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COMPUTER SIMULATION OF THE LIQUID Li_4Pb ALLOYG. Jacucci, M. Ronchetti and W. Schirmacher^{†*}*Dipartimento di Fisica, Università di Trento, 38050 Povo, Trento, Italy**†Institute Max von Laue - Paul Langevin, 156 X, 38042 Grenoble Cedex, France*

Résumé - Une simulation sur ordinateur de l'alliage liquide Li_4Pb à 1085. K est présentée. Le calcul est fondé sur les potentiels de paire utilisés par Copestake et al. pour décrire la structure de ce système : interactions de Coulomb écrantées plus une répulsion de coeur mou. Les coefficients de diffusion ainsi que les fonctions de structure statiques et dynamiques sont évalués et comparés aux résultats expérimentaux. Les fonctions de corrélations de paires sont aussi calculées. Les facteurs de structure dynamique mettent en évidence l'existence d'un mode propagatif, surtout visible sur la fonction de Van Hove partielle Li - Li, et qui est probablement un mode optique dans le liquide.

Abstract - We present a computer simulation of the partially ionic liquid alloy Li_4Pb at 1085K. The calculation is based on the pairwise potentials used by Copestake et al. to describe the structure of this system: screened Coulomb interactions plus a soft core repulsion. Diffusion coefficients and static and dynamical structure functions are evaluated and compared with experimental results. Pair correlation functions are also presented. The dynamical structure factors show in addition to the interdiffusion mode a propagating mode which is most strongly visible in the Li-Li partial van Hove function. We interpret this mode as an optical-like mode in the liquid.

1 - Introduction

An important and well studied binary metallic fluid is the liquid alloy Li-Pb. Many of its properties have been measured over the last ten years; all of them vary in a non ideal way with the composition, and show a maximum deviation close to the composition $\text{Li}_{0.80}\text{Pb}_{0.20}$ (Li_4Pb for short). (For a review of the experimental data, see ref.1). In particular, the system deviates strongly from the ideal mixing behaviour. The particles in the melt are not distributed at random: unlike atoms are preferred as nearest neighbours.

The nature of the bonding in Li_4Pb has been investigated by several authors, following mainly two different approaches. In the first approach the existence of chemical complexes with finite lifetime has been conjectured /2-5/; in the second one it has been suggested that bonding might be partially salt-like /6,7/. While direct evidence for the existence of chemical complexes has not emerged, many experiments indicate that there is charge transfer.

It has been suggested /1/ that the experimental concentration - concentration structure factor $S_{CC}(q)$ can provide informations about the intermediate-range part of the "ordering" or "interchange" potential defined as $v(r) = c_1c_2(U_{11}+U_{22}-2U_{12})$ where U_{ij} is the pairwise potential. Applying this procedure to Li_4Pb Copestake et al. /8/ found by using the mean spherical (MSA) and hypernetted-chain (HNC) approximations that the structure can be well described using a screened Coulomb (Yukawa) potential (plus a short range

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repulsive part). This corresponds to a model in which negative charge is transferred from Li to Pb.

At the composition Li_4Pb the Li and Pb atoms are expected to have similar diameters d (chosen equal to 2.65\AA from the experimental S_{CC} data). The pair potential used by Copestake et al. /8/ in their HNC calculation which forms the basis of our simulation /9/ is of the form

$$U_{ij}(r) = k_B T a \exp\{(d-r)/p\} + Q_i Q_j e^2 \exp(\lambda(d-r))/r \quad (1)$$

where a and p are soft core parameters that were arbitrarily fixed to values similar to those used for molten alkali halides ($a=2$, $p=3.3\text{\AA}$). The values of λ , Q_1 and Q_2 were directly estimated from the experimental $S_{CC}(q)$ data to be $\lambda=1.1\text{\AA}^{-1}$, $Q_1=Q_{\text{Li}}=.533$ and $Q_2=Q_{\text{Pb}}=-2.134$. For a detailed description of how this potential was obtained we refer to /8/.

In this work we adopted this potential to simulate the model on the computer using the method of Molecular Dynamics (MD). The double aim is to check the analytical results obtained by Copestake et al. against the computer simulation data, and to extend the calculation to the dynamical structure factors, to compare with recent neutron scattering data /10/.

II - The computer simulation

We used the MD method which consists in the integration of the classical equation of motion for all the particles in the system. A constant force approximation for very small time intervals (0.5×10^{-14} sec) is assumed, and the trajectories of the particles in phase space are accurately followed.

We started our calculation using a cubic box composed by 250 particles: 200 Li atoms and 50 Pb atoms. The temperature was 1085K and the number density $.04558\text{\AA}^{-3}$. The system was subjected to periodic boundary conditions: in such conditions the maximum possible wavelength is equal to the box length. Correspondingly the only allowed values of the wavevector \vec{q} are $(n_x, n_y, n_z)q_{\text{min}}$, where n_x , n_y and n_z are integers and q_{min} is equal to $2\pi/(\text{max.wavelength})$. In our case q_{min} was $.36\text{\AA}^{-1}$.

After equilibration we started collecting data. In order to get the dynamical structure factor it is necessary to run a long job (at least 10000 steps) recording on tape the position of all the particles every few steps. These data are then used to evaluate the space-time Fourier transform for each desired value of q . We run the system for 10000, 20000 and 50000 steps.

In order to check the influence of the finite size of our system we doubled the linear dimension of the box: our "large" system was composed of 2000 particles, and it took one hour to run it for 500 time steps. We used this system only to get more extended and accurate $g(r)$ and $S(q)$.

To investigate the dynamical behaviour of the system for smaller values of the wavevector q without increasing too much the number of particles we used a rectangular box. In arbitrary program units this "long" box was $4 \times 4 \times 16$, while the "regular" box was $5 \times 5 \times 5$ and the "large" one was $10 \times 10 \times 10$. So we were able to gain a factor 3 in length (and hence to decrease by a factor 3 our smallest q) by only doubling the number of particles: the long box contained 510 atoms. Data were collected during a 20000 steps run after equilibration.

III - Results and discussion

In fig. 1 we have plotted the static partial radial distribution functions $g_{ij}(r)$.

It is evident that hetero-coordination is preferred. Unlike atoms exhibit a peak at 2.6\AA , and while Li-Li nearest neighbours are found at 2.9\AA , there are no Pb-Pb

nearest neighbours: although Pb has the same soft-core radius as Li, the first peak of the $g_{Pb-Pb}(r)$ is at 4.9\AA .

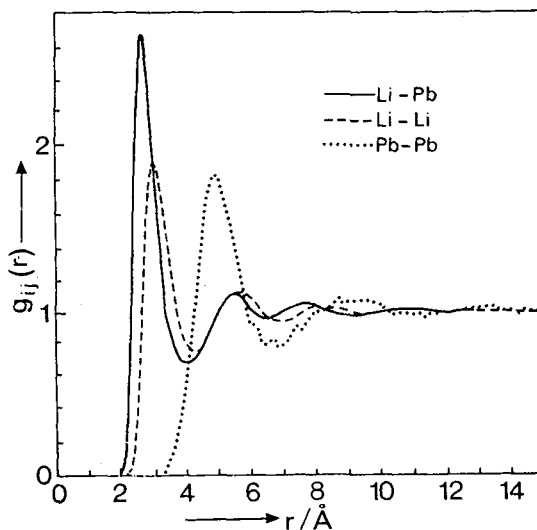


Fig.1:
partial radial
distribution
functions $g_{ij}(r)$

In fig. 2 we have plotted the Bhatia-Thornton /11/ structure factors which describe the correlations of concentration and density fluctuations. The first peak of the S_{CC} lies at $q \sim 1.6\text{\AA}^{-1}$ whilst that of the S_{NN} is at $q \sim 2.6\text{\AA}^{-1}$. These results are typical for systems with strong hetero-coordination and are of the kind obtained strongly charge-ordered systems /12/.

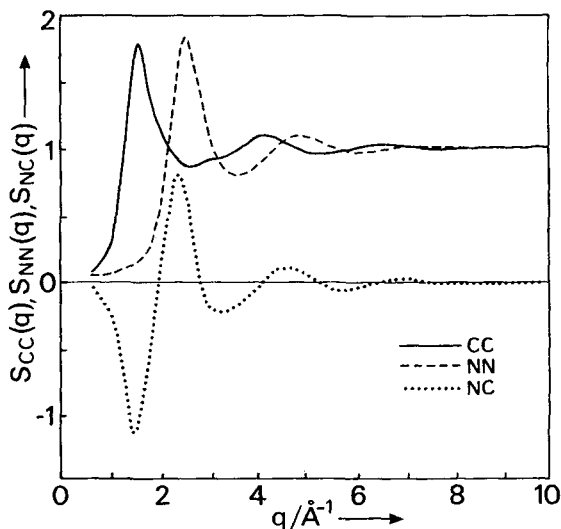


Fig.2:
The Bhatia-Thornton
structure factors

The S_{CC} can be compared with the experimental result (see fig. 1 in ref.1). The position of the peaks is in accord to the experiments, and the characteristic plateau for $2.6\text{\AA}^{-1} < q < 3.5\text{\AA}^{-1}$ is well reproduced by our calculation. The height of the main peak is, however, too low (by 30%), as in the case of the hyper-netted chain calculations (Fig.8 in ref.8). This might be due to the choice of the soft core parameters: the calculations performed in the MSA using the same potential but with a hard repulsive core show much higher peaks /8/.

We turn now to the discussion of our results for the dynamical structure factors. These can be compared with the experimental results obtained by Soltwisch et al./10/.

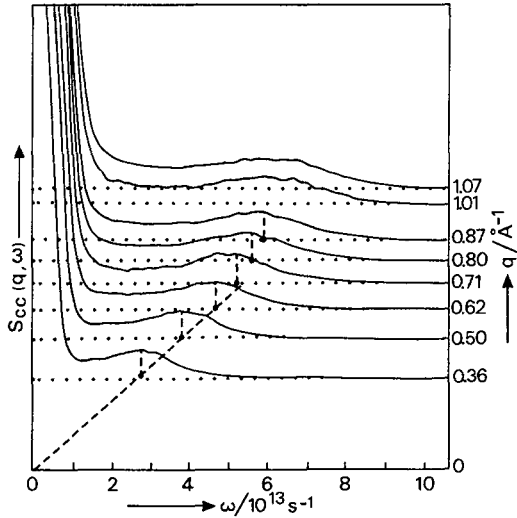


Fig.3: Dynamic concentration-concentration structure factors.

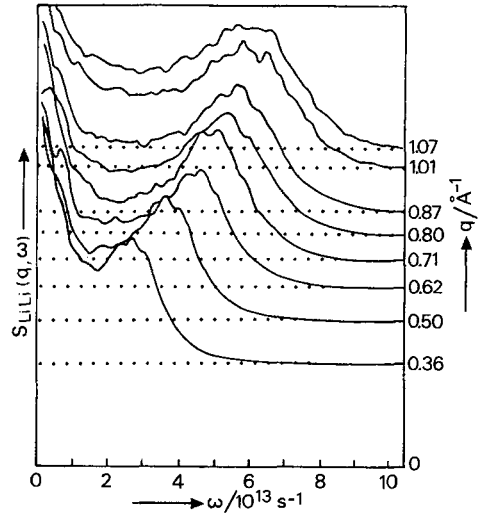


Fig.4: Partial Li-Li dynamic structure factors.

The $S_{cc}(q, \omega)$ (fig. 3) is dominated by a central peak. Beside this diffusive mode we see clearly also a propagating mode, which was not observed in the experiment: experimental results are reported for ω up to $.15 \times 10^{13} \text{sec}^{-1}$ while this mode occurs at far higher energy.

To investigate the origin of this peak it is very interesting to look at the partial structure factors $S_{LiLi}(q, \omega)$ (fig.4) and $S_{PbPb}(q, \omega)$ (this last is shown in fig.5 for only low values of ω because for larger ω it becomes indistinguishable from zero).

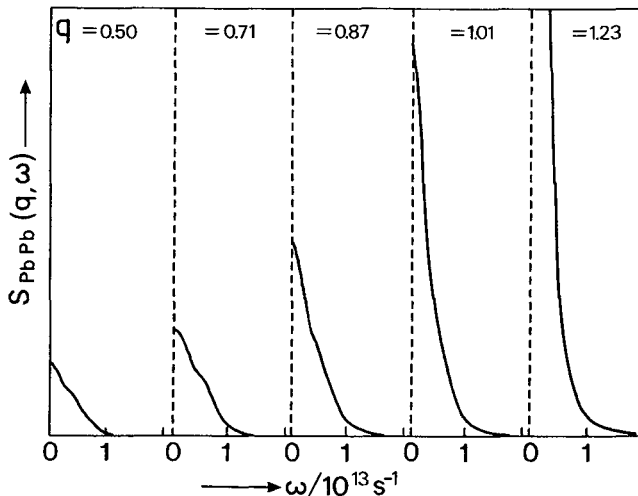


Fig.5: Partial Pb-Pb dynamic structure factors

The propagating mode is present in Li, and completely absent in Pb, while the low frequency interdiffusion mode is present in both species. This unforeseen fact comes probably from the great difference between the masses of the two species.

Pb is in fact 30 times heavier than Li, and therefore the atomic motion time scales of the two elements are separated in a Born-Oppenheimer like fashion: short-period short-wavelength density waves are supported by Li atoms alone.

The "sound velocity" extracted from the dispersion curve given by the maxima of $S_{cc}(q,\omega)$ or $S_{LiLi}(q,\omega)$ is 7500 m/sec: almost four times the experimental value /13/, which is 2000 m/sec. To explain this discrepancy we decided to check whether the behaviour of the dispersion curve was linear also for lower values of q . A bending in the curve could have revealed this mode as an optical one, due to the light, fast and "positively charged" Li atoms vibrating against the heavy, still and "negatively charged" Pb atoms. So we devised our "long" box and we evaluated the $S(q,\omega)$ for three lower values of q (.11, .22 and .34 \AA^{-1} , not shown in the figures). For all the new values of q we observed a linear behaviour of the dispersion curve: we are therefore not able to either prove or disprove this conjecture as far as the q dependence of the dispersion curve is concerned (we cannot see what happens for still lower values of q).

On the other hand, it is interesting to look more closely at the $S_{PbPb}(q,\omega)$ for low values of q : it presents in fact an outstanding deviation from a simple Lorentzian spectrum. The bumpy shape of this curve is also observable in the $S_{cc}(q,\omega)$ (when plotted on a scale different from that in fig.3), and a similar deviation has also been reported in the experimental results (see the discussion in terms of "fast and slow relaxation channels" in /10/). This could be the signature of the "real" sound mode. The dispersion curve obtained by this shoulder gives a sound velocity much nearer to the experimental one.

We used our simulation data to evaluate also the self diffusion coefficients, calculated as $D = \langle x^2 \rangle / 6t$. We obtained $D_{Li} = 20 \times 10^{-5} \text{cm}^2/\text{s}$ and $D_{Pb} = 3.5 \times 10^{-5} \text{cm}^2/\text{s}$, which are in good agreement with the experimental results obtained /10/ for the Li from incoherent scattering intensity and for Pb from an extension of Darken's relation ($D_{Li,exp} = 21 \times 10^{-5} \text{cm}^2/\text{s}$ at 1098K and $D_{Pb} = 3.3 \times 10^{-5} \text{cm}^2/\text{s}$).

IV - Summary and conclusion

The usefulness of the model potential proposed by Copestake et al. /8/ has been shown. Static structure factors which are in qualitative accord with the experiments have been obtained. Good agreement with the experiments is obtained also for diffusion data. Dynamical structure factors have been shown, presenting a rather peculiar behaviour: a propagating mode to which only Li atoms contribute has been found. This is due to the vast difference between the atomic masses of Li and Pb. A possible interpretation of this mode as an optic or a plasma mode has been suggested.

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