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1995 J. Phys.: Condens. Matter 7 L19

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## LETTER TO THE EDITOR

# ***Ab initio* simulations of liquid NaSn alloys: Zintl anions and network formation**

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Received 28 October 1994

**Abstract.** Using the Car–Parrinello technique, *ab initio* molecular dynamics simulations are performed for liquid NaSn alloys in five different compositions (20, 40, 50, 57 and 80% sodium). The obtained structure factors agree well with the data from neutron scattering experiments. The measured prepeak in the structure factor is reproduced qualitatively for most compositions. The calculated and measured positions of all peaks show the same trend as function of the composition.

The dynamic simulations also yield information about the formation and stability of  $\text{Sn}_4$  clusters (Zintl anions) in the liquid. In our simulations of compositions with 50 and 57% sodium we observe the formation of networks of tin atoms. Thus, isolated tin clusters are not stable in such liquids. For the composition with 20% tin only isolated atoms or dimers of tin appear; ‘octet compounds’ of one Sn atom surrounded by four Na atoms are not observed.

A large amount of work has been done in the past decades on so-called Zintl systems; for a review see [1]. In general, these systems are binary alloys which contain the (so-called) Zintl ions [2]. These (an)ions are characterized as isoelectronic to typical neutral molecular configurations, for example, the  $\text{P}_4$  molecule.

The alloys of alkali metals with post-transition group IV elements are typical examples of Zintl systems: here the atoms of the group IV elements form anionic Zintl clusters (especially, tetramer anions isoelectronic to  $\text{P}_4$ ). These alloys played a central role in the development of models for compound formation and therefore of the concept of polyanion formation (anion clustering) in liquid anionic alloys.

In this letter we consider the alloys of sodium and tin for which the first indication of anion clustering in those systems was found [3, 4]. The Na–Sn alloys were investigated experimentally by Alblas *et al* [5]; the structures of their solid phases were determined experimentally by Müller and Volk [6, 7]. Theoretical examinations of these alloys were mostly done by means of simple models [5]. A first *ab initio* simulation with the method of Car and Parrinello (CP) [8] of the equiatomic NaSn liquid was published in [10]. Here we extend these CP calculations to different compositions of liquid Na–Sn alloys and discuss their structures, pair correlation functions and structure factors systematically. In particular, we investigate the stability of the Zintl anions  $\text{Sn}_4^{4-}$  and other clusters in the liquids as a function of the sodium (or tin) concentration. In this letter we consider alloys of compositions with 20, 40, 50 (again), 57, and 80% of sodium. For these concentrations experimental (neutron scattering) data are available [5].

Similar work has been done with *ab initio* molecular dynamics for the alloys K–Si [12], Li–Si [13] and Cs–Pb [14] and with empirical molecular dynamics for alkali–Pb alloys [15].

The method and computational details are briefly summarized next. Then the results for the structure factors are presented and compared with the experimental results and the

short-range order, i.e. the cluster stabilities and coordination numbers, is discussed. Finally a summary is given.

For our simulations we used the Car–Parrinello method [8], which was found to be an *effective tool for performing ab initio molecular dynamics; for details of this scheme see* [9]. We applied the MOTECC-90 computer code [11]. The pseudopotentials of Bachelet *et al* [16] were used, and the exchange and correlation (XC) energy was treated within the local density approximation (LDA). The plane wave basis was taken up to a cut-off energy of 6 Ryd, which we found to be sufficient (see below). For the Brillouin zone sampling in the  $k$  space summation for the calculation of the electronic density we only used the  $\Gamma$  point (as in [10]).

To determine the cut-off energy and to estimate the error due to supercell, pseudopotential and LDA effects we calculated the following quantities.

(i) The equilibrium bond lengths of the dimers  $\text{Na}_2$ ,  $\text{Sn}_2$  and  $\text{NaSn}$  with three different cut-off energies using a large supercell, to avoid spurious interactions between the dimers. Furthermore, these bond lengths are calculated with an LCAO program [17] (where the dimers are considered without supercell effects) with (a) LDA and (b) LDA plus gradient corrections (GC).

**Table 1.** Equilibrium bond length (in au) for the dimers  $\text{Na}_2$ ,  $\text{Sn}_2$  and  $\text{NaSn}$  calculated with several cut-off energies by the PWPP method and the LCAO method (for explanation see text) compared to experimental values from [18].

	PWPP-LDA			LCAO		Experiment
	6 Ryd	8 Ryd	10 Ryd	LDA	GC	
$\text{Na}_2$	5.484	5.483	5.482	5.67	5.84	5.82
$\text{Sn}_2$	5.014	5.007	5.030	5.29	5.37	5.30
$\text{NaSn}$	5.430	5.439	5.440	5.69	5.83	

The results—including the available experimental data—are given in table 1. The bond lengths, obtained by the plane wave pseudopotential (PWPP) scheme, applied in this work, agree within about 5–7% with the experimental and LCAO values and are, in general, slightly too small. The effect due to the gradient corrections is small compared to this deviation ( $\leq 3\%$ ). It is obvious from table 1 that a cut-off energy of 6 Ryd is sufficient.

(ii) The equilibrium lattice constants of the supercell of the Na and Sn bulk, respectively, for different cut-off energies. The lattice constants obtained show a similar trend as the dimer bond lengths. They converge in a similar manner with the cut-off energy as the dimer bond lengths and are about 5–10% smaller than the experimental values.

As starting configuration for the simulations we took a cubic supercell with 64 atoms. For the composition with 50% Na we used the geometry of the solid phase of  $\beta$ -NaSn as described by Müller and Volk [6] rescaled to a cubic cell with a length of  $a = 23.4$  au, keeping the same volume as the original cell. Therefore, in the case of the equiatomic composition we used the experimentally known density of the solid [6]; see also [10]. This geometry contains Sn tetrahedra which form Zintl tetramer anions.

Other compositions were achieved by replacing in the same cell with the same atomic positions some atoms from Na to Sn or vice versa. Specifically, we used the following cell configurations:  $\text{Na}_{52}\text{Sn}_{12}$  for 80% Na,  $\text{Na}_{36}\text{Sn}_{28}$  for 57% Na,  $\text{Na}_{32}\text{Sn}_{32}$  for 50% Na,  $\text{Na}_{28}\text{Sn}_{36}$  for 40% Na and  $\text{Na}_{13}\text{Sn}_{51}$  for 20% Na. As the effective atomic radii of Na and Sn are very similar the cell size was kept equal for all compositions.

Having assigned the initial positions, the geometry of the starting configuration was relaxed with a steepest-descent technique for the electronic and ionic systems. After this, the system was equilibrated in order to obtain the desired average temperature which was chosen to be the temperature for which the neutron scattering experiments of [5] have been performed. Firstly the system was heated to a finite temperature by scaling the velocities of the nuclei. Then the Car–Parrinello (CP) dynamics was started for some 500–1000 steps of molecular dynamics. After that the velocities were scaled again, and the ‘heating equilibration’ process was repeated until the averaged temperature over the equilibration CP run was near (within  $\pm 50$  K) the desired value.

During this process the total (kinetic and potential) energy  $E_{\text{cons}}$  of the nuclei had to be monitored. The parameters—the time step  $\delta t$  and the fictitious mass of the orbitals  $\mu$ —were optimized on the one hand to get a simulation with a sufficiently constant energy  $E_{\text{cons}}$ —basically this means with small (fictitious) ‘orbital kinetic energies’—and on the other hand to get a simulation time large enough to extract physical quantities of a liquid. Time steps  $\delta t$  of 5–10 atu with a  $\mu$  in the range of 300–500 au proved to be suitable ( $1 \text{ atu} = 2.4 \times 10^{-17} \text{ s}$ ).

After that the data for the forthcoming analysis could be collected from a ‘production run’ of at least 10 000 steps of CP dynamics. Hence, the total simulation time was about 2 ps. Although this time is too small to simulate a real flow of the liquid, it is sufficient to have an evolution of the system over a time long enough to describe the fluctuations of the interatomic distances. The CPU time per simulation (per production run) was approximately 7 d on an IBM-RS6000 workstation.

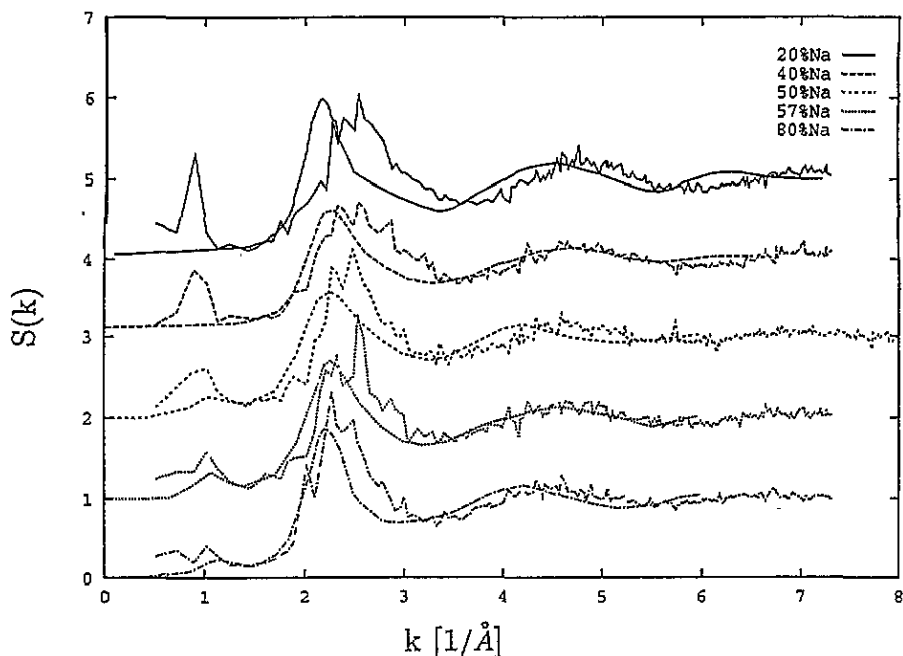
As a check of the ‘liquidness’ of the system the time dependence of the mean square displacement of the atoms from their starting positions was monitored. In liquids, this property increases nearly proportionally with the simulation time.

Each ‘production run’ yielded a phase space trajectory of the system. From the atomic positions of this trajectory the pair correlation functions and the structure factors were obtained as described for example in [5]. Furthermore, the coordination numbers and the bond angle distributions between the atoms could be investigated via a nearest-neighbour analysis; these quantities give information for example about the stability of clusters in the liquid. These results are presented and discussed in the following.

The calculated structure factors for the five considered compositions are plotted in figure 1 together with the experimental ones. The experimental curves were obtained for temperatures of 25 K above the liquidus temperature. These temperatures and the final averaged temperatures of the ‘production runs’ corresponding to our curves are given in table 2.

**Table 2.** Systems and temperatures discussed in this letter. For each system the averaged temperature  $\bar{T}_{\text{MD}}$  of the simulation is compared to the temperature  $T_{\text{exp}}$  for which neutron scattering experiments in [5] have been performed. In addition the liquidus temperature  $T_{\text{liq}}$  is given.

System	Atomic % Na	$\bar{T}_{\text{MD}}$ (K)	$T_{\text{exp}}$ (K)	$T_{\text{liq}}$ (K)
Na <sub>13</sub> Sn <sub>51</sub>	20.3	726	623	580
Na <sub>26</sub> Sn <sub>38</sub>	40.6	818	813	783
Na <sub>32</sub> Sn <sub>32</sub>	50.0	921	873	851
Na <sub>36</sub> Sn <sub>28</sub>	56.3	796	778	752
Na <sub>52</sub> Sn <sub>12</sub>	81.3	748	713	681



**Figure 1.** Static structure factors obtained from CP simulations compared to those from neutron scattering experiments [5] for different NaSn alloys. The atomic percentage for each composition is given. For details on the systems see table 2.

The general agreement between calculations and experiment is good for all cases. The trends of the peak positions as functions of the concentration are reproduced rather well—see figure 2. However, the calculated peak positions (except for the prepeak) are slightly shifted towards larger  $k$  values compared to the experimental ones, see figure 2. Such an effect was also found in the systems Li-Si [13] and Cs-Pb [14]. This shift can be explained by the occurrence of too small distances in real space because these distances correspond with too large distances in the reciprocal lattice. As can be seen from table 1, the interatomic distances (bond lengths) obtained from PWPP calculations are too small. Hence, the shift in the structure factor could be due to pseudopotential effects. Another possible explanation could be that the density of the system used for our simulations is too large compared to the experiments. For each system the simulation yields a prepeak. In general, the prepeak is connected to a superstructure in the liquid. Alblas *et al* suggested that the prepeak corresponds to an ordering of Sn clusters [5]. However, as already shown in [10], the existence of a prepeak is not necessarily connected with the ‘survival’ of such clusters (tetrahedra). For further discussion of these Zintl clusters see the next subsection.

The calculated positions of the prepeaks show the right trend, see figure 2. However, for small Na concentrations (20 and 40%) no prepeak is measured; furthermore, the heights of the prepeaks have the wrong trend. The reason for these differences could be the statistical noise in our simulated structure factors, a too small supercell, i.e. a too broad mesh of  $k$  points for small  $k$  or a ‘superstructure effect’ of the periodicity imposed by the supercell treatment of the system, which could cause a prepeak for all compositions independently from the experiment. On the other hand, the measured structure factors show for the small Na concentrations a rather strong noise for small  $k$  values; therefore a prepeak for these two compositions might be possible, too.

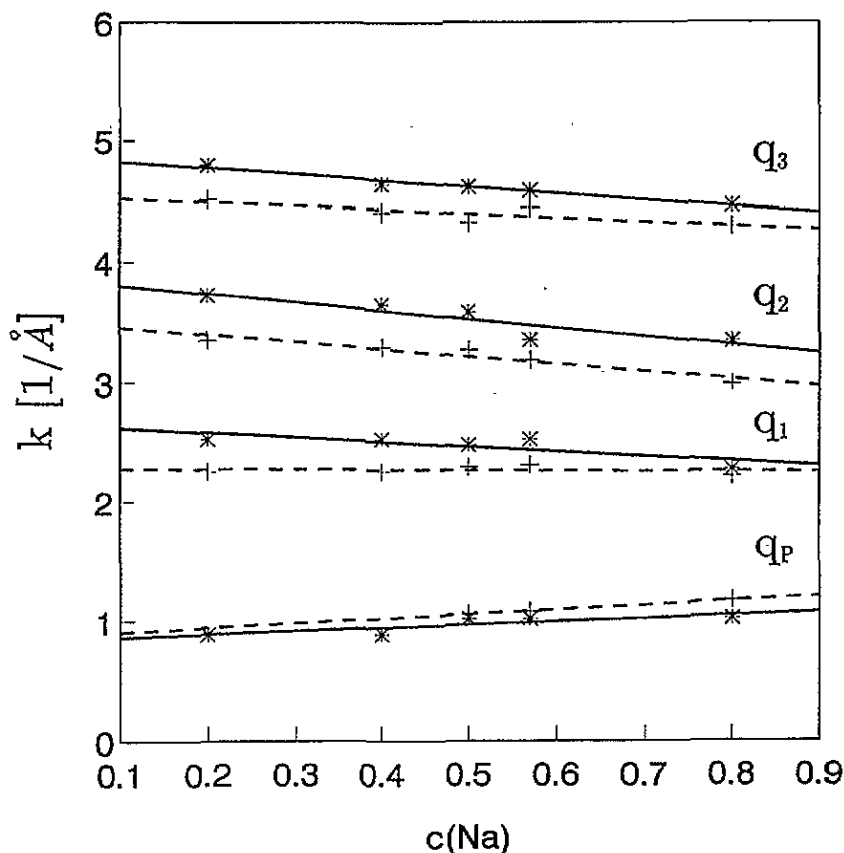


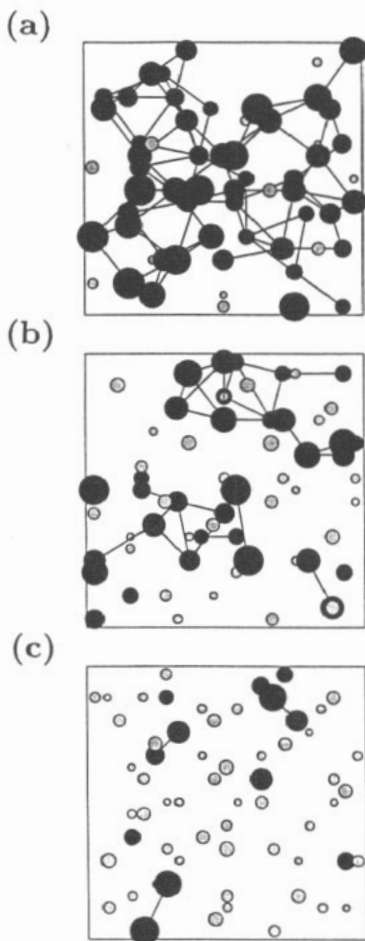
Figure 2. Peak positions in the static structure factors shown in figure 1 plotted as functions of the sodium concentration.  $q_p$ : prepeak,  $q_1$ : main peak (maximum),  $q_2$ : next minimum,  $q_3$ : next maximum. The lines indicate the trend of the peak positions. Dashed lines refer to experimental data [5]; solid lines refer to CP simulations.

Furthermore, we investigated the temperature dependence of the structure factors. It was found for each composition that the structure factor changes only within our numerical accuracy (i.e. within the statistical fluctuations) for temperature differences up to 100 K. Such small changes with the temperature agree with the measurements [5].

The structure factors obtained from neutron scattering experiments as performed in [5] yield no direct information about the geometric structure of the substances. In MD simulations one gets the complete structural information about the system and so it is possible to analyse for example the short-range order which could be helpful for the understanding of certain physical properties.

In this letter we mainly focus on the Sn-Sn correlations. Figures 3(a)-(c) gives snapshots of typical system configurations with 20, 50 and 80% sodium, respectively, taken from our simulations. The bonds between Sn atoms with a distance less than 6 au are shown.

In systems with excess tin (20 and 40% sodium) the Sn atoms form 'dynamic' networks characterized by strong fluctuations in the bondings. We observed only a few atoms with more than fourfold coordination and about as many with two- as with threefold coordination. This and the bond angle distributions indicate that the Zintl anions ( $\text{Sn}_4^{4-}$ ), with which our simulations started, now form larger networks of tin. There is no evidence for the existence



**Figure 3.** Snapshots of system configurations with 20 (a), 50 (b) and 80 (c) % sodium. The Na atoms are plotted as smaller and lighter. The Sn-Sn bonds within the cut-off distance of 6 au are shown.

of isolated Zintl anions in these systems. Figure 3(a) gives an impression of how complex the networks are in the case of the configuration with 20% sodium.

The analysis of the data taken from the simulation with 57% sodium supports the results for the equiatomic composition already published in [10]: the Sn atoms form larger networks than in the case discussed above. The  $\text{Sn}_4^{4-}$  Zintl anions which exist in the solid phase [6] practically do not survive in the liquid. Only a few  $\text{Sn}_4$  tetrahedra remain, and they are parts of a network and not isolated; see figure 3(b). This trend to network formation is again supported by the bond angle distribution analysis, see [10]. Similar results were found for the alloys K-Si [12], Li-Si [13] and Cs-Pb [14]. Their Si and Pb tetrahedra, respectively, tend to build blocks (networks) in the liquid.

When we reduced the proportion of tin in the system (80% Na) neither networks nor Zintl Anions could be observed. Instead we found that the tin atoms preferably stay isolated or form dimers. There is no remarkable trend for a dimer separation, but some evidence for the formation of new dimers ('dumb-bells') during our simulations (see figure 3(c)). So

these dimers seem to be relatively stable with an oscillating bond length with an average of about 5.5 au.

For this composition we also investigated the existence and stability of the so-called 'octet compounds' ( $\text{Na}_4\text{Sn}$  clusters) which were suggested by Alblas *et al* [5]. From our data we could not confirm the existence of such stable complexes.

More detailed discussions on the pair correlation functions, bond angle distributions and coordination numbers and especially results on the electronic structure will be given in a forthcoming paper [19].

In this letter five different compositions of liquid Na-Sn alloys were investigated by means of *ab initio* (Car-Parrinello) simulation. The obtained structure factors agree well with the experimental data. The peak positions show the correct trend as functions of the concentration. The systematic shift can be explained as a (small) pseudopotential effect. In particular, the measured prepeak could be reproduced. Deviations between simulation and experiment concerning the height or the disappearance of the prepeak could be due to noise in the experiment or to statistical fluctuations in the simulation. The structure factors show a very small temperature dependence—within the statistical noise of our simulations—which is also in agreement with the experiment.

We find that  $\text{Sn}_4$  clusters are not stable but form networks in the liquid with 50 and 57% Na. In the case of 80% Na no stable  $\text{Na}_4\text{Sn}$  clusters are observed—which disagrees with suggestions of Alblas [5]: their picture of isolated  $\text{Sn}_4$  tetrahedra and  $\text{Na}_4\text{Sn}$  octet compounds, respectively, does not seem to be an appropriate description of the atomic structure of liquid NaSn alloys.

Our theoretical method has the following limitations: (i) the (finite) supercell, which leads to a broad mesh of the  $k$  points for small  $k$ , (ii) the finite simulation time which causes a statistical noise of the results, (iii) the limited accuracy due to the pseudopotential—which we used without the so-called 'non-linear core corrections' [20] to have a smaller cut-off energy to economize on computer time. To overcome these problems one could use a softer pseudopotential, see e.g. [21], or one could look for approximate methods which allow the simulation of larger times and larger supercells.

On the other hand, our method has the advantage that the electronic structure is considered directly, without empirical parameters (*ab initio* method). Furthermore, the resulting trajectories of the *ab initio* simulations with the corresponding electronic structure (wavefunctions, eigenvalues) allow us to calculate other quantities of physical interest, for example, the resistivity, charge distribution, specific heat, susceptibilities and the Knight shift. For some of these quantities experimental data are available. Especially the resistivity (or conductivity) is known to show a strong dependence on changes in composition.

As next steps, we are going to extract these quantities from our data. Furthermore, we may extend our investigations to other binary (Zintl) alloys.

The authors thank D Hohl, Institut für Festkörperforschung, Jülich, for providing us with his Cornell version of the CP code based on the MOTECC-90 program collection by IBM and are grateful to G Pastore, ICTP Trieste, for helpful discussions and support concerning the computer programs. This work was supported by the Deutsche Forschungsgemeinschaft (DFG).

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