MOLECULAR DYNAMICS SIMULATION OF SUPERIONIC CONDUCTOR BaF_2

A. K. IVANOV-SHITZ, AND S. KH. AITYAN

Institute of Crystallography, USSR Acad. Sci., Moscow

INTRODUCTION

The superionic conductors are of interest from the standpoint of both their intrinsic scientific problems of solid state physics and their technological importance. It should be noted that these systems are very difficult to treat using simple analytic theory because they have a high degree of disorder.

On the other hand, the computer simulation is suited for studying such strong anharmonicity systems and we report on how molecular dynamics simulation has been used to investigate superionic conductors.

It should be stressed that fluoride conductors with the fluorite structure appear to be a suitable model for studying features of ionic transport in solids, because they have a simple crystal structure.[1] Fluoride materials such as Ca, Sr, Ba, Pb fluorides (as well as Sr chloride $-SrCl_2$) crystallize in the fluorite structure. These compounds are ordinary ionic conductors at low temperatures and only just before melting point they undergo the so-called diffuse transition, accompanied by a significant increase in conductivity and a pronounced peak in specific heat.[2] The new high-temperature modification is retained up to the melting poin T_m.

At present structural and transport characteristics of BaF_2 at high temperatures appear to be studied insufficiently. That is why it was rather important to study specific features of the crystal structure and ion transport just in this compound, in order to confirm the existence of the superionic state.

To do this we carried out a computer simulation by the molecular dynamics technique. The power of MD in interpreting the properties of superionic conductors with the fluorite crystal structure CaF_2, SrF_2, PbF_2 and $SrCl_2$ was shown in ref. 3.

MOLECULAR-DYNAMICS SIMULATION

One of the methods of computer simulation technique is molecular dynamics technique[4,5] which consists in calculation of particle motion in the system. So, we have a system of N particles interacting with one another under defined interaction potential, the motion of each ion being governed by Newton's equation of motion. The force applied on each ion is obtained by summing the forces exerted on it by all the ions in the system. These forces can be derived from specified interionic potentials. Solving the equations of motion we obtain trajectories of all the particles in the system, from which we can determine all the required thermodynamic and kinetic characteristics of the system.

In general, the iterative simulation proceeds as follows. Initially, the ions are placed at sites near their regular lattice positions and random velocities are given. The time evolution is produced by integration of the equation of motion, that is, the velocities and coordinates of the particles may be determined at a time, Δt, between times $n\Delta t$ and $(n + 1)\ \Delta t$, using a suitable numerical algorithm. The process is then continued. In our work we used the predictor-corrector type algorithm[6] for numerical integration of equations of motion. The conservation of the total energy was used as a criterion of correctness of the trajectories generated.

In each particular realization of MD it is possible to consider rather small amount of particle – dozens, hundreds, and, only in some cases, thousands. In order to eliminate the surface effects associated with a very small system, the system is made pseudo– infinite by the use of periodic boundary conditions. In this case N particles are confined in a simulation box and the box is repeated by periodic replicas of itself. In evaluating the interactions in the system we consider only the pairs separated by a distance less than some cut-off radius r_c beyond which the interaction can be assumed to be negligible.[6] To avoid the rupture of forces and potentials, special correction procedures should be used.

Many fluorites can be regarded as crystals with purely ionic character of bonding, that enables the use of a simple "rigid– ion" model.[5,7] In this case the potential energy of the lattice may be obtained as a sum of pair potentials. Interionic potentials (to be more exact the potental energy) may be written as the Born-Mayer-Huggins potential in the form:

$$V_{ij} = z_i\, z_j\, e^2 / r + A_{ij} \exp(- r / \rho_{ij}) - C_{ij} / r^6 \qquad (1)$$

where z_i, z_j are the effective charges of interacting i and j ions that are positioned at r distance, e is electron charge, A_{ij}, ρ_{ij} and C_{ij} are constants. The first term in Eq. (1) describes the Coulombic interaction, the second one –the repulsive interaction form the overlapping electron shells, the third one –the attraction energy due to van-der-Waals (dipole-dipole) interaction.

The Ewald sum algorithm[5] was used to calculate the contribution of the electrostatic energy.

We have written a "SUPERION" program package for carrying out molecular dynamics simulation. Three logical stages are made using this program. To exclude effects due to randomly given initial configuration, the first stage –evolution– has been introduced. At the second state– thermalization –the system is brought to a required temperature. The temperature is obtained by averaging over the time step and set of particles, i.e.

$$3\,kT/2 = \left(\frac{m_\alpha v_\alpha^2}{2} \right)_{N,t}$$

where k is the Boltzman constant, T is the absolute temperature, m_α is the mass of particles of species α, V_α is the velocity of particles of species α.

If the average temperature remains constant and the system is in thermal equilibrium, the third stage– run– can be started. The results obtained in run stage are analyzed to calculate the thermal averaged values.

Let us consider real system characteristics that were used for simulations on barium fluoride crystals. In our work the calculation box was a cube with linear dimensions twice as large as unit cell sides, i.e. the box consisted of eight unit cells and contained 32 cations and 64 anions. The cut-off radius was half box linear size.

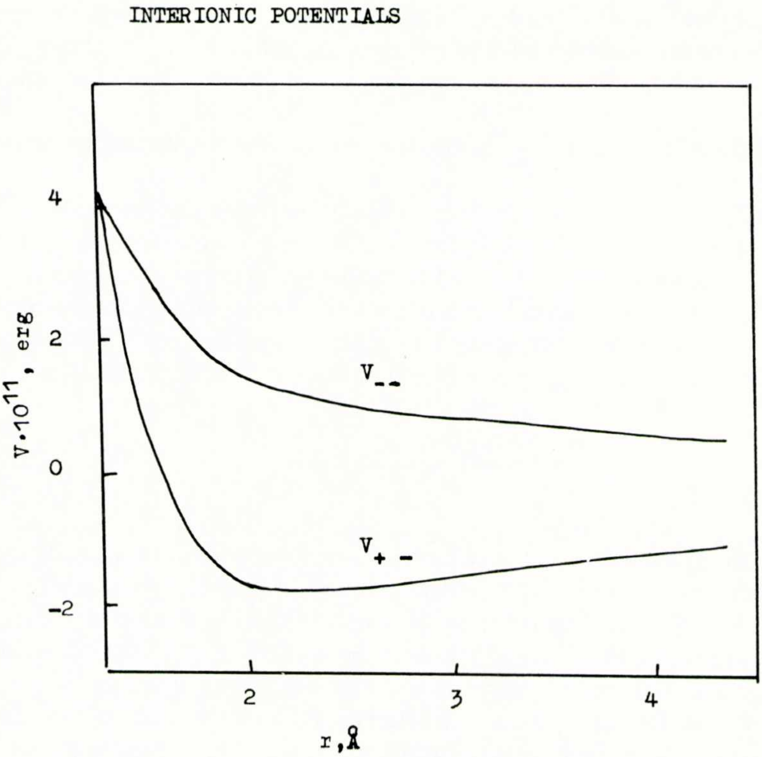
Parameters of the interactions were taken from[8,9], they are listed in Table 1, $V_{ij}(r)$ plots are shown in Fig. 1.

While carrying out MD-simulations over a wide temperature range one should take into account a change of system density. Box size was varied according to behaviour of the temperature dependence of lattice constant (Fig. 2) obtained by neutron diffraction studies.[10]

The simulation time of the system was 3-10 ps, that was sufficient for

Table 1. Interionic potentials for BaF_2 used in simulations.

A_{--} x 10^{12}, erg	ρ_{--}, Å	C_{--} x 10^{12}, erg Å^6	A_{+-} x 10^{12} erg	ρ_{+-}, Å	ref
7001,177	0.2753	230.7024	8414,229	0.2792	9
1806.688	0.2753	25.3612	8320.185	0.2795	8



$$V_{ij}(r)=q_iq_j/r + A_{ij}\exp(-r/\rho_{ij}) - C_{ij}/r^6$$

$A_{--}=7001.177\cdot10^{-12}$ erg; $\rho_{--}=0.2753$ Å ; $C_{--}=230.7024\cdot10^{-12}$ erg/Å^6

$A_{+-}=8414.229\cdot10^{-12}$ erg; $\rho_{+-}=0.2792$ Å ; $C_{+-}=0$

Fig. 1. Interionic potentials V_{--} and V_{+-} [9].

studying thermodynamic, structural and kinetic properties. The fluctuations in the total energy were less 10^{-5} for time step $\Delta t = 10^{-15}$ s and 10^{-4} for $\Delta t = 5{*}10^{-15}$ s (which possessed a temperature accuracy within ± 20K).

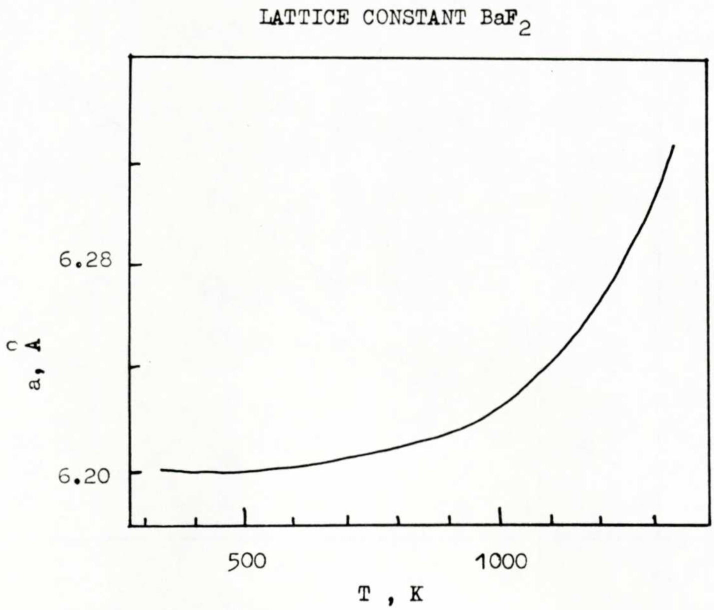


Fig. 2. The lattice constant of BaF_2 as a function of temperature.

RESULTS AND DISCUSSION

Thermodynamics

As metioned above, measurements of specific heat indicate a peak C_p at T = 1250K, that is why it was interesting to analyze the thermodynamic characteristics of BaF_2, obtained form MD-simulations. Fig. 3 shows a temperature dependence of the total energy. There are abrutp changes in the energy near T = 1250K and T = 1800K; these anomalies are due to phase transitions. The appropriate value of energy jump at the first transition is a $\Delta U = (18.8 \pm 0.2)$ kJ/mole. This value is close to the value of latent heat at 1275K, determined experimentally from specific heat measurements:[11] $\Delta Q = 18.36$kJ/mole. The second transition, as we shall see later, is a melting point.

Structural Characteristics

The information on the system structural characteristics has been obtained from the consideration of radial distribution functions g_α (RDF).

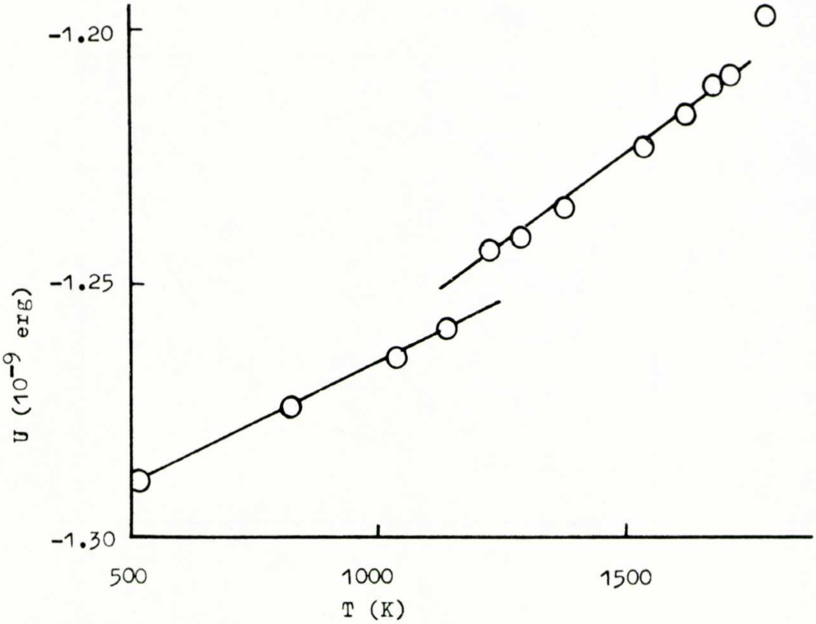


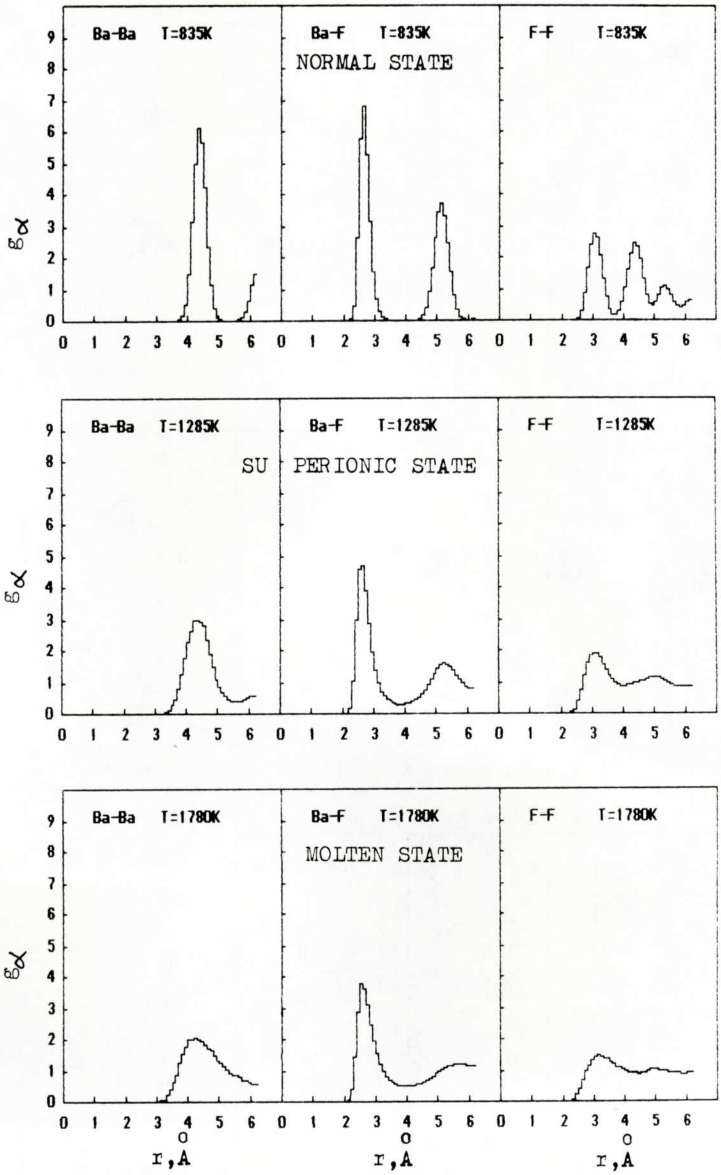
Fig. 3. The temperature dependence of the total energy.

The use of these functions makes it possible to describe the crystal structure and the disorder of one sublattice. Fig. 4 presents RDF at different temperatures. At low temperatures, on all g(r) curves there are well resolved sharp peaks. Such RDFs are typical of ordinary solids. The distances between peak centres correspond to appropriate distances between ion sites in a regular fluorite lattice. The peaks are flattened with increasing temperature, due to more active thermal vibrations of ions near centres of crystallographic sites.

An increase in temperature results mostly in the changes of anion-anion correlation function $g_{--}(r)$ (fig. 4), namely, after a phase transition the first peak (characterizing the position of nearest neighbours) is observed in the high-temperature modification, while all the other are flattened. This shape of RDF is similar to that found in liquids, indicating that the anions form a weakly correlated subsystem.

Ionic Motion

Fig. 5 presents trajectories of ions at different temperatures. At a low temperature, as seen from Fig. 5, cations and anions are in thermal motion



RADIAL DISTRIBUTION FUNCTIONS

Fig. 4. RDFs at different temperatures.

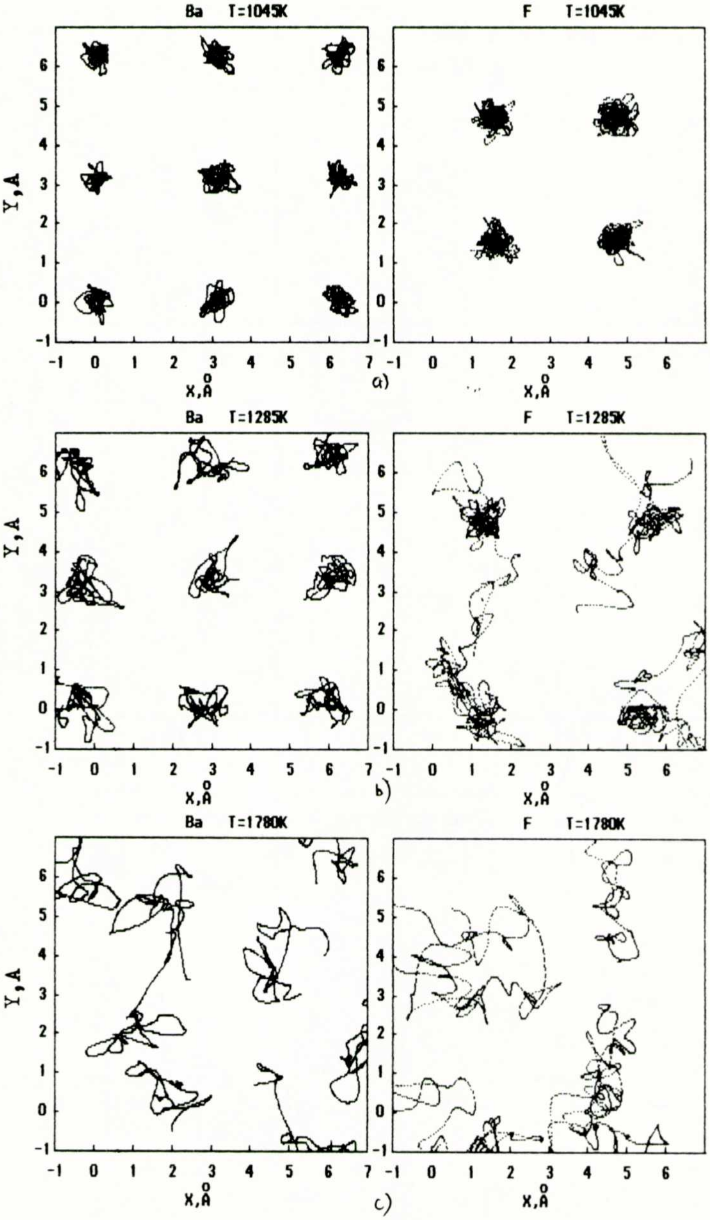


Fig. 5. Trajectories of ions for simulated BaF_2 at different temperatures: a) low-temperature phase. b) high-temperature superionic phase. c) molten state.

about regular positions; the vibrational amplitude of fluorine exceeding that for barium. In the high-temperature phase barium ions continue vibrating about their equilibrium positions, while fluorine anions begin diffusing between nearest– neighbour sites (although they spend most of their time in the vibration about the crystallographic sites). In this case, we can speak about the disordering of the anionic sublattice. At T = 1780K cations are also disordered, that is, the crystal is melted.

It is very convenient to describe the ion motion using mean-square displacements $<\Delta r_\alpha^2(t)>$. As is known, the asymptotic form $<\Delta r_\alpha^2(t)>$ for large t is:

$$6\,D_\alpha t + A_\alpha = <\Delta r_\alpha^2(t)> \tag{2}$$

The coefficient A describes particle thermal fluctuations and is connected with the Debay-Waller factor B_α.

In fig. 6 we show $<\Delta r_\alpha^2(t)>$ for cations and anions. These results confirm that the cations do not diffuse up to 1680K; they are only vibrating. According to eq. (2), knowing the mean value $<\Delta r_\alpha^2(t)>$ one can calculte the Debay– Waller factors B_{Ba}. After the transition to the high-temperature phase cationic thermal vibrations significantly increase, however, no diffusion is observed. (Certainly, in real BaF_2 crystal the cation diffusion constant is not exactly zero, but, due to a high activation energy, the value of D_{Ba} is much smaller than could be detected i our MD simulations).

The calculated B_{Ba} and B_F Debay-Waller factors, together with those determined from neutron diffraction data, are shown in Fig. 7. There is a good agreement between calculated and experimental values in the low-temperature phase, while in the high-temperature phase the calculated values exceed the observed ones.

The anionic motion in the low-temperature phase (up to 1200K) is vibrational. In the high-temperature phase, anions are diffusing. The form $<\Delta r_F^2(t)>$ for anions is similar to that found in liquids or melts. Self-diffusion constants can be obtained directly from the slopes of lines $<\Delta r_\alpha^2(t)>$ (the errors in calculating D are roughly 10%), their value is 10^{-5} cm^2/s. Such values of D are typical of superionic conductors, that is why the high-temperature phase can be called superionic, the phase transition – a superionic phase transition. Fig. 8 presents the temperature dependence of diffusion coefficient obeying the Arrhenius equation.

At present there are no experimental data for self-diffusion constant in BaF_2, however, there are results of the conductivity σ measurements. The anion diffusion constant can be obtained from the Nernst-Einstein correlation:

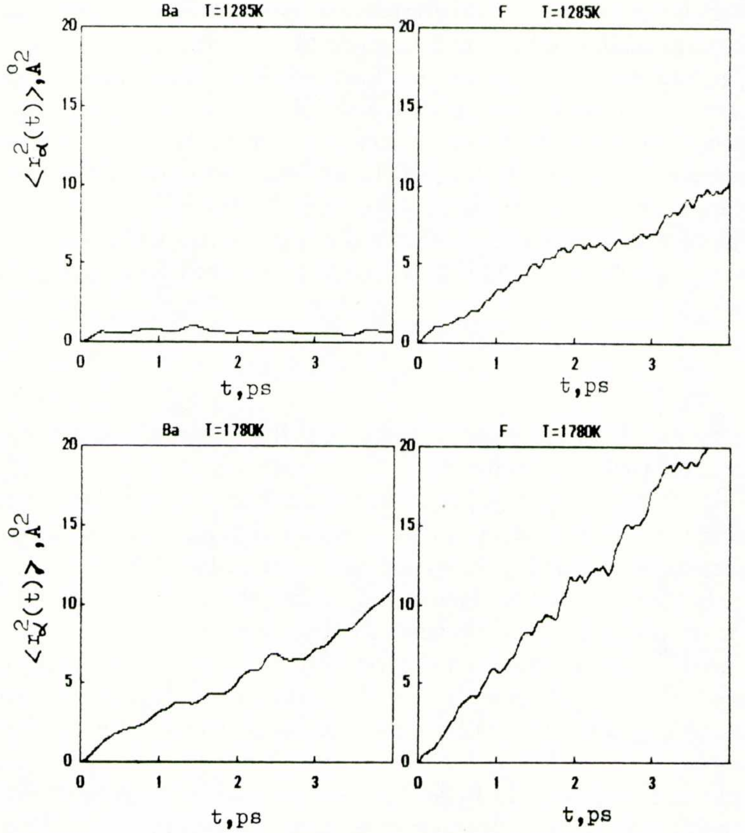


Fig. 6. Mean-square displacements Δr_α^2 (t) for cations and anions for simulated BaF_2 at different temperatures.

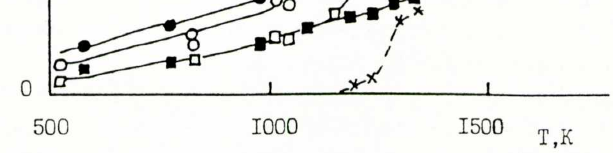


Fig. 7. Temperature dependences Debay-Waller factors: neutron diffraction data from [10] for Ba^{2+} (■), F^-(●) and F'(x); MD simulation results for Ba^{2+} (□) and F^- (○).

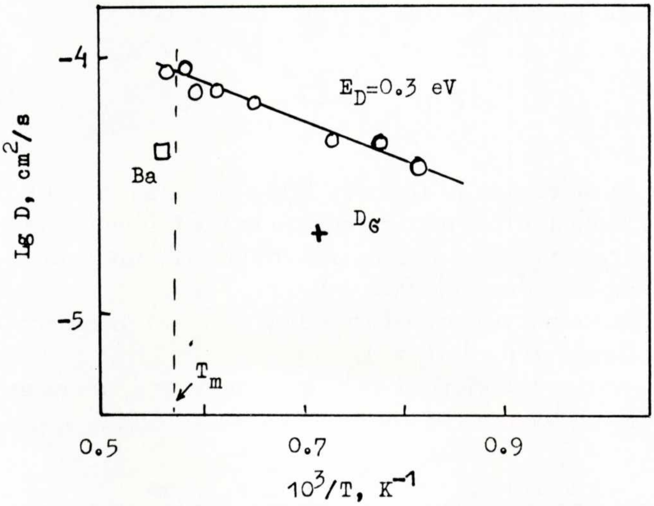


Fig. 8. Temperature dependences for anion diffusion constant of simulated BaF_2: ○ = simulation results. □ = simulation results for cations Ba^{2+}. + = results, derived from conductivity measurements.

$$D_\sigma = f \frac{k\,T\,\sigma}{n\,q^2}$$

where n is the concentration of charge carriers, q and f is the correlation factor. The f value is unknown, but it is assumed that it only slightly differs from 1.[2] We see from fig. 8, presenting also the calculated values of D_σ, that the simulated D_F is at least in qualitative agreement with experiment.[12,13]

Activation energy of conductivity E_σ depends on temperature and is $E_\sigma = 0.4$ eV near the melting point. This value agrees with the value of activation energy of diffusion $E_D = 0.3$ eV, obtained from MD-simulation.

Dynamics of Ionic Motion

It was shown above that anions diffuse in the superionic phase. However, the question is: whether the mechanism of particle motion is the quasi continuous liquid-like motion or the discrete hopping motion? To solve this microscopic task we examine the spherically averaged self-correlation van-Hove function G_s (r, t).

The second moment of this G_s (r, t) function is

$$P(t) = \frac{3 <\Delta r^4>}{5 <\Delta r^2>^2}$$

Simple consideration of function P(t) permits analysis of a possible microscopic mechanism of particle motion in the following way.

1) if the motion in the system is harmonic vibrations or is random-walk diffusion, then the value P(t) = 1.

2) if the motion is performed according to some other mechanism, for instance, by hopping, the P (t) ≠ 1.

Fig. 9 presents the plots of P (t) for cations and anions at different temperatures. It is seen that at low temperatures (<1200K) P (t) is close to

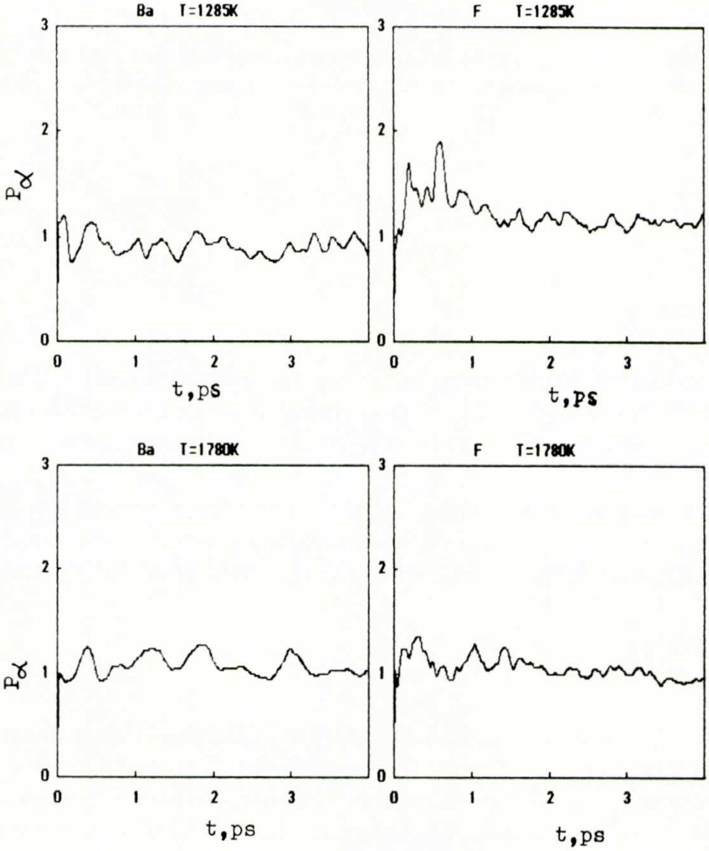


Fig. 9. Moments P_α (t) for Ba^{2+} and F^- ions at different temperatures.

unity both for cations and anions. Thus, bearing in mind the known information, we can make a conclusion about the ionic vibrations near their equilibrium sites. A more significant deviation of P (t) from unity for anions indicates that, apparently, there is a strong anharmonicity of fluorine vibrations. In the superionic phase P_+ (t) = 1, i. e. there are no principle changes in Ba motion. P (t) for F anions show strong deviations from unity, one may suppose that the mechanism of anionic diffusion, being the hopping one, differs from that of particle diffusion in simple liquids.

We have carried out simulations of a lower-density system, the potential parameters being the same. The main difference of the results obtained was a lowering of the superionic phase transition temperature by 250K. Fluoride ion diffusion is also observed in the high-temperature phase. We have also carried out MD-simulations with altered parameters of the short-range Born-Mayer potential, taken from[8]. The behaviour of the temperature dependence of the total energy suggests a possible superionic phase transition at T = 1050K. The fluoride ion diffusion constant in the high–temperature phase is of the same order of magnitude.

CONCLUSION

Basing on the results of MD simulations we suppose that, as a result of a phase transition, BaF_2 crystal exhibits a state characterized by a high ionic conductivity due to anion diffusión. Barium ions ensure preservation of the fluorite crystal structure, while fluoride anions in the high–temperature phase are engaged in two kinds of motion: they vibrate about equilibrium positions and perform hoppings to neighbouring nodes and interstitial sites.

ABSTRACT

The specific features of the thermodynamic, kinetic properties and crystal structure of BaF_2 were situdied by molecular dynamics simulation. The results obtained evidence the phase transition to the superionic state. This phase transition is accompanied by changes of radial distribution functions. The Debay-Waller factors in low-temperature phase are in good agreement with those obtained by neutron diffraction data. Fluoride self-diffusion constant is about $10^{-5} cm^2/s$ in superionic state.

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