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LETTER TO THE EDITOR

Ab initio molecular dynamics simulation of liquid NaSn alloy

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Abstract. A first-principles molecular-dynamics study of liquid NaSn alloy is presented. The structural properties (static structure factor, bond angle distribution) are discussed. The calculated static structure factor is in good agreement with that from neutron diffraction experiments. The calculations show a tendency of network formation of threefold and fourfold coordinated tin atoms in the liquid. Tetrahedral Sn_4 complexes—Zintl anions $[\text{Sn}_4^{4-}]$ —which are typical structural units in solid NaSn are nearly absent in the liquid. As a consequence of the network formation there is an indication of a 'bimodal' bond angle distribution for the tin atoms.

Alloys of alkaline metals and group IVA elements are characterized by cluster-like groups of the group IV elements (the so-called Zintl anions [1]) in the solid phase. It proves to be interesting to investigate how far these complexes are also apparent in the liquid phase. There are a number of interesting properties of such alloys, so, for example, they show a rather strong concentration dependence of the electric resistivity, ranging from a clearly metallic conductivity down to a nearly semiconductor one [2]. And this variability of the conductivity is probably closely connected with the compound formation in these systems.

A suitable way to study such alloys even in the liquid state is the application of an *ab initio* molecular dynamics scheme as the unified approach to molecular dynamics (MD) and the density functional theory (DFT) [3]. This method allows the study of structural as well as electronic properties; it has been successfully applied to series of problems (see e.g. [4]).

In this letter we will report the results of such MD simulations of liquid NaSn as a first stage of investigation of the structural and electronic properties of liquid I-IV alloys. NaSn in equiatomic composition forms a tetragonal crystal in the solid phase with Sn_4 clusters as typical structural units [5]. $\text{Na}_x\text{Sn}_{1-x}$ alloys have also been investigated widely in the liquid phase—see especially [6].

The unification of DFT and MD became in practice realizable by introducing fictitious orbital dynamics [3]. In this way the Lagrangian \mathcal{L} for the system of one-particle orbitals and ions is:

$$\mathcal{L} = \sum_i \mu_i \int_{\Omega} d\mathbf{r} |\dot{\psi}_i|^2 + \sum_I \frac{1}{2} M_k \dot{\mathbf{R}}_k^2 - E[\{\psi_i\}, \{\mathbf{R}_k\}] + \sum_{ij} \Lambda_{ij} \left(\int_{\Omega} d\mathbf{r} \psi_i \psi_j^* - \delta_{ij} \right). \quad (1)$$

The second term in (1) describes the real dynamics of the nuclei with masses M_k on the potential energy surface $E[\{\psi_i\}, \{\mathbf{R}_k\}]$, and the first term is associated with the fictitious dynamics of the orbitals with a 'mass' μ . The third term follows from the orthonormality constraint on the orbitals ψ_i , and the energy surface E is calculated using DF theory with a local density approximation for the exchange–correlation energy. From this Lagrangian we obtain the equations of motion:

$$\mu_i \ddot{\psi}_i(\mathbf{r}, t) = -\delta E / \delta \psi_i^*(\mathbf{r}, t) + \sum_j \Lambda_{ij} \psi_j(\mathbf{r}, t) \quad (2)$$

$$M_k \ddot{\mathbf{R}}_k = -\partial E / \partial \mathbf{R}_k. \quad (3)$$

(For a detailed description of the method see e.g. [4].) To solve these equations in practice it is necessary to expand the orbitals ψ_i in a suitable basis. Usually, a plane-wave representation for the ψ_i is used. The energy cut-off in the plane-wave expansion was chosen to be 8 Ryd. This cut-off gives reliable for the lattice constants of pure sodium and pure tin. The MD simulation was performed applying periodic boundary conditions with a constant volume cubic elementary cell. This cell contained 32 Na and 32 Sn atoms. We used only the Γ point to sample the Brillouin zone of the supercell. The norm-conserving pseudopotentials according to [7] were used for Na and Sn, considering only the *s*-non-locality. A fictitious mass μ of 300 au was used, and the time step for the numerical integration of the equations of motion was taken to be 6 atu (1 atu = 2.4×10^{-17} s). This choice of parameters guarantees an accurate adiabatic evolution of the system over a rather long time during the MD simulation.

We started the simulation with a geometrical arrangement of the atoms according to a structure obtained from that of the elementary cell of solid β -NaSn [5] by homogeneously rescaling the Na coordinates and the positions of the centres of mass of the Sn tetrahedra with different scaling lengths in the *x*-*y* and *z* directions to transform the original orthorhombic cell into a cubic one and keeping the same intra-tetrahedral distances in order to preserve the tetrahedra. After a small random displacement of the initial ionic coordinates, the system was equilibrated for 12000 time steps (2 ps) at a temperature of 921 K. The data for the statistics were collected in a 'production' run of 10000 time steps (1 ps). The temperature of 921 K (648 °C) is about 70 K above the experimental melting point of β -NaSn [8].

Figure 1 shows the calculated static structure factor from our MD simulation in comparison with that obtained from neutron scattering experiments [6]. There is a good overall agreement between the theoretical and the experimental curves. In particular, our simulation also gives a prepeak in the structure factor at 1 \AA^{-1} in good agreement with the experimental results. Such a prepeak is commonly a characteristic for some ordering in the liquid system and may be ascribed to the concentration–concentration structure factor $S_{CC}(q)$ [9]. We can directly verify such an assignment in figure 2. Alblas *et al* [6] interpreted the prepeak as an indication of the existence of Sn_4 tetrahedra separated by Na atoms, as in the solid compound. From the simulation we indeed find a dominance of the threefold coordination for tin, as it is in the solid. But one half of all Sn atoms is not threefold coordinated: about one quarter is twofold coordinated and, also, about one quarter is fourfold coordinated. The bond angle distribution for the threefold coordinated Sn atoms shows a distinct maximum at 60° (see figure 3(a)), which is also the bond angle in Sn_4 tetrahedra. But there is also a tail to larger bond angles. The bond angle distribution for the fourfold coordinated

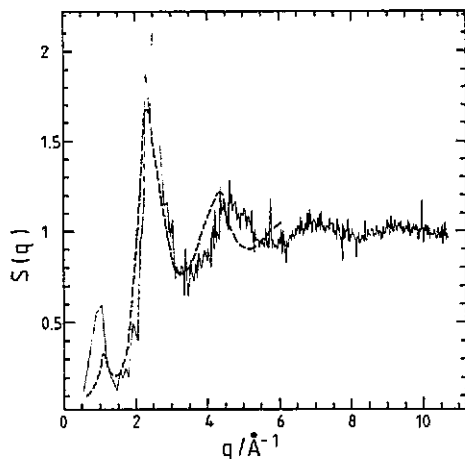


Figure 1. Neutronic structure factor $S(q)$ for NaSn at 648 °C from MD simulation (full curve) and from experimental data (at 650 °C) ([6]) (broken curve).

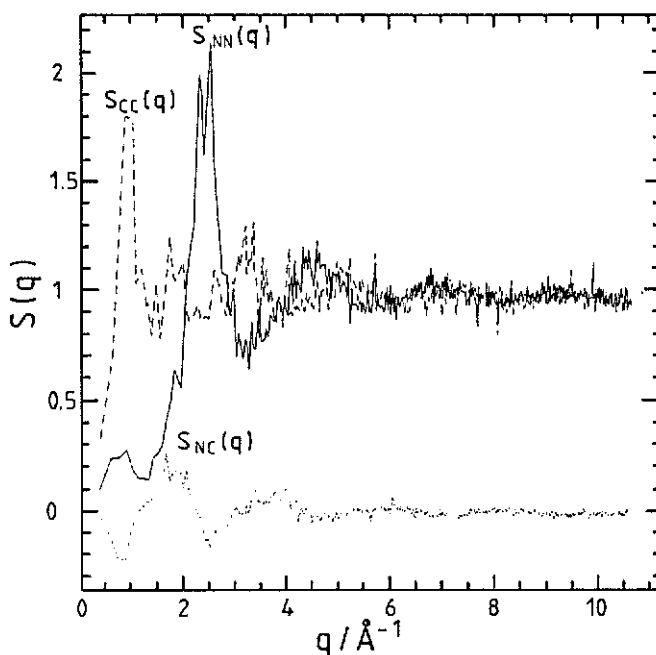


Figure 2. Bhatia-Thornton structure factors [9] $S_{NN}(q)$, $S_{NC}(q)$, $S_{CC}(q)$ for NaSn.

Sn atoms shows a second maximum around the tetrahedral bond angle (109° —see figure 3(b)). In summary this leads to a bimodal bond angle distribution for the tin atoms (see figure 3(c)). This is a clear indication that the ideal isolated tetrahedra—as they exist in the solid—no longer exist in the liquid phase. The analysis of the data from our simulation shows that there are no isolated Sn_4 clusters in the molten alloy. One can find relics of Sn_4 complexes, but always connected with other Sn atoms or groups of Sn atoms. There is a clear tendency to network formation between the tin atoms. An illustrative picture of this behaviour is given by a snapshot of the structure during the simulation (see figure 4).

Thus, the structure of liquid NaSn seems to be a little bit more complex than

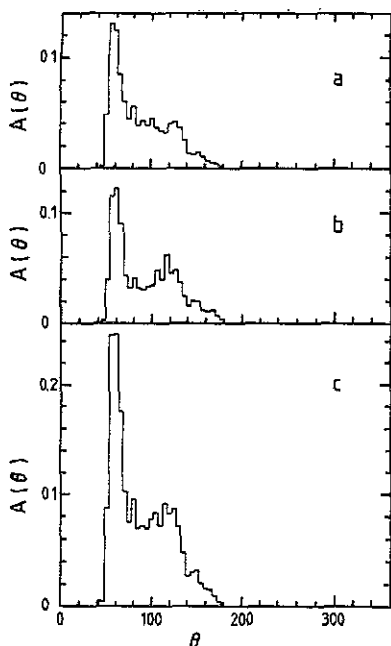


Figure 3. Bond angle distribution [$A_{Sn,Sn}(\theta)$] for tin atoms in NaSn: (a) threefold coordinated atoms, (b) fourfold coordinated atoms, (c) total.

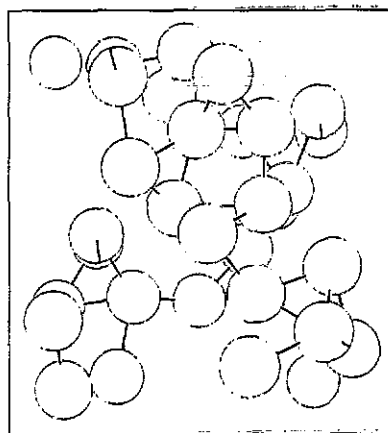


Figure 4. Snapshot of the ionic positions during the MD simulation (Sn atoms only). Tin atoms with interatomic distances less than 3.2 Å are connected by straight lines.

assumed from previous investigations [6]. Similar results were obtained quite recently for a related system (molten KSi), also using the *ab initio* MD scheme [10]. In the case of KSi the Zintl ion stability is expected to be larger than in the present case. The finding of Galli and Parrinello of an 'oscillation' between a configuration containing distorted tetrahedra and another containing a 'percolating' network of Si atoms and the absence of the distorted tetrahedra in our sample are in agreement with such an expectation. In conclusion, from the simulation of KSi [10] and NaSn (presented here) it follows that the assumption of the existence of stable Zintl ions in the liquid phase may be inappropriate. Nevertheless, in the liquid phase there are clear indications of a persistence of features related to the original β -NaSn crystalline structure. A more detailed analysis of the simulation results considering also the electronic properties is in progress.

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References

- [1] Zintl E 1939 *Angew. Chem.* 1 1
- [2] Van der Marel C, Van Oosten A B, Geertsma W and Van der Lugt W 1982 *J. Phys. F: Met. Phys.* 12 2349
- [3] Car R and Parrinello M 1985 *Phys. Rev. Lett.* 55 2471

- [4] Car R and Parrinello M 1988 *Simple Molecular Systems at Very High Density (NATO Advanced Study Institute Series B 186)* p 455
- [5] Müller W and Volk K 1977 *Z. Naturf. b* **32** 709
- [6] Alblas B P, Van der Lugt W, Dijkstra J, Geertsma W and Van Dijk C 1983 *J. Phys. F: Met. Phys.* **13** 2465
- [7] Bachelet G B, Hamman D and Schlüter M 1982 *Phys. Rev. B* **26** 4199
- [8] Hansen M and Anderko K 1958 *Constitution of Binary Alloys* (New York: McGraw-Hill) 1958
- [9] Bhatia A B and Thornton D E 1970 *Phys. Rev. B* **2** 3004
- [10] Galli G and Parrinello M 1991 *J. Phys.: Condens. Matter* **2** SA227