Ab initio calculations for mixed clusters of lead and alkali elements, and implications for the structure of their solid and liquid alloys

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Abstract

Ab initio density functional calculations for mixed clusters of Pb and alkali elements demonstrate the high stability of the octet clusters $A_4Pb$ in the case of light alkali metals, that is for $A = Li$ or $Na$. This justifies the observed anomalies at the composition of 20% Pb in the liquid alloys of Pb with Li and Na. The calculations also show the high stability of the Zintl clusters $A_4Pb_4$, which explains the crystalline structure of the equiatomic solid compounds of Pb with Na, K, Rb and Cs, and the persistence of the Zintl complexes in the melt. The absence of Zintl clustering in the Li alloys is due to an atomic size effect.

The class of alloys formed by lead and alkali metals is characterized by properties that have been interpreted as indicating the presence of clustering [1]. In the solid phase, Na–Pb, K–Pb, Rb–Pb and Cs–Pb form equiatomic ordered compounds in which the Pb atoms group together forming Pb tetrahedra in a tetrahedral configuration and these tetrahedra are kept apart by the alkali atoms [1,2]. Around each Pb tetrahedron are four alkali atoms arranged in a larger tetrahedron with the opposite orientation; each alkali atom is shared by two Pb tetrahedra. The chemical view of this clustering effect goes back to Zintl and Woltersdorf [3]. Due to the large difference of electronegativity between Pb and the alkali atoms, each alkali atom transfers its valence electron to one Pb atom. The corresponding Pb$^-$ anions become isoelectronic with the P and As atoms, which in the gas phase form tetrahedral P$^-$ and As$^-$ molecules. Note that 20 electrons is a magic number for clusters with Td symmetry. Group-symmetry arguments favour tetrahedral structures for pentavalent atoms. It is assumed that, in a similar way, the Pb$^-$ anions group together in the crystal forming $(Pb)_4^{3-}$ polyanions. Li–Pb is, however, an exception to this rule. Evidence also exists for the survival of the Zintl polyanions when the solid compounds melt. Neutron diffraction experiments in the liquid give radial distribution functions consistent with the presence of Pb tetrahedra [4,5]. Again in the liquid alloys, the electrical resistivity shows a sharp maximum as a function of Pb concentration at 50% Pb in the alloys with K, Rb and Cs [1] indicating a departure from metallic character at that composition. Other properties, such as density, specific heat and Darken stability (the second derivative of the Gibbs free energy with respect to concentration of one component) also
display pronounced features at the equiatomic concentration.

Liquid Li–Pb alloys behave differently. Structural, electronic and thermodynamic properties display pronounced features at a concentration of 20% Pb [1] and this behavior has been interpreted in terms of the formation of "octet" clusters Li\textsubscript{4}Pb\textsubscript{2}, with eight valence electrons closing the 6s, 6p shell of lead. Finally, the Na–Pb alloys mark the transition between the two groups (Li–Pb on one side and K–Pb, Rb–Pb, Cs–Pb on the other) with properties like the electrical resistivity or the Darken stability showing a pronounced maximum at 20% Pb and also a smaller second maximum, or a shoulder, at the equiatomic (50% Pb) composition.

In this Letter we wish to show how these clustering features in the condensed phases can be explained by appealing only to calculations for appropriately selected "free" clusters. To this end we have performed ab initio Density functional calculations [6] using nonlocal norm-conserving pseudopotentials [7], a superlattice geometry (cubic lattice of cell parameter 34 au) and a plane wave basis set [8] with an 8 Ry energy cut-off. The selfconsistent determination of the wavefunctions used Car–Parinello optimization techniques [9] and the local density approximation (LDA) for exchange and correlation effects [10]. The pertinent computational details can be found in a previous paper [11]. The results of ab initio calculations on related clusters [11–14] appear to explain the relative abundance of Na\textsubscript{n}Pb clusters produced by aggregation in the gas phase in mass spectrometry experiments [15], which gives us confidence in the treatment of the clusters in this work.

We begin with an analysis of the octet clusters. Fig. 1 shows the energy required to evaporate an alkali atom (A) from A\textsubscript{n}Pb clusters which is defined to be

$$E_e(A_n\text{Pb}) = E(A_{n-1}\text{Pb}) + E(A) - E(A_n\text{Pb})$$

(1)

in terms of the total ground state energies of the fragments A\textsubscript{n−1}Pb and A and the parent cluster A\textsubscript{n}Pb. A large value of $E_e$ is associated with high stability of the corresponding parent cluster. The main observation is that the only maximum of $E_e$ in the series of Li clusters occurs for Li\textsubscript{4}Pb, which is an exceptionally stable cluster with a filled HOMO

level and a substantial HOMO–LUMO gap. Its electronic configuration can be described in simple terms as the (6s\textsuperscript{2})(6p\textsuperscript{6}) configuration of the simple shell model [16] even though the ionic skeleton of Li\textsubscript{4}Pb is not spherical-like – the calculated ground state structure is a deformed triangular bipyramid with $C_2\text{v}$ symmetry and with the Pb atom forming part of the base (see inset in Fig. 2). Contours of constant electron density in two representative planes of the cluster (the two reflection planes) are given in Fig. 2. One of the planes (Fig. 2(a)) is the common base of the bipyramid and the other is the plane orthogonal to the base of the bipyramid and containing the lead atom and the apex atoms of the two pyramids. The 6s electrons as denoted above are localized around the Pb atom. The density contours of the 6p shell, which are also centered on the Pb atom, are roughly spherical and display maxima in regions midway between the Pb and the Li atoms. These features are due to the strongly attractive pseudopotential of Pb as compared to Li and justify the approximate validity of the simple shell model. An analysis of density difference plots shows that charge is transferred from the Li atoms to Pb so the bonding is partly ionic. An isomer in which the Pb atom is enclosed at the center of a tetrahedron of Li atoms, which evidently is more spherical than the ground state, is however 0.5 eV higher in energy. This is because the Li–Li distances in this case are much larger (1.5–2.0 au larger) than the corresponding Li–Li distances in the ground state structure and the residual bonding interaction between the Li atoms is greatly reduced.
Fig. 2. Contours of constant valence electron density for Li, Pb in its minimum energy structure, which is a deformed triangular bipyramid with \( C_{2v} \) symmetry. The structure of the cluster is illustrated in the inset. (a) Contours in the common basal plane of the bipyramid and (b) contours in the vertical plane containing the lead atom and the apex atoms of the two pyramids. The most external contour is \( \rho = 0.001 \) e/au\(^3\); the interval between contours is \( \Delta \rho = 0.002 \) e/au\(^3\); the maximum density (+ symbol) is (a) \( \rho = 0.0415 \) e/au\(^3\) and (b) \( \rho = 0.0388 \) e/au\(^3\).

Turning to the case of Na, Pb clusters we see in Fig. 1 that Na, Pb is again a stable cluster. For instance the difference \( \Delta E_v \) in evaporation energy between Na, Pb and Na, Pb, which is another local maximum of \( E_v \), is 0.46 eV. The corresponding difference in the lithium clusters is 0.88 eV. Finally, we notice for the K clusters that K, Pb is no longer highly stable with respect to other clusters of the K, Pb series. We can confidently extrapolate these results and predict that Rb, Pb and Cs, Pb will be even less distinguished in the corresponding Rb and Cs series. These features of the clusters account for the pronounced effects observed at 20% Pb in the liquid alloys with Li and Na, and the absence of effects at this concentration in the alloys containing K, Rb and Cs. Only in the Li and Na cases are the octet clusters, Li, Pb and Na, Pb, highly stable with respect to competing complexes and only in these two cases can one expect a substantial amount of octet clustering in the liquid.

Considering now the Zintl clusters A, Pb, we see that these are also stable. For instance, plotted in Fig. 3 is the energy required to evaporate an alkali atom from Na, Pb and K, Pb:

\[
E_v(A, Pb) = E(A_{n=1}Pb) + E(A) - E(A, Pb),
\]

(2)

and we notice local maxima at \( n = 4 \) and large drops from \( n = 4 \) to \( n = 5 \). The enhanced stability of the
Fig. 4. Electronic energy levels for Pb$_{4}$ in the tetrahedral (T) and rhombus (R) configurations, and for Na$_{n}$Pb$_{2}$ in their ground state ($n = 1$–$5$). The numbers give the degeneracies of some levels. The arrows mark the HOMO level. The vertical bar in Pb$_{4}$(T) indicates the large gap that exists above the LUMO level. This becomes the HOMO–LUMO gap in Na$_{4}$Pb$_{4}$.

Zintl cluster can also be explained as an electronic shell-closing effect. Fig. 4 shows a diagram of the orbital energy levels for Na$_{n}$Pb$_{4}$ ($n = 1$–$5$) in their respective ground state structures and for two isomers of Pb$_{4}$, the first one having a tetrahedral structure (T) and the second is a planar rhombus (R). The ground state of Pb$_{4}$ is the rhombus and although both isomers have the HOMO level filled and a HOMO–LUMO gap, the gap is larger for the rhombus structure. We also see that the tetrahedral isomer has degenerate LUMO and LUMO + 1 levels followed by a large gap of nearly 3 eV separating this doubly degenerate level from the next higher one. This gap is indicated by a vertical bar in Fig. 4. This suggests that the filling of the LUMO and LUMO + 1 levels would stabilize the tetrahedral isomer and this is what actually occurs when alkali atoms bind to Pb$_{4}$. First, in NaPb$_{4}$ the Na atom simply sits above the Pb$_{4}$ rhombus and the valence electron contributed by the Na atom occupies the LUMO of rhombic Pb$_{4}$. When a second Na atom binds to the cluster, the repulsion between the two Na$^{+}$ ions above the rhombus induces a folding of the rhombus into a Pb$_{4}$ tetrahedron with the two Na atoms capping two faces of the tetrahedron. Adding two more Na atoms completes the capping of the four faces of the Pb$_{4}$ tetrahedron in such a way that the four Na atoms form another tetrahedron with opposite orientation. The energy gap mentioned above becomes a fully operative HOMO–LUMO gap in Na$_{4}$Pb$_{4}$ and stabilizes this cluster. In contrast, Na$_{3}$Pb$_{2}$ and Na$_{3}$Pb$_{4}$ have only partially filled HOMO levels accounting for the sharp decrease in stability be-

Fig. 5. Valence electron density plots for (a) Li$_{4}$Pb$_{4}$ and (b) K$_{4}$Pb$_{4}$ in the plane containing two Pb atoms, labelled 1 and 2 in the inset and two alkali atoms, labelled 3 and 4. The outermost contour is $\rho = 0.001$ e/au$^{3}$ and the interval between contours is $\Delta\rho = 0.002$ e/au$^{3}$. Density maxima occur in the regions of the + signs. Circles around the position of the alkali cations represent the size of these cations.
between Na$_4$Pb$_4$ and Na$_4$Pb$_5$ evident in Fig. 3. Calculations for A$_n$Pb$_m$ clusters with $n = 1$–5, varying now the number of Pb atoms, were reported in a previous paper [17] using a simplified model in which the total ionic pseudopotential of the cluster was spherically averaged around its center of mass. Those calculations reinforce the view that the Zintl clusters, A$_n$Pb$_m$, are highly stable with respect to other clusters with $n \neq 4$.

The high stability of the “free” Zintl clusters is not restricted to the heavy alkalis: Na, K, Rb and Cs, for Li$_4$Pb$_4$ is also predicted to be stable. The charge density plots, given in Fig. 5 for Li$_4$Pb$_2$ and K$_4$Pb$_2$ in a plane containing two Pb atoms, labelled 1 and 2 in the inset, and two alkali atoms, labelled 3 and 4, look remarkably similar. The positions of these two alkali atoms with respect to the outer density contours confirm that electronic charge is transferred to the Pb tetrahedron, in agreement with the chemical model [3], but the alkali cations are embedded (more Li$^+$ than K$^+$) in the valence cloud of the cluster, which serves to screen the cation-cation repulsion. However, the structure of the solid compounds and the properties of the liquid alloys indicate that only in the cases of Na, K, Rb and Cs are Zintl polyanions present in the bulk phases. We propose, in accord with Geertsma [18] that the exceptional behavior of the Li alloys is an atomic size effect. The Pb–Pb bond distances are similar in the Zintl clusters of the three alkalis Li, Na and K, with values ranging between 5.83 and 5.89 au i.e. differing by no more than 1%. However, the distances $d$(Pb–A), between the Pb and the nearest alkali atoms depend greatly on the alkali partner. The calculated average values are $d$(Pb–Li) = 5.06 au, $d$(Pb–Na) = 5.71 au and $d$(Pb–K) = 6.43 au. Furthermore, there is a drastic increase of the cation volume as we move down the alkali column of the periodic table. In this way, the external alkali tetrahedron sets an exclusion region around the inner Pb$_4$ tetrahedron whose volume increases from Li to Na to K. The size of the cations has been indicated in Fig. 5 by thick circles drawn around each alkali site, of radius $R$ equal to the ionic radius of Li$^+$ and K$^+$ respectively: R(Li$^+$) = 1.28 au, R(K$^+$) = 2.51 au [19]. In a condensed environment in which the Zintl clusters can interact with each other the cations will not remain in the ideal positions optimizing packing and minimizing mutual repulsion and in the liquid phase they will, in addition, be mobile. In the case of the potassium alloy, each Pb$_4$ tetrahedron is well separated from other Pb$_4$ units by the shielding effect of the large K cations, setting a large exclusion region around the Pb$_4$ polyanions. The interaction between Pb atoms belonging to different tetrahedra is then sufficiently weak to leave the different Pb$_4$ tetrahedra intact in the condensed phase (the radii $R$(Rb$^+$) = 2.80 au, $R$(Cs$^+$) = 3.19 au are even larger than $R$(K$^+$), enhancing the shielding effect). Thus, our picture of the solid is an arrangement of the Pb$_4$ tetrahedra surrounded and kept apart by the K cations and similarly for the Na, Rb and Cs alloys. Similar reasoning suggests the survival of Zintl polyanions in the liquid alloy. By weak interaction between the Pb$_4$ polyanions we mean that the electronic structure of the condensed phases (solid or liquid) can be understood in terms of the overlap of the polyanion orbitals, whose charge density is plotted in Fig. 5. Due to the large size of the cations surrounding the Pb$_4$ polyanions in the alloys with Na, K, Rb and Cs, the orbital overlap is small and, in fact, solid state calculations confirm the non-metallic character of these alloys [20,21]. However, Li$^+$ is the smallest alkali cation (see Fig. 5) and does not prevent the Pb atoms in different tetrahedra becoming close enough to interact strongly in the condensed phase. This leads to energy band broadening, a drastic rearrangement of the whole structure and the energetic favouring of a new solid phase with the CsCl structure [20] and to the absence of Zintl polyanions in the liquid.

Our calculations are based on the use of the LDA for exchange and correlation [10] and one may ask about the effect of gradient corrections. A comparison between the results obtained with the LDA and the more sophisticated GGA (generalized gradient approximation) of Perdew et al. [22] has been presented for the cluster Na$_4$Pb$_4$ [23]. Complete agreement was obtained for the lowest energy structures, although, as usual, GGA bond distances were 0.2 au larger and total binding energies 1.1 eV smaller (the LDA binding energy is 9.7 eV). These results suggest that the LDA treatment of other Pb–alkali clusters is adequate for our purposes.

In summary, using results of ab initio calculations of gas-phase clusters only, we have provided theoretical support for the observed occurrence of clustering.
in solid and liquid alloys of Pb with the alkali metals. Also accounted for are the observed trends in stoichiometry as we progress from Li to Na and through the alkalis. In the liquid Li–Pb alloys the octet cluster Li Pb is favoured, whereas the clusters in the solid and liquid alloys of heavy alkali metals are the K Pb , Rb Pb and Cs Pb Zintl clusters, with the Na alloys as an intermediate case.

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