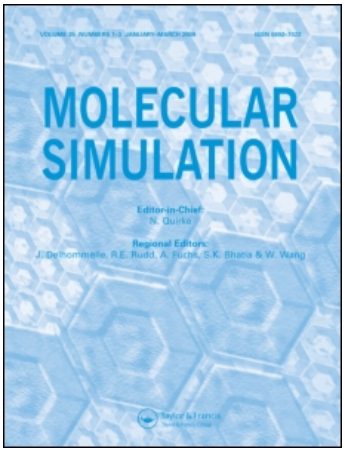

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Molecular Dynamics Simulation of CaF_2 Structure in Crystalline, Superionic and Molten Phases

Zhaonian Cheng[a]; Jing Chang[a]; Zhengming Jia[a]; Nianyi Chen[a]
[a] Shanghai Institute of Metallurgy, Chinese Academy of Sciences, Shanghai, P.R. China

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MOLECULAR DYNAMICS SIMULATION OF CaF_2 STRUCTURE IN CRYSTALLINE, SUPERIONIC AND MOLTEN PHASES

ZHAONIAN CHENG*, JING CHANG, ZHENGMING JIA AND NIANYI CHEN

Shanghai Institute of Metallurgy, Chinese Academy of Sciences, 865 Changning Road, Shanghai 200050, P.R. China

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We describe here a number of molecular dynamics simulations on calcium fluoride over a range of temperatures spanning the transitions to the superionic and molten state. The simulation temperatures are 1400, 1590, 1800, 2000, 2200 K. By using the bond spherical harmonics method with equal neighbor number, we have studied the structure and bond orientation of cation sublattice and anion sublattice in superionic conductor CaF_2. The bond order parameters Q_l have been calculated both for the computer generated instantaneous configurations from the simulation system and for the standard configurations from the normal distribution model of bond orientation. The comparison of Q_l between the molecular dynamics simulation and the normal distribution model shows that not only the cation sublattice but also the anion sublattice can be described by the normal distribution model. The cations keep their original fcc frame, but in the anion case there is a great deal of random distortions from the original anion sublattice.

KEY WORDS: molecular dynamics simulation, calcium fluoride, superionic phase, molten salt, bond order parameters

1 INTRODUCTION

Alkaline earth metal fluorides such as CaF_2, which has a fluoride structure, undergo a phase transition from the low temperature insulating phase to the high-temperature superionic phase, accompanying the specific heat anomaly [1]. The structure and transport properties of this type of superionic conductor were widely studied both theoretically and experimentally. A number of exmperiments showed that in the superionic phase the structure of cation sublattice is the same as that in the insulating phase, while the anions move in the cation frame. As a preliminary molecular dynamics (MD) simulation study of calcium fluoride system, some years ago, Rahman [2, 3] performed MD simulation and showed that the cations form a stable structure and the value of the mean square root displacement of cations is very limited, only about 0.3 A, while the motion of anions has a self-diffusion coefficient $D = 2.6 \times 10^{-5}$ cm^2/sec, which is a typical liquid-like value of D. The simulation given by Dixon and Gillan [4] indicated that in spite of their very high mobility, the anions do not occupy the octahedral interstitial site to any appreciable

*to whom correspondence should be addressed

extent. Recent neutron scattering experiments [9] showed that there is a strong quasi-elastic (i.e. low frequency) contribution to the scattering, which is intimately connected with the superionic conduction phase. The experimental results indicated that there are some dynamic correlations between interstitial anions and their near neighbor anions in the superionic phase of calcium fluoride. In order to compare the intensity and width of the quasi-elastic peak observed in the simulation with those in the corresponding experimental quantities, Gillan [5, 6] performed molecular dynamics simulation and demonstrated that the results of his simulation are in reasonable agreement with the experimental values. The simulation indicated that the mobile ions accompany the defect induced lattice distortion and the collective motions are responsible for the peak observed in the CaF_2 superionic phase. Recently, Ueda and his collaborators [7, 8] performed MD simulation and showed that the diffusion occurs mainly by ⟨100⟩ hops accompanying the correlated jumps of neighboring anions in the direction of diffusion. However, the details of the anion distribution and diffusion dynamics are complex and have not been fully elucidated for superionic conductor systems.

Early in the 80's, Nelson and his collaborators [10, 11] developed a method of bond spherical harmonics to measure both local and extended orientational symmetries in computer-generated models of dense liquids and glasses. Using this method we investigated the bond-orientational order and local structure in some molten salts [12]. By "bond" we do not mean chemical bonds, but rather lines resulting from some convenient assignation of near neighbors. Provided that the number of bonds of center particle is N and the polar angle of i-th bonds is θ_i and φ_i, the bond order parameters can be expressed as:

$$Q_l = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\bar{Q}_{lm}|^2 \right]^{\frac{1}{2}} \tag{1}$$

and

$$\bar{Q}_{lm} = \frac{1}{N} \sum_{i=1}^{N} Y_{lm}(\theta_i, \varphi_i) \tag{2}$$

where the $\{Y_{lm}(\theta, \varphi)\}$ are spherical harmonics, and $l = 0, 1, 2, \ldots$ The Q_l histogram of the first several nonzero even l is enough to describe the bond-orientational order ($l = 2, 4, 6, 8, 10$) since for all odd l, $Q_l = 0$ and for $l = 0$, $Q_l = 1$.

The instantaneous coordinates of the particles can be obtained from MD simulation. The Q_l value of N near neighbors in every computational step can be calculated from the momentary coordinates of the particles. By averaging the Q_l value of every particle and every step, the statistical description of the bond-orientation and spacial structure can be obtained.

In this work, we have carried out a number of molecular dynamics simulation on calcium fluoride system over a range of temperatures spanning the transitions to the superionic and molten state. The bond order parameters have been calculated from the instantaneous configurations generated by MD simulation and the spatial structures of the system simulated have been investigated by means of the bond order parameters.

2 BOND NORMAL DISTRIBUTION MODEL

In our previous work [12], we suggested a model with a parameter of square deviation to compare with the Q_l diagram obtained from MD simulation of molten salts. In this work we will present a small improvement and call it the bond normal distribution model. The crystal configuration at 0 K is called the standard configuration and every bond in the standard configuration is called a standard bond. All real bonds in the normal distribution model are random bonds. We denote θ_0 and φ_0 the spherical coordinates of the standard bond, θ and φ that of the random bond, $\theta = \theta_0 + \Delta\theta$, $\varphi = \varphi_0 + \Delta\varphi$. Figure 1 gives the generation of the random bond. The dashed line is the standard bond and the solid line is the random bond in Fig. 1(a). The angle between the standard bond and random bond is α, which satisfies the normal distribution and its average is 0 (random bond coincides with standard bond) with square deviation σ (an angle degree). The relative direction angle of each random bond with the same α is β, which satisfies the equalizational distribution with the range $0 - 2\pi$. The relationship among α, β and $\Delta\theta$, $\Delta\varphi$ is shown in Fig. 1(b), where the standard bond is denoted as OA while the random bond as OB in the ΔABC at unit spherical surface, $AB = \alpha$, $AB = \Delta\theta$, $BC = \Delta\varphi$. So $\Delta\theta = \alpha\cos\beta$, $\Delta\varphi = \alpha\sin\beta$. The spherical coordinates of the random bond can be generated as following: $\theta = \theta_0 + \alpha\cos\beta$, $\varphi = \varphi_0 + \alpha\sin\beta$. In such a model, the standard configuration is its "average" and the square deviation would measure the "confusion" magnitude of the system.

The space group of the fluorite structure is Fm3m, with the lattice constant of the face-centred cub (fcc) a_0, and a basis of a cation at the origin and anions at $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ positions. It may be viewed as a simple cubin (sc) array of anions, with alternate cube centers occupied by cations. According to the crystalline structure of calcium fluoride, we have calculated the model values of bond order parameters Q_l for cation-anion bonds, cation-cation "bonds", and anion-anion "bonds". The coordination number of the first shell of anions around every cation is 8 in the CaF_2 crystal structure and there are $N_b = 8$ anions as cation's near neighbor for cation-anion frame. The bond order parameters Q_l for cation-anion bonds have been calculated and listed in Tab. 1 with the σ range from 0° to 60°. In the fcc sublattice of cations there are $N_b = 12$ cations as "near neighbor" around every cation with equal distance from it. We have also calculated the model values of Q_l of cation-cation "bonds" with different σ and listed them in Tab. 1. In the

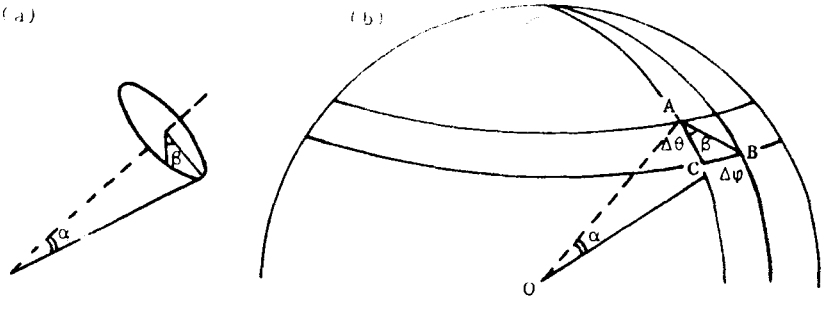

Figure 1 Generation of the random bond.

sc frame of anions there are $N_b = 6$ anions around every anion and the modei Q_l of anion-anion "bonds" are also listed in Tab. 1.

Table 1 Bond order parameters Q_l of bond normal distribution model.

ions	*σ (degree)*	Q_2	Q_4	Q_6	Q_8	Q_{10}
	0.0	0.0000	0.5092	0.6285	0.2128	0.6501
	4.0	0.0330	0.5035	0.6105	0.2310	0.6027
	8.0	0.0657	0.4873	0.5641	0.2671	0.5051
	12.0	0.0977	0.4636	0.5076	0.2996	0.4296
	16.0	0.1283	0.4366	0.4576	0.3209	0.3198
	20.0	0.1574	0.4111	0.4216	0.3308	0.3739
$Ca^{++} - F^-$	24.0	0.1843	0.3897	0.4002	0.3363	0.3642
	28.0	0.2091	0.3730	0.3875	0.3408	0.3583
$N_b = 8$	32.0	0.2312	0.3609	0.3803	0.3434	0.3565
	36.0	0.2512	0.3523	0.3747	0.3451	0.3548
	40.0	0.2689	0.3463	0.3697	0.3464	0.3546
	44.0	0.2849	0.3425	0.3653	0.3481	0.3565
	48.0	0.2988	0.3399	0.3619	0.3493	0.3567
	52.0	0.3117	0.3389	0.3605	0.3498	0.3547
	56.0	0.3222	0.3374	0.3608	0.3497	0.3517
	60.0	0.3321	0.3374	0.3619	0.3491	0.3495
	0.0	0.0000	0.1909	0.5745	0.4039	0.0129
	4.0	0.0270	0.1922	0.5585	0.3870	0.1151
	8.0	0.0539	0.1958	0.5162	0.3507	0.1991
	12.0	0.0803	0.2019	0.4615	0.3204	0.2454
	16.0	0.1057	0.2104	0.4102	0.3047	0.2659
	20.0	0.1298	0.2213	0.3702	0.2983	0.2749
$Ca^{++} - Ca^{++}$	24.0	0.1527	0.2322	0.3425	0.2954	0.2790
	28.0	0.1737	0.2422	0.3250	0.2944	0.2810
$N_b = 12$	32.0	0.1924	0.2502	0.3140	0.2933	0.2823
	36.0	0.2097	0.2565	0.3063	0.2914	0.2834
	40.0	0.2252	0.2617	0.3014	0.2901	0.2851
	44.0	0.2388	0.2660	0.2982	0.2901	0.2864
	48.0	0.2509	0.2698	0.2957	0.2904	0.2866
	52.0	0.2617	0.2729	0.2942	0.2914	0.2858
	56.0	0.2714	0.2754	0.2937	0.2926	0.2856
	60.0	0.2794	0.2773	0.2936	0.2940	0.2852
	0.0	0.0000	0.7637	0.3535	0.7180	0.4114
	4.0	0.0390	0.7531	0.3573	0.6853	0.4094
	8.0	0.0775	0.7231	0.3665	0.6101	0.4078
	12.0	0.1153	0.6795	0.3779	0.5372	0.4096
	16.0	0.1506	0.6316	0.3880	0.4904	0.4113
	20.0	0.1844	0.5848	0.3959	0.4633	0.4104
$F^- - F^-$	24.0	0.2158	0.5447	0.4004	0.4483	0.4082
	28.0	0.2439	0.5140	0.4032	0.4389	0.4080
$N_b = 6$	32.0	0.2694	0.4905	0.4037	0.4318	0.4084
	36.0	0.2912	0.4752	0.4034	0.4264	0.4093
	40.0	0.3109	0.4649	0.4038	0.4232	0.4091
	44.0	0.3281	0.4579	0.4035	0.4202	0.4077
	48.0	0.3429	0.4530	0.4041	0.4186	0.4068
	52.0	0.3556	0.4492	0.4057	0.4185	0.4067
	56.0	0.3663	0.4459	0.4082	0.4179	0.4063
	60.0	0.3744	0.4434	0.4105	0.4185	0.4048

3 MOLECULAR DYNAMICS SIMULATION

In our simulations we examined temperature dependence of both static- and dynamic-properties of calcium fluoride in the crystal, superionic and molten phase. Our results will be compared with that of the experiments and the molecular dynamics simulations given by Rahman, Gillan, and Ueda and their collaborators.

The simulation was performed by the standard molecular dynamics techniques and the program MDIONS3 used in this work was similar to our previous work on the simulation of three molten salts [12]. The computational cell was a cubic box and the number of particles in the box was 324 (108 cations and 216 anions). The periodic boundary condition was used and the Ewald summation technique was adopted to deal with the long-range force [13, 14].

The side length of the box is determined by the density data of the fluoride. The densities used in the present simulation are $d=2.793$, 2.525, 2.475, 2.397 and 2.319 g/cm^3 for $T=1400$, 1590, 1800, 2000, 2200 K, respectively. The densities used in our simulation are taken from experimental data [17, 18] or from Rahman [2].

A simple potential, Born-Mayer-Huggins (BMH) potential was used in our simulation,

$$U(r_{ij}) = Z_i Z_j \frac{e^2}{r_{ij}} + \left(1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}\right) b \exp\left(\frac{\sigma_i + \sigma_j - r_{ij}}{\rho}\right) \tag{3}$$

where r_{ij} is the distance between i ion and j ion, Z_i and Z_j the charge of ions in units of the protonic charge e, n_i and n_j the number of electrons in the outer shell, σ_i and σ_j the parameter representing the ionic radius, b the repulsion parameter and ρ the softness parameter.

Since CaF_2 is close to being fully ionic, we set the charges to $z_+ = 2$ and $z_- = -1$. The coefficients b, ρ, and σ were determined empirically. The double charge on the Ca^{++} ions ensures that these are always well separated from one another, and their repulsive interactions can be neglected: $b_{++} = 0$. The parameters of the interactions between the F^- ions were taken from the model 1 given by Busing [20] in his study of the crystal structure of Li_2BeF_4: $b_{--} = 0.190 \times 10^{-19}$ J/mole, $\rho_{--} = 0.290$ Å and $\sigma_- = 1.237$ Å, where the parameters b_{--} and ρ_{--} were taken from the common value given by Tosi and Fumi for alkaline fluorides [21]. Although the model 1 of Busing omitted the van der Waals term, the stable minima of 23 independent distance parameters were found closed to the experimental structure very well [20]. For unlike ions the van der Waals parameter was not included, on the grounds that unlike nearest neighbours are close enough for the van der Waals interaction to be quenched [5]. In the remaining three parameters, the parameters b_{+-} and ρ_{+-} were taken as common value: $b_{+-} = 0.190 \times 10^{-19}$ J/mole, $\rho_{+-} = 0.290$ Å, which very closed to the corresponding parameters given by the model 1 of Catlow and Norgett [22]. In their study Catlow and Norgett fitted potential to the properties of three alkaline earth fluoride and the potential reproduced the elastic properties of the three materials [22]. Thus we require only one further parameter σ_+ to describe the cation-anion interaction. Using above parameters of anion and cation and lattice parameter $a_0 = 5.444$ Å, we adjusted the parameter σ_+ to fit the experimental lattice energy $E = 2609$ kJ/mol at zero temperature and obtained the value $\sigma_+ = 1.46$ Å. The

elastic properties (in 10^{11} dyn cm^{-2}) calculated from this simple potential model are: bulk modulus $K = 8.11$ and elastic constant $c_{11} = 15.66$, $c_{12} = 3.92$, and $c_{44} = 3.79$, while experimental value [22, 23] are $K = 8.8$, $c_{11} = 17.12$, $c_{12} = 4.68$, and $c_{44} = 3.62$, respectively. The values calculated are reasonable agreement with experiment. Generally, the potential model used in present work are very close to the model 1 given by Catlow and Norgett [22].

We began the simulation of $T = 1400$ K and took the crystal structure of calcium fluoride at 0 K as the initial configuration. The initial velocities of the particles were given by thermal velocities $\sqrt{3kT/m}$, while the directions were given at random.

The motion equation set was solved numerically with the leapfrog algorithm [15]. The temperature of the system was adjusted by scalling the velocities [16] and the total energy was maintained at a certain value automatically when its fluctuation was out of the given range. In the simulation the time interval was 5×10^{-15} s and at each temperature the system was first equilibrated for 5000 time step. When the equilibrium reached, the system was relaxed for 1000 steps in equilibrium to record the instantaneous positions and velocities of ions in every step for the computations of radial distribution functions, transport properties, and bond order parameters, and other properties.

4 SIMULATION RESULTS

The mean square displacements (MSD) generated from the MD process, which may be useful to reflect the ionic diffusivity, have been calculated for five temperatures simulated. Figure 2 gives the MSD calculated from a certain time after equilibrium. It can be seen from Figure 2 that the MSD of cations and anions at $T = 1400$ K are in the range of thermal motion about equilibrium position, the MSD being found to be constant and small in the simulation time, about 0.28 Å for cations and 0.57 Å for anions.

The displacements of cations at $T = 1590$ and 1800 K are also in the range of thermal motion in equilibrium around its lattice point of original sublattice, while the MSDs of anions monotonically increase with time step. The anion diffusion coefficient calculated from the MSD at $T = 1590$ K is $D = 2.33 \times 10^{-5}$ cm^2/s, which is a typical liquid-like value of the constant of self-diffusion. It is a characteristic property of superionic conductors that the mobile species have liquid-like constants of self-diffusion. At $T = 1590$ K the electrical conductivity deduced from the Nernst-Einstein relation is $1.07/\Omega$ cm, which is coincident with the experimental value of about $1.5/\Omega$ cm [19]. The MSDs of both cations and anions at $T = 2000$ and 2200 K increase with the time step, which indicates the calcium fluoride system simulated has melted and transformed into molten phase.

The transition temperature to the superionic phase is $T_c = 1423$ K and the melting temperature is $T_m = 1691$ K. The calculation of the present simulation shows that the T_c and T_m fell into the regions 1400–1590 K and 1800–2000 K, respectively. This indicates that the transition to the superionic region occurs at roughly the right temperature, but the temperature range of the superionic phase shifts a little to high T. The potential used in this simulation may be somewhat too simple.

Figure 3 shows the radial distribution functions (RDF) between two kinds of ions.

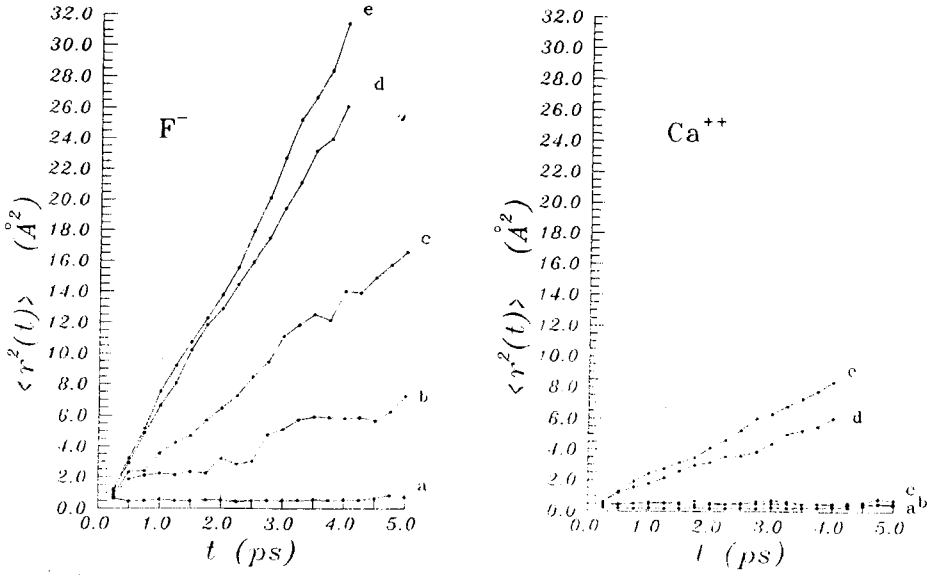

Figure 2 Mean square displacemment for anions and cations as a function of MD time from a certain time after equilibrium.
The temperature are: (a) 1400 K, (b) 1590 K, (c) 1800 K, (d) 2000 K and (e) 2200 K.

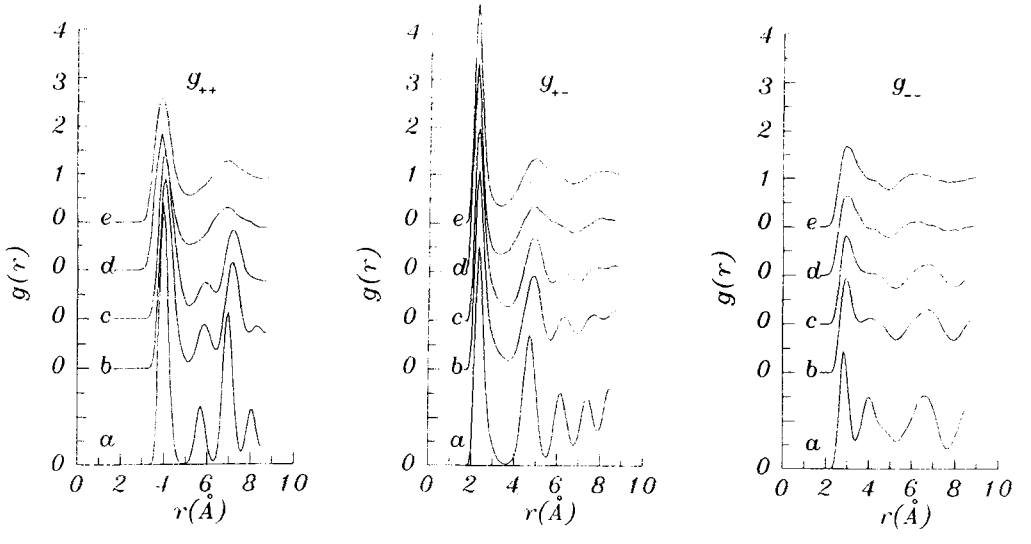

Figure 3 Radial distribution functions g_{++} (cation-cation), g_{+-}(cation-anion) and g_{--}(anion-anion).
The temperature are: (a) 1400 K, (b) 1590 K, (c) 1800 K, (d) 2000 K and (e) 2200 K.

The RDF at $T = 1400$ K gives a description of crystalline phase of calcium fluoride. At $T = 1590$ and 1800 K, the cation-cation's RDFs clearly show that cations form a thermally agitated fcc lattice: three successive peaks correspond to the first, second and third nearest neighbor distances, and no structural change is predicted. The

anion-anion's RDFs have much less clearity in its peak structure than those of cation-cation's or cation-anion's and the second peaks are gradually smoothing down. In the case of cation-anion, the first peaks of RDF are very high, which shows each cation has a well defined shell of nearest neighbor anions with a distance between cations and anions similar to that of the crystalline phase. The second peaks, and even the third peaks are also very clear. At $T = 2000$ and 2000 K, the system has been melted. The second peaks of cation-cation's RDF have disappeared and the first and third peaks smoothed down. For cation-anion's RDF, the third peaks disappeared and the second peaks smoothed down. In the anion-anion's RDF, the first and third peaks smoothed down, and the position of third peaks became smaller than those of crystalline and superionic phase. From superionic to molten phase, the variations in cation-cation's and cation-anion's RDF are very obvious but for the anion-anion case, the RDF of molten phase is not distinct from superionic phase.

General features of our RDF are found to be similar to those of Rahman [1] and Hiwatari-Ueda [7], but they did not calculate the RDF of crystalline and molten phase nor compare them with the superionic phase.

The bond order parameters (BOP) were calculated for cation-anion, cation-cation and anion-anion frame based on the method of bond spherical harmonics with equal neighbor number [12]. For cation-anion bonds, we took every cation in computational cell as center particle and found 8 nearest anions around it with the neighbor image conversion and the periodic condition. Then the θ_i and φ_i of 8 bonds of cation-anion can be calculated and the bond order parameters Q_l can be obtained in accordance with the equation (1). The Q_l values of every instantaneous configuration were calculated by averaging 108 cation center ions and the molecular dynamics averages $\langle Q_l \rangle$ were obtained by averaging all the instantaneous Q_l. The procedure for cation-cation and anion-anion "bonds" was the same as for cation-anion bonds, but the number of near neighbors is taken as 12 for cation-cation frame and 6 for anion-anion frame.

The bond order parameters of calcium fluoride system calculated from the present simulation are given in Figure 4(b) for cation-anion bond. Figure 5(b) for cation-cation "bond", and Figure 6(b) for anion-anion "bond".

We denote the Q_l from the bond normal distribution model as $Q_l^M(\sigma)$ and the Q_l from the MD simulation as Q_l^S, and calculated the square deviation σ by minimizing the quantity

$$\sum_l [Q_l^S - Q_l^M(\sigma)] \tag{4}$$

to obtain the square deviations of bond orientation in the simulation system. The model Q_l^M histograms with square deviation calculated are given in Figure 4(a), 5(a) and 6(a) corresponding to the simulation Q_l^S. From comparison between the model Q_l^M and the simulation Q_l^S in the Figs. 4–6, we can see that the Q_l^M of the model is very similar to Q_l^S of the simulation. This means that the bond normal distribution model can describe very well the cation and anion sublattice in calcium fluoride superionic phase.

The square deviations of bond orientation in the simulation system are given in Figure 7 for three bonds at different temperatures. We note from the Figure 7 that there are some "abrupt" changes of slope upon entering the superionic region and molten region.

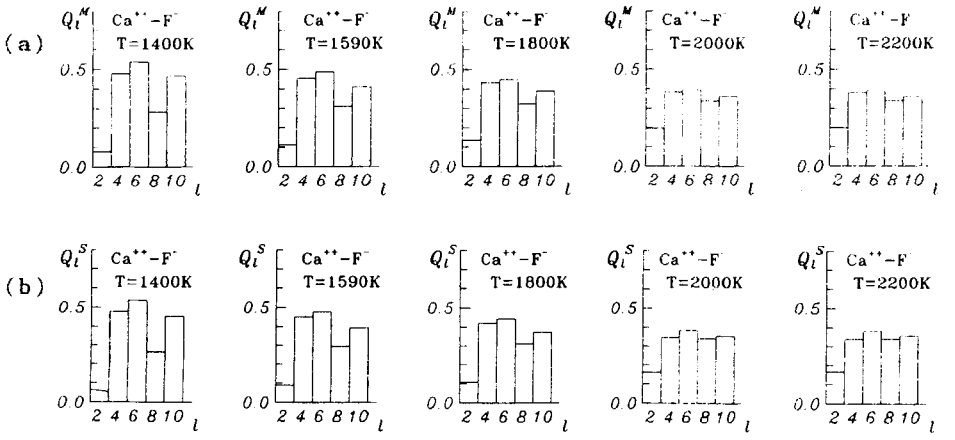

Figure 4 Bond order parameters Q_l^M (model) and Q_l^S (simulation) histograms for cation-anion bond at five temperatures.

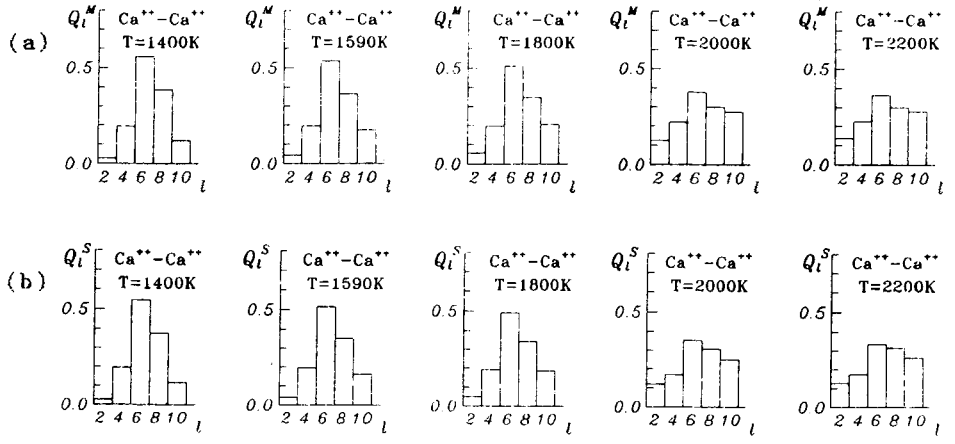

Figure 5 Bond order parameters Q_l^M (model) and Q_l^S (simulation) histograms for cation-cation "bond" at five temperatures.

5 DISCUSSION

(1) Suppose an anion moved to the middle point between two anions. If the motion was along ⟨100⟩ direction, then the fluctuation of the bond angle would be 26.6°; if along ⟨110⟩, then 45°; if ⟨111⟩, then 63.4°. The small values of square deviation of fluctuation of the anion-anion "bond" angle, (only 23.2° and 27.3° in the superionic phase given by present work), indicate that anion diffusion occurs by means of correlated hops predominantly in the ⟨100⟩ directions, coinciding with some molecular dynamics simulations [2-8] and neutron-scattering experiments [9].

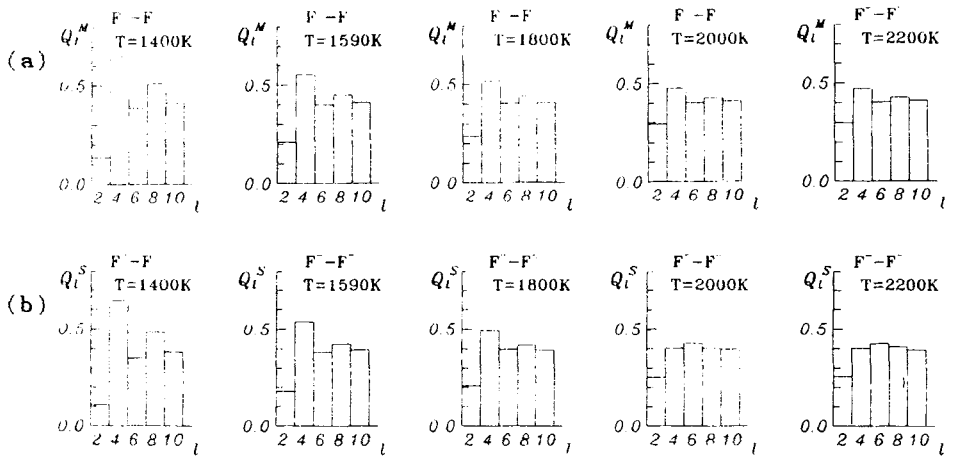

Figure 6 Bond order parameters Q_l^M (model) and Q_l^S (simulation) histograms for anion-anion "bond" at five temperatures.

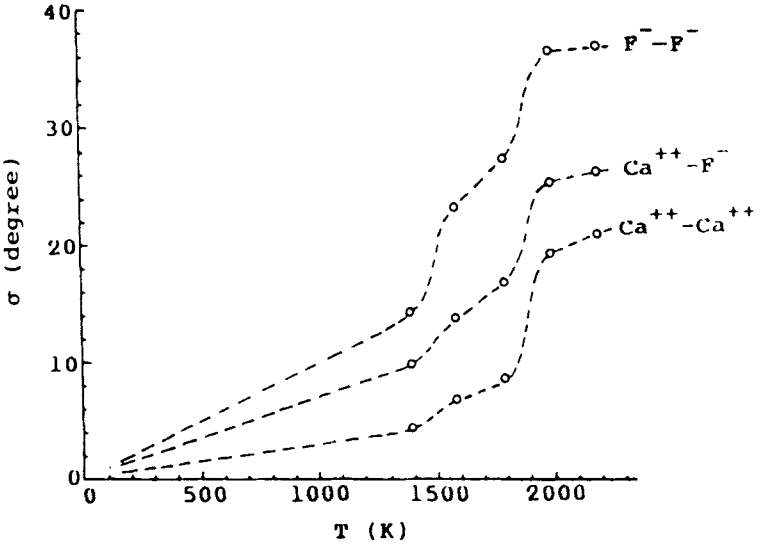

Figure 7 Square deviation of bond orientation in the simulation system for cation-anion bond, cation-cation "bond' and anion-anion "bond' as a function of temperature.

Meantime, the tetrahedral positions in cation's fcc sublattice are occupied by anions, while the octahedral positions are empty. If anions occupied the octahedral positions (the middle point between two anions along ⟨111⟩ direction), some characteristics near about 63.4° of bond angle would have appeared. But such characteristics are not found in the bond order parameters. This means that the

anions do not occupy the octahedral interstitial sites to any appreciable extent, coinciding with the simulation results of Dixon and Gillan [4].

(2) The stability of the cation and anion sublattice in superionic phase could be examined by studying the square deviations of the "bond" orientation. The length of cation–cation "bond" is 3.86 Å and the square deviations σ of the "bond" orientation of cation–cation's fcc sublattice in this simulation are only 6.6° and 8.4°. These angles correspond to 0.44 Å and 0.56 Å of the cation's displacement, which are much less than half of the length of cation–cation "bond". This indicates that the cations are keeping their original fcc sublattice steadily. The usual way to demonstrate the stability of cation sublattice in molecular dynamics simulations is to show that the displacement of cations is very small. In the calculation of the mean square displacements we examined every instantaneous displacement $r(s+t)$ of every ion at time $(s+t)$ from the original position $r(s)$ itself at time s, while in the computation of bond order parameters we could examine the related displacements between center ions (all the ions in the computational cell are taken as centers) and their neighbors in every momentary configuration. Perhaps, the bond order parameters might describe the cation sublattice more reasonably.

(3) The length of anion–anion "bond" is 2.73 Å and in the superionic phase of this simulation, the square deviations σ of the "bond" orientation of anion–anion's sc sublattice are 23.2° and 27.3°. These angles correspond to 1.08 Å and 1.25 Å of the anion's displacements. Although these displacements are about half of the length of anion–anion "bond", they are still less than it. This means that in the calcium fluoride system, the anions might continue their original sc sublattice to some extent. We can say from the similarity between Q_l^S and Q_l^M that the strong fluctuation of anion sublattice is observed in the system rather than a complete disorder, and there is no evidence for liquid-like behaviour of the anions, arising from a sublattice melting. It is surprising that not only the cation sublattice but also the anion sublattice can be well described by the bond normal distribution model. This indicates that in the anion frame there is a random distortion, of which the "average" is sc sublattice, rather than a distortion tending to some certain deformation. Such as picture given by our bond normal distribution model is fully coincident with the trajectory figure from the simulation of Kaneko-Ueda (Figure 3(b) in [8]). However the bond order parameters can give a more quantitative description than the trajectory figure can do.

It is usually said from the neutron diffraction data that the interstitials do not participate significantly in the rapid diffusion of the ions, which is due to vacancies, and the clusters do not have any direct connection with the conduction mechanism. The present result which we stress is based on absolute comparison of bond order parameters free of any arbitrary factor, the anion frame can also be described by the bond normal distribution model and there is scarcely any significant distortion tending to some certain deformations, provides again evidence that the spatial characteristics of collective fluctuations in the simulated system are closely similar to those in real calcium fluoride, as Gillan had pointed out in his paper [5, 6] by comparing his simulation with the experiments of Hutchings *et al.* [9].

(4) There are 216 anions altogether in the computational cell. If only one of anion diffused into its near neighborhood position, the value of displacement would be 2.73 Å (the distance between anions), and its square would be 7.45 Å. Thus, one of the anions displaced contributes 7.45/216 = 0.0345 Å to MSD of the system. It may be interesting to see that in Figure 2(a) at $T = 1590$ K there is a small "jump"

in the curve of mean square displacement around $t = 3$ ps. The quantity of "jump" is about 2Å^2, implying that about 60 anions among 216 ions diffused successively into their near neighborhood position at a short time. Such a picture supports Kaneko-Ueda's conclusion: the diffusion occurs mainly by ⟨100⟩ hops accompanying the correlated jumps of neighboring anions aligned in the direction of diffusion ([8], Figure 6). The time of jump could reflect the time in flight of anions from the original position to its near neighborhood position, which is about 1 ps from Figure 2, and coincident with the result of Kaneko-Ueda, also.

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