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Atomic motions in liquid KPb: A molecular-dynamics investigation

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A molecular-dynamics computer simulation is used to determine velocity and current-density autocorrelation functions for a liquid system consisting of K^+ and Pb_4^{4-} ions. The calculated structure of this system is in excellent agreement with that determined experimentally for liquid KPb alloys. The calculations provide an interpretation for recent inelastic-neutron-scattering results, which do not show any distinct vibrational modes characteristic of Pb_4^{4-} tetrahedra.

INTRODUCTION

Recent electrical-resistivity,[1] heat-capacity,[2] and neutron-diffraction measurements[3] performed on liquid equiatomic KPb alloys have given strong support for the presence of polyanionic species in the liquid namely, the Zintl ions, Pb_4^{4-}. According to powder-diffraction measurements, the structure of the crystalline phase is tetragonal, with the Pb atoms forming nearly regular Pb_4 tetrahedra; the K atoms are situated opposite the faces of the Pb_4 tetrahedra, forming larger tetrahedra oppositely oriented.[4] An attempt was made to determine the internal vibrations of these tetrahedral units by inelastic neutron scattering. The results on both solid and liquid KPb did not show any sharp peaks that could be ascribed to vibrations of a molecular character.[4]

In this work, we report preliminary molecular-dynamics (MD) calculations of atomic motions in a liquid system composed of K^{1+} and Pb_4^{4-} ions. This simulation reproduces surprisingly well the measured structure factors, especially the first sharp diffraction peak at 1 Å^{-1}.[5] We have calculated the velocity and current-density autocorrelation functions to probe the effect of the liquid milieu on the molecular motions of Pb_4^{4-}.

POTENTIAL MODEL

The potential model employed is based upon a central force pair potential. The tetrahedral Pb structural units are formed by incorporating harmonic springs between the Pb atoms of the same unit. The intramolecular potential used is of the form

$$V_{ij}(r)=\tfrac{1}{2}K(r-r_0)^2 . \tag{1}$$

Values for K (spring constant) = 0.8 mdyn/Å and r_0 (equilibrium bond distance) = 3.25 Å were determined from recent measurements of the static structure factor $S(Q)$.[4] To account for charge transfer in the liquid alkali-metal–lead alloys, a charge of $-1e$ is assumed for each Pb atom in the system and $+1e$ for each K atom.

The intermolecular Pb-Pb interactions consist mainly of a repulsive core-core body-body potential in addition to the repulsive coulombic interactions due to the localized charges on the tetrahedral units. The core-core body-body potential has a simplified Tosi-Fumi form similar to that employed for molten salts.[6] Hence, the total Pb-Pb intermolecular interaction potential is taken as

$$V_{ij}(r)=A_{ij}\exp[\alpha(\sigma_i+\sigma_j-r)]+\frac{Z_iZ_je^2}{r} , \tag{2}$$

where

$$A_{ij}=\left[1+\frac{Z_i+Z_j}{8}\right]A_0 ,$$

$$A_0=0.338\times10^{-12}\text{ erg} ,$$

Z_i,Z_j (charges on interacting atomic pair) $=-1e$ for Pb, $\alpha=3\ \text{Å}^{-1}$, and σ_i,σ_j (respective Pauling radii) $=2.42$ Å for a Pb ion.

Interactions between the Pb and K atoms are accounted for by using an identical form to Eq. (2) with a Pauling radius of 1.33 Å (Ref. 5) and a charge of $+1e$ for the K ion. The K-Pb Coulombic interaction is essential for reproducing the intermediate-range ordering present in the K ions as determined experimentally.[5] For the K-K interactions, Eq. (2) is used with the appropriate values for the K parameters. Equation (2) is well suited for reproducing the measured neutron structure factors to good accuracy in the alkali-metal–lead equiatomic alloys.[5]

MOLECULAR-DYNAMICS SIMULATIONS

A system of 128 Pb and 128 K atoms corresponding to equiatomic KPb in a cubic simulation cell of side 22.76 Å, corresponding to a density of 4.43 g/cm^3, was studied by MD simulations. Well-equilibrated liquid samples were modeled at a temperature of 870 K starting from a random atomic configuration. The integration step in time was 1×10^{-15} sec, and each run was on the average 10 000 time steps long. The short-range part of the interaction was cut off at a range of 11.35 Å. Periodic boundary conditions were used across the constant-volume simulation cell. Standard Ewald summation techniques were employed to sum over the long-range coulombic interactions with a conversion constant $\gamma=0.22$ Å^{-1}.

To interpret the recent neutron inelastic measurements, we focused on the calculation of the vibrational density of states and the dynamic structure factor for the liquid KPb system. The velocity autocorrelation functions of the Pb and K atoms, defined in the usual way by

$$A(t)=\langle \mathbf{V}_j(\tau)\cdot\mathbf{V}_j(t+\tau)\rangle / \langle \mathbf{V}_j(\tau)\cdot\mathbf{V}_j(\tau)\rangle \ , \tag{3}$$

were calculated over 2500 time steps and averaged over four cycles and over the particles in the simulation cell. We calculated the vibrational density of states for the Pb and K atoms as

$$\Phi(\omega)=(1/\pi)\int_0^\infty A(t)\cos(\omega t)dt \ . \tag{4}$$

Figure 1(a) shows a typical power spectrum for the Pb (dashed line) and K (dotted line) atoms obtained by Fourier transformation of the velocity autocorrelation function calculated previously, together with a weighted average for KPb (solid line), with each component spectrum weighted by scattering cross section and atomic mass. The Pb and KPb spectra clearly show two main bands centered at 6.5 and 15.5 meV, respectively. As discussed in the next section, these bands can be interpreted as arising from librational modes due to the liquid milieu and from internal modes of the tetrahedral units, respectively.

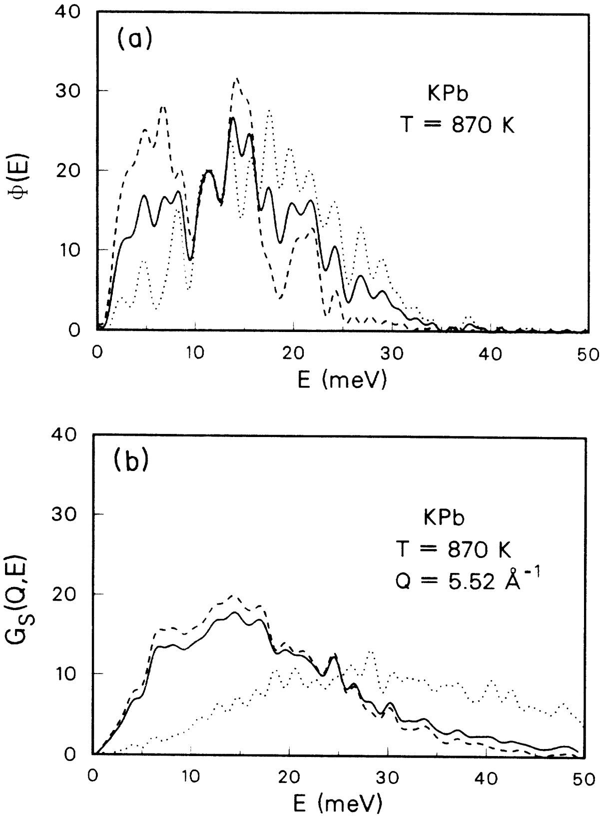

FIG. 1. MD results for liquid KPb simulated using the potential defined by Eqs. (1) and (2). Dashed lines refer to Pb, dotted lines to K, and solid lines to weighted average for KPb. (a) Energy spectrum for the velocity autocorrelation function [Eq. (4)]. (b) Energy spectrum for the current-density function at $Q=5.52$ Å^{-1} [Eq. (6)].

The effect of a finite momentum transfer Q on the measured neutron spectrum was determined. The single-particle current-density autocorrelation function, $J_S(Q,t)$, was also calculated for 2500 time steps. It is defined as

$$J_S(Q,t)=\frac{\langle[\mathbf{Q}\cdot\mathbf{V}_j(t+\tau)][\mathbf{Q}\cdot\mathbf{V}_j(\tau)]\exp\{i\mathbf{Q}\cdot[\mathbf{r}_j(t+\tau)-\mathbf{r}_j(\tau)]\}\rangle}{\langle[\mathbf{Q}\cdot\mathbf{V}_j(\tau)][\mathbf{Q}\cdot\mathbf{V}_j(\tau)]\rangle} \ , \tag{5}$$

where $\mathbf{V}_j$ and $\mathbf{r}_j$ refer to the velocity and the position of the jth particle in the system. The $\mathbf{Q}$ vector in Eq. (5) is determined from the relation $\mathbf{Q}=(2\pi/L)(\mu,\upsilon,\Delta)$, $\mu,\upsilon,\Delta=0,\pm1,\pm2,\ldots$, where L is the length of the cubic simulation cell. The choice of the Q values as given above is a consequence of the periodic boundary conditions imposed on the simulation cell. The scalar quantity $J_S(Q,t)$ in Eq. (5) is obtained by averaging over all possible orientations of the momentum-transfer $\mathbf{Q}$ for a given Q value. Thirty orientations of the wave vector Q were considered for $Q=5.52$ Å^{-1}.

The Fourier transform of the current-density autocorrelation function $G_S(Q,E)$ can be shown to be related to the particle self-dynamic structure factor $S_S(Q,E)$ by

$$G_S(Q,E)=\frac{\hbar\langle V^2\rangle}{3\pi}\int_0^\infty J_S(Q,t)\cos(\omega t)dt$$
$$=E^2S_S(Q,E)/Q^2 \ . \tag{6}$$

From a practical point of view, $G_S(Q,E)$ is a natural quantity to calculate for the high-frequency modes for particle motions because the low-frequency part of $S_S(Q,E)$ is attenuated by the factor E^2. This leads to a rapid decay of the time correlation function $J_S(Q,t)$, which allows the Fourier transform of this function to be computed from relatively short time histories.

Figure 1(b) shows the calculated functions $G_S(Q,E)$ at a Q value of 5.52 Å^{-1} for the Pb and K atoms and the scattering-cross-section-weighted average for KPb. Band broadening and attenuation at the larger Q value are clearly evident when compared with the more distinct bands at the $Q \rightarrow 0$ limit.

DISCUSSION

The power spectrum depicted in Fig. 1(a) clearly shows two main distinct bands centered at 6.5 and 15.5 meV. In the higher-energy band centered at 15.5 meV, three distinct peaks at 10.6, 14.5, and 20.7 meV are evident for Pb (dashed line) and KPb (solid line). To help in interpreting the data, an MD simulation was run for a free molecular gas consisting of K atoms and Pb_4 tetrahedra, with coulombic and intermolecular interactions neutralized for both Pb and K. The power spectrum of the molecular gas motion is shown in Fig. 2, where three major bands are present at 10.6, 14.5, and 20.7 meV in the Pb spectrum (dashed line). No significant features are exhibited in the K spectrum (dotted line). These major bands are identical to those previously detected in the vibrational density of states spectrum for the liquid [Fig. 1(a)]. This indicates that the broad energy band at 15.5 meV in the liquid is due to the internal vibrational modes of the Pb tetrahedral units.

To confirm this assignment, a separate calculation was carried out for the internal vibrational modes of the tetrahedral unit. Following Herzberg,[7] three distinct modes are predicted for the molecular gas-phase medium, given by

$$\omega_1 = \sqrt{K/m}\ , \quad \omega_2 = \sqrt{2K/m}\ , \quad \omega_3 = \sqrt{4K/m}\ ,$$

where K is the spring force constant of the interacting Pb pairs, and m is the mass of a Pb atom. Substituting the value of $K = 0.8$ mdyn/Å from Eq. (1), one obtains the following vibrational frequencies for the Pb tetrahedral unit:

$$E_1 = 10.05 \text{ meV},\ E_2 = \sqrt{2}E_1 = 14.25 \text{ meV},$$

$$E_3 = 2E_1 = 20.1 \text{ meV}\ .$$

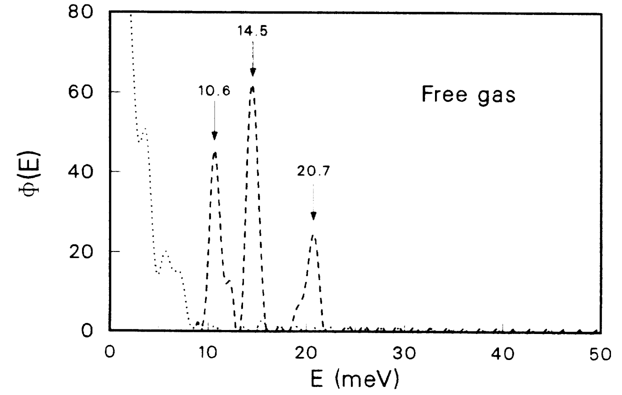

FIG. 2. Energy spectrum of the velocity autocorrelation function calculated by MD for the free molecular gas of K atoms and Pb_4 tetrahedra, with coulombic and intermolecular interactions neutralized for both K and Pb atoms. Dashed lines refer to Pb, dotted lines to K.

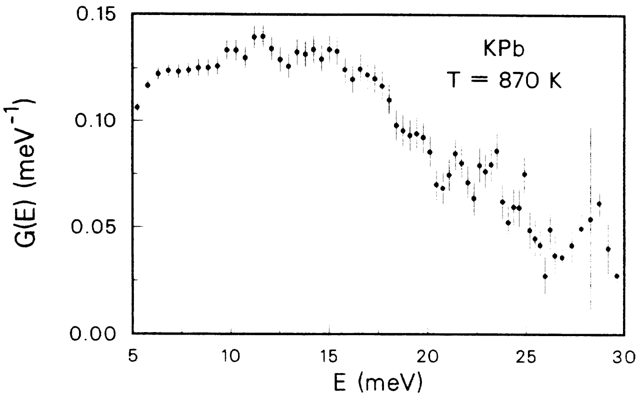

FIG. 3. Q-averaged energy-distribution function obtained from an inelastic-scattering measurement on liquid KPb at $T = 870$ K.

It is evident that the characteristics of the molecular gas structure are still preserved in the liquid state for the alkali-metal–lead alloys, as indicated by the results of the MD simulations.

The other major band, present in the liquid spectrum at 6.5 meV, is undoubtedly a signature of the liquid milieu, since it is nonexistent in the molecular gas spectrum. This band is clearly due to the librational modes of the Pb atoms as they drift around in the liquid. The electrostatic Coulombic charge-transfer interaction between the Pb and K atoms is the source of this band.

Results of inelastic-neutron-scattering measurements on KPb, made on the low-resolution medium-energy chopper spectrometer (LRMECS) at IPNS, are shown in Fig. 3. The incident energy was 58 meV and the data shown represent an average over scattering angles from 3° to 30°, corresponding to a Q range of 1.0–2.7 Å^{-1}. Some structure of the type predicted by the MD calculations is evident in the measured spectrum with suggested peaks centered at 15.5, 23, and 28.5 meV. Although the vibration frequencies are approximately in the calculated ratios, their values are about 40% higher than expected. However, the quality of the data is limited by the conditions of the low-Q measurements, namely the low inelastic-scattering cross section and the high incident energy required to reach low Q. The statistics will improve at higher Q but the Doppler broadening smears out the structure as shown by the MD results [Fig. 1(b)].

CONCLUSIONS

These calculations help to explain the negative results obtained from the inelastic-neutron-scattering measurement that showed no distinct vibrational modes due to $Pb_4{}^{4-}$ tetrahedra. Additional calculations will be conducted with a less-rigid potential, e.g., a Morse potential,[8] which will take into account anharmonicity effects in order to examine diffusion. MD calculations will also be carried out on other systems where tetrahedra are known to survive in the liquid state but where the energy separation is such that the vibrational modes will be clearly separated from the librations.

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