [10], measured at $T = 858$ K. (b) Ashcroft-Langreth partial structure factors $S_{\text{Pb-Pb}}(q)$ (full curve), $S_{\text{K-Pb}}(q)$ (long broken curves) and $S_{\text{K-K}}(q)$ (short broken curve), calculated with $l = 21$ Å. (c) Bhatia-Thornton partial structure factors $S_{\text{NN}}(q)$ for density fluctuations (full curve), $S_{\text{cc}}(q)$ for concentration fluctuations (dotted curve), and cross-term $S_{\text{Nc}}(q)$ (broken curve), calculated with $l = 21$ Å.

$g_{ij}(R)$ are very close to the corresponding nearest-neighbour distances in the crystalline compound. Note that while the Pb-Pb distances are very sharply defined, the first peak in the K-K correlation function is much broader and lower. This shows that the local order is dominated by the lead atoms. The relative amplitude of the peaks varies strongly with l . For an infinitely long mean free path the Pb-Pb interaction is so strong that it leads to a formation of large Pb clusters (in the structure factors (figure 3) this is reflected in long-wavelength density fluctuations). As the mean free path decreases the number

Table 1. Average coordination numbers in the crystalline compound KPb and in liquid KPb alloys, calculated as a function of the electronic mean free path l .

		K	Pb	Total
Crystal				
	K	4.5	7	11.5
	Pb	7	3	10.0
Liquid, molecular dynamics				
$l = \infty$	K	6.7	5.5	12.2
	Pb	5.5	4.8	10.3
$l = 32 \text{ \AA}$	K	5.9	6.1	12.0
	Pb	6.1	3.8	9.9
$l = 21 \text{ \AA}$	K	5.8	6.0	11.8
	Pb	6.0	3.5	9.5
$l = 16 \text{ \AA}$	K	5.6	6.1	11.7
	Pb	6.1	3.1	9.2

of Pb atoms in a cluster is reduced and for $l \approx 21 \text{ \AA}$ (corresponding to 5 to 6 interatomic distances) the number of Pb atoms in a cluster is about four (see table 1 for the value of the partial coordination numbers in the melt as compared to those in the crystal). Let us note that a mean free path of the order of a few interatomic distances is in good agreement with the measured electrical resistivity of $\approx 900 \mu\Omega \text{ cm}$ [15]. However, we should not forget that the mean free path entering the self-energy is not identical to the transport mean free path determining the resistivity.

The analysis of the bond-angle distributions shows that many Pb–Pb–Pb triplets enclose a bond-angle of about 60° so that we find indeed approximately tetrahedral units (figure 4). The trend to a reduction of the Pb–Pb coordination is paralleled by an increasing tendency to heterocoordination—the K ions separating the small Pb clusters. However, the distribution of the coordination numbers is a rather broad one. Although the average number of atoms in a Pb cluster is four, we also find a substantial number of three- and five-atom clusters. The same follows from the analysis of the bond angles. The distribution of the bond angles shows peaks at the crystalline bond angle and a similar, but substantially broader distribution.

In the neutron-weighted composite structure factor $S(q)$ (figure 3(a)) we find for $l = \infty$ a very strong peak at small momentum transfers indicating a trend to the formation of extended Pb clusters and ultimately segregation. As l decreases we find a broad plateau extending from $q \approx 0.5 \text{ \AA}^{-1}$ to $q \approx 1.6 \text{ \AA}^{-1}$ reflecting the formation of clusters of various sizes. With a still shorter l this plateau develops into a single peak near 1.2 \AA^{-1} . From the partial Ashcroft–Langreth and Bhatia–Thornton structure factors (figure 3(b) and (c)) we find that the prepeak is dominated by the arrangement of the Pb atoms and that it does not represent a chemical, but a topological short-range order: the prepeak is due to the number-density-fluctuation structure factor $S_{NN}(q)$ and not to the concentration-fluctuation structure factor $S_{cc}(q)$. The agreement with the neutron scattering data [10] is only semi-quantitative—the prepeak is slightly shifted and we do not find the deep minimum between the prepeak and the main peak of $S(q)$. Again this reflects the greater regularity of the Pb clusters in the real alloy than in the theoretical model.

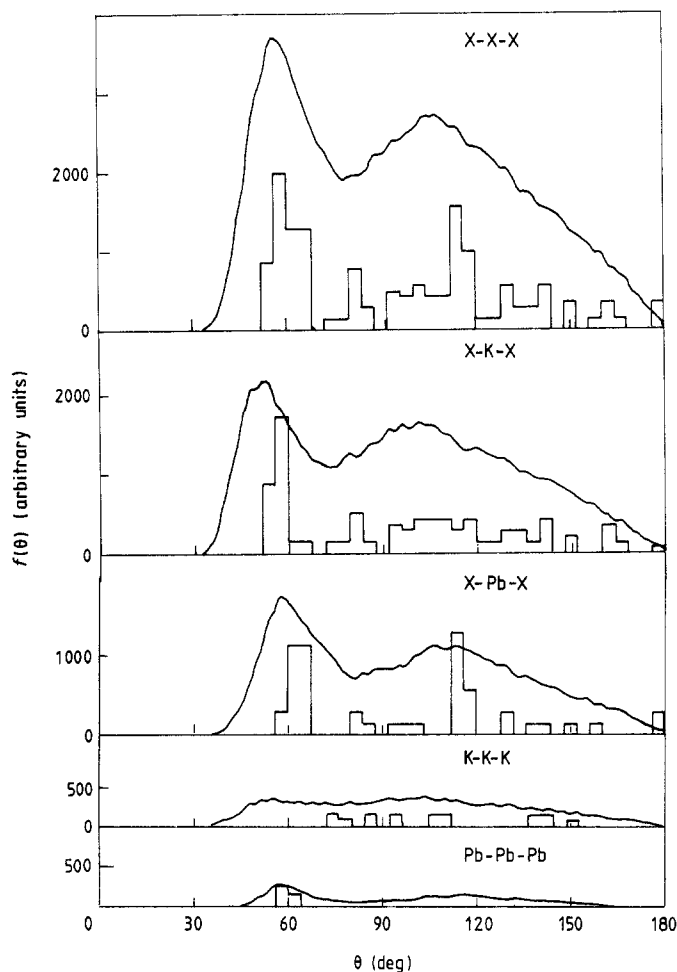


Figure 4. Total and partial bond-angle distribution for KPb alloys: full curve, liquid alloy at $T = 880$ K calculated with $l = 21$ Å, histogram, crystalline intermetallic compound.

In this Letter we have demonstrated that strong alloying effects can lead to a preferential interaction between the polyvalent ions and to the formation of polyanionic clusters in liquid alloys. For the first time it has been shown that the limitation of the electronic mean free path by strong disorder scattering has a pronounced influence on the effective interatomic interactions and hence on the structure of a liquid alloy. We do not achieve a fully quantitative agreement with the experiment—this is due mainly to the neglect of three-body forces. Angular-dependent interactions contribute to the rigidity of the bond-angles and to a greater regularity of the polyanionic clusters. It is important however to realise that the main chemical and structural trends are set already by the pair interactions. We are currently working to extend our investigations to include three-body forces.

Similar effects are observed in liquid Rb–Pb and Cs–Pb alloys [11, 12]. Preliminary results indicate that our approach describes their structure rather well and that the variation of the electronic mean free path inferred from the resistivity data parallels the

evolution of the topological short-range order in the sequence KPb–RbPb–CsPb. This work has been supported by the Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich (Austrian Science Foundation) under project no 6191.

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