A computer simulation of LiKSO₄

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Abstract. Molecular-dynamics computer-simulation of an ionic molecular solid LiKSO₄ has been carried out at 300 and 1000 K using the atom-atom potentials obtained from lattice dynamical studies. We observe hopping of lithium ions to interstitial positions which is related to reorientations of sulphate tetrahedra.

Keywords. Molecular dynamics; computer simulation; lattice dynamics; diffusion; reorientation; LiKSO₄; superionic conductor.

1. Introduction

Lithium potassium sulphate is known to undergo a superionic conducting phase transition at $T_c \sim 700$ K when the conductivity increases by an order of magnitude (Ando 1962). This is likely to be due to diffusion of the vacancies and interstitials of lithium ions because of the small size of these ions. It is also possible that the rotational diffusion or reorientation of sulphate radicals plays an important role in helping lithium diffusion. Recently, the phase transition at 700 K has been studied by Raman scattering (Bansal *et al* 1983) and abrupt changes in frequencies and line-widths of phonons have been observed at the transition.

Molecular-dynamics computer-simulation appears to be the most appropriate technique to study such complex dynamical phenomena (Chaplot 1983). In this technique (Rao and Chaplot 1979) one simulates the system by setting up in a computer a macrocell of a number of formula units (of LiKSO₄) and applying the periodic boundary conditions around the macrocell. The dynamics of the system is then studied by solving the Newton-Euler equations of motion. The dynamics is studied for a long enough time by dividing the total time interval into a number of small time steps, each time step being sufficiently small as determined by the nature of dynamics. Some details of the simulation technique for an ionic molecular solid are given in §2.

The essential input for the computer simulation is a suitable potential function to represent the interatomic interactions. We have recently obtained a potential function for LiKSO₄ by lattice dynamical studies on this system in the room temperature and low temperature phases (Chaplot *et al* 1984). The suitability of this potential function is discussed in §3.

We have carried out the simulation studies on LiKSO₄ at 300 K and 1000 K. Limited results available so far are described in §4. A more complete paper will appear elsewhere.

2. Molecular dynamics method

We consider a macrocell formed by the vectors $n_1\mathbf{a}$, $n_2\mathbf{b}$ and $n_3\mathbf{c}$ where $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, are the primitive cell vectors of the crystal and n_1, n_2, n_3 are integers which determine the total

number of primitive cells $n = n_1 \times n_2 \times n_3$ in the macrocell. As each primitive cell of $LiKSO_4$ in the room temperature phase of space group $P6_3$ contains two formula units, the macrocell would contain $2n\,Li^+$, $2n\,K^+$ and $2n\,(SO_4)^{2-}$ ions and in all $14n$ atoms. We have used a $3 \times 3 \times 2$ macrocell in these studies.

We initialize the system with atoms located at their crystallographically determined equilibrium positions and the atoms are provided with some random velocities scaled to the square root of the temperature of simulation. Time evolution of the system is then calculated at steps of suitable time intervals using the classical equations of motion, namely the Newton's equations for translational motion of the centres of mass and the Newton–Euler equations for rotational motion of rigid bodies like $(SO_4)^{2-}$. Accelerations at each time step are obtained from a suitable atom-atom potential function. The periodic boundary conditions are imposed to remove the surface effects and thus simulate, in effect, an "infinite" crystal with periodicity of the macrocell.

While the translational coordinates are taken as the conventional cartesian coordinates x, y, z, the rotational coordinates used are not the conventional Euler angles ψ, θ, ϕ, as these are known to produce singularities in the equations for large rotations. Instead we use the quaternian coordinates L_1, L_2, L_3 and L_4 (where $L_1^2 + L_2^2 + L_3^2 + L_4^2 = 1$) as these produce singularity-free equations (Evans 1977).

The time step of calculation is chosen as a small fraction of the minimum vibrational period in the system which is the inverse of the maximum phonon frequency of external modes. The values chosen for the simulations at 300 K and 1000 K were respectively 1 $\times 10^{-14}$ sec and 0.75×10^{-14} sec as higher values of time steps resulted in too close atomic contacts producing unstable kinetic energy in the calculations. In the simulation, various physical quantities like temperature, mean square amplitudes, orientations of sulphates, etc have been monitored. The results are presented in §4.

3. Potential function for LiKSO$_4$

We shall now discuss the suitability of the potential function obtained from a lattice dynamical calculation (Chaplot *et al* 1984) for use in the simulation studies. The form of the potential function is the simplest with minimum parameters for use in a complex ionic molecular solid like $LiKSO_4$. The potential energy between two non-bonded atoms (Kk) and $(K'k')$ separated by a distance r is given by

$$V(r) = \frac{e^2}{4\pi\varepsilon_0} \frac{Z(Kk)Z(K'k')}{r} + a\exp\left\{\frac{-br}{R(Kk)+R(K'k')}\right\}$$

where $Z(Kk)$ is the effective charge and $R(Kk)$, the radius parameter associated with the atom (Kk) belonging to the rigid unit K.

The above potential produces a potential minimum for the positions of Li and K atoms and molecular positions and orientations of (SO_4) rigid units corresponding to the structure determined by crystallographic experiments (Bhakay Tamhane *et al* 1984). The potential also predicts proper Raman frequencies and the LO-TO splitting of modes (Chaplot *et al* 1984) reasonably in agreement with experiments. It may be mentioned that a much better agreement would be obtained with an improved potential model or a shell model (Chaplot 1983) but it is at present difficult to obtain the parameters for such a model and also too (computer) time consuming at present to use such a model in simulation work.

The lattice dynamical calculation (Chaplot *et al* 1984) which used the above potential predicts a soft mode at an irrational phonon wave vector and involving librations of the sulphate molecules about axes in the hexagonal plane. The potential thus provides an understanding of possible easy rotations of molecules in the crystal and such easy rotations may be related to observed phase transitions in LiKSO$_4$ involving reorientations or orientational disorder of sulphates. While we need not at present go into details of such explanations of the phase transitions, the predictive utility of the potential suggests that it may be used in simulation work with some confidence.

Additional support for the potential comes from the results of calculation of *partial* density of phonon states (Choudhury *et al* 1984). These results at room temperature show substantial Li motions at low energies and coupling of Li translations and sulphate rotations, indicating possible trends at higher temperatures.

4. Results

We present the results corresponding to the simulation temperature of 1000 K. The calculated mean kinetic energies of both the translational and rotational motions reach their equilibrium values fairly quickly. Larger fluctuations are observed in the rotational kinetic energy as compared to the translational part as would be expected due to a smaller total number of degrees of freedom of the rotational motions in the macrocell.

Figure 1 shows the mean square displacement $\langle u^2(t) \rangle$ of the lithium ions averaged over all the 36 lithium ions in the macrocell as a function of simulation time up to 7·5 $\times 10^{-12}$ sec. The figure indicates a small rise in $\langle u^2(t) \rangle$ as the time increases; however, no appreciable diffusion is observed at this temperature. Examination of individual lithium ions shows that the ions move to interstitial positions and vibrate there for fairly long times of a few pico-seconds and then some of the ions return to their lattice positions. This phenomenon of lithium movement appears to be closely related to the orientations of the neighbouring sulphate tetrahedra which are found to rotate and reorient by large angles of up to 180°. Interestingly the rotation or reorientation about the hexagonal axis is found to be about twice as favourable as about any one axis in the hexagonal plane.

In figure 2 we show a plot of one of the quaternians L_3 of a typical sulphate tetrahedron. L_3 represents sin $(\theta_z/2)$ when $L_1 = 0 = L_2$, θ_z being the angle of rotation about the hexagonal axis. We notice that this particular sulphate has first reoriented by
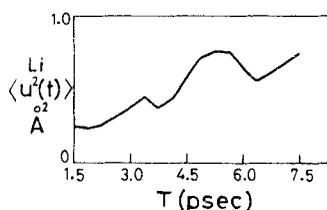

Figure 1. Mean square displacement of lithium ions in LiKSO$_4$ at 1000 K as a function of time as obtained by molecular dynamics simulation.
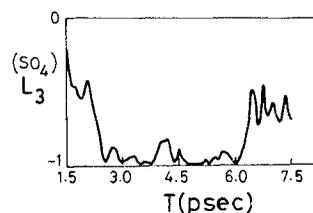
Figure 2. The quaternian L_3 of a typical sulphate tetrahedron in LiKSO$_4$ at 1000 K as a function of time as obtained by molecular dynamics simulation.

60° and then after about 0·5 psec has reoriented by another 120°, then again after 3 psec it has reoriented back by 60°. The time taken in carrying out a reorientation is about 0·5 psec.

Simulation at the room temperature has been carried out for a simulation time of 3 psec. In this duration we have not observed any reorientations although the vibrations have large amplitudes. Also the lithium displacements are found to be small.

We have also calculated the dynamical structure factors $S(Q, w)$ and vibrational density of states. The details of these results along with simulation at other temperatures and annealing of the system will be published elsewhere.

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