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CaF₂ 熔化温度的分子动力学模拟*

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摘要: 利用壳层模型分子动力学方法,研究了高温高压条件下 CaF₂ 的熔化温度,同时计算了温度为 300 K、压强上升到 100 GPa 时 CaF₂ 的状态方程. 研究中考虑了分子动力学模拟的过热熔化,通过晶体的现代熔化理论,对 CaF₂ 的分子动力学模拟熔化温度进行了修正,获得了高温高压下 CaF₂ 的熔化温度. 因此,常压下壳层模型分子动力学方法为研究物质熔化提供了一个很好的方法.

关键词: 熔化温度; 分子动力学模拟; 状态方程; 高压

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Molecular Dynamics Simulations for Melting Temperatures of CaF₂ *

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Abstract The molecular dynamics method has been applied to simulate the melting temperatures of CaF₂ at elevated temperature and high pressure and to calculate the $P \sim V$ equation of state of CaF₂ up to 100 GPa at 300 K. The interatomic potential was taken to be the sum of pairwise additive Coulomb, van der Waals attractions, and repulsive interactions. In addition, the shell model was used in molecular dynamics simulation. The pressure dependence of the melting temperature of CaF₂ was predicted up to 4 GPa. However, in order to account for the superheating melting of the molecular dynamic simulation, the simulated melting temperatures of CaF₂ were corrected by the modern theory of melting. Consequently, the melting temperatures of CaF₂ were accurately obtained at elevated temperature and high pressure. Therefore, it is shown that shell-model molecular dynamics simulation at constant pressure indeed provides a useful tool for studying the melting temperatures of other materials under high pressures.

Keywords Melting temperature, Molecular dynamics simulation, Equation of state, High pressure

1 Introduction

As a mysterious phenomenon in nature, melting has attracted much attention for a long time^[1-4]. The

prediction of the pressure dependence of the melting temperature for a solid material is a problem, however, it is very important for the description of Earth's evolution, especially in case that one adopts the hypothesis

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of an early magma ocean^[5]. In order to describe the timing and sequence of crystallization from the protomelt^[6], it is necessary for us to know the pressure dependence of the melting temperature of minerals forming the Earth's minerals. Here, we only focus on CaF_2 because CaF_2 is one of the major constituents of the Earth's mantle, and the properties of CaF_2 at elevated temperature and pressure are of interest to the geophysicist^[7].

There have been significant progresses lately in the experimental determination of the pressure dependence of the melting temperatures of MgO , NaCl , and MgSiO_3 under the physical conditions of the Earth's mantle and core using a diamond-anvil cell (DAC) with laser heating and shockwave techniques^[8-10]. At present, it has been still difficult to measure available results at the extreme condition of high pressure and elevated temperature for all kinds of materials, such as CaF_2 and so on. Therefore, computer simulations based on interionic interactions have been applied extensively to investigate the microscopic structures and the macroscopic thermodynamics of a wide variety of chemical and physical properties. In addition, numerical computations are particularly useful and powerful for problems that may be inaccessible to direct experimental studies. As is known, a theoretical approach can provide independent information to support experimental determinations.

In this work, we have calculated the melting temperatures of CaF_2 by shell-model molecular dynamics simulation at constant pressure. Molecular dynamics (MD) simulation allows substantial metastable superheating of perfect crystals without suffering from surface/interfaces as heterogeneous nucleation sites for melting^[11]. MD simulation further allows tracking the physical properties of the atoms not only as global but also local average. This capability is indispensable for exploration of a correction between the theories and the atomic-level mechanisms at the onset of melting.

2 Theoretical method

MD simulation is a well-established technique in mineralogy, especially for studying the effects of high

pressure and elevated temperature on the properties of solid and their melts. A detailed description of the molecular dynamics method has been reported elsewhere^[12,13]. In short, the molecular dynamics method consists in solving numerical equations of atomic motion, assuming initial coordinates and velocities of atoms and a model of interactions between them. Normally, as is also the case in MD calculations, periodic boundary conditions are applied.

MD simulation in its classical modification is quite suitable for calculation of thermoelastic properties of a solid or a melt. However, as a complex phenomenon, melting is believed to initiate around defects that include various point defects and extended defects including the surface. In view of the complexity, various techniques have been applied to judge the melting, such as the two-phase, bulk transition, radial distribution functions (RDF), snapshot, and so on. Whereas the bulk transition is rather direct and convenient to consider defects. The two-phase method^[14,15] allows for melting at the interface of an ideal lattice and melt. However, it does not allow for defects to be generated within the ideal lattice. Superheating of a crystal in MD simulation of melting is a well-known phenomenon^[16,17]. Superheating is required for several reasons. At first, a nucleus of melt is instable unless it reaches a certain size^[18], which might be quite large compared with the size of the computation box (which usually does not exceed a few dozen angstroms). Therefore, the appearance of melt is suppressed by the size of a stable nucleus. Secondly, the creation of an interface between solid and melt requires excessive energy, which can be provided only by increasing the temperature. Thirdly, simulations at constant volume might lead to instability of both solid and liquid phases (the volume is too small for a liquid and too large for a solid).^[19] Therefore, we believe that bulk transition simulation at constant pressure indeed provides a useful tool for studying the melting transition.

Following our previous studies^[20, 21], the crystal lattice energy is taken to be the sum of interactions between atoms as follows:

$$V(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8} \quad (1)$$

where Z_i or Z_j is an effective charge of the i th atom, e the electronic unit charge, A_{ij} the magnitude of repulsion force, B_{ij} the softness parameter, C_{ij} and D_{ij} the parameters of dipole-dipole and dipole-quadruple dispersion forces. The first term represents the Coulomb interaction; the second one is due to overlapping repulsion. Here r_{ij} is the interatomic distance between the i th atom and the j th atom. The parameters in Eq. (1) are given in the literature^[7].

MD simulations were performed in the NTP (N : number of particles, T : temperature, and P : pressure) ensemble^[22]. The results of shell-model MD simulations in the NTP ensemble with the chosen model of the interatomic interaction depended on slightly, apart from the initial arrangement of particles, the size of time step Δt , number of particles N , and temperature of windows t_{win} , which allowed temperature window for equilibration dynamics, in K. Therefore, the influence of these parameters was carefully studied by carrying out test run at various temperatures and pressures. It was found that the correct results can normally be obtained with $\Delta t = 1$ fs, $N = 216$, $t_{\text{win}} = 23$ K. The results might have been affected by the choice of the above parameters; we varied them to verify that the final results are stable. In this work, we have simulated the $P \sim V$ equation of state of CaF₂ up to 100 GPa at 300 K, as shown in figure 1, where $V_0 = 23.368$ cm³/mol is the simulated molar volume of CaF₂ at ambient temperature and pressure.

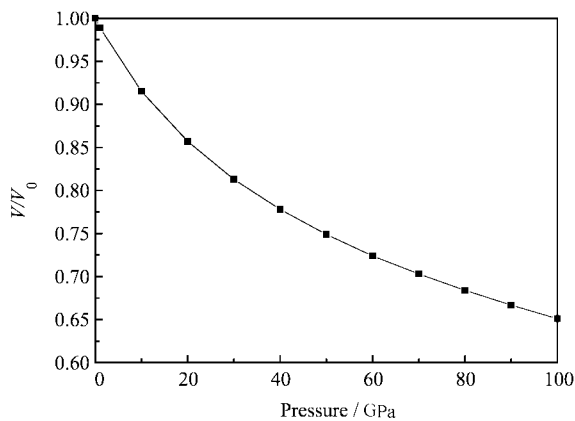


Fig. 1 The $P \sim V$ equation of state of CaF₂ up to 100 GPa at 300 K

3 Results and discussions

The first-order melting transition of CaF₂ manifests themselves at 2543 K under the pressure of the 101 kPa, where the mean atomic volume undergoes a sudden upward jump, as marked in figure 2. Note that these are higher than normal melting. The reason is that MD simulations in free space are known to exhibit high hysteresis^[23], which prevents us from judging how well the experimental value of melting temperature at 0.1 kPa pressure is reproduced. Cohen and Gong noted the high hysteresis at 0.1 kPa, which decreased

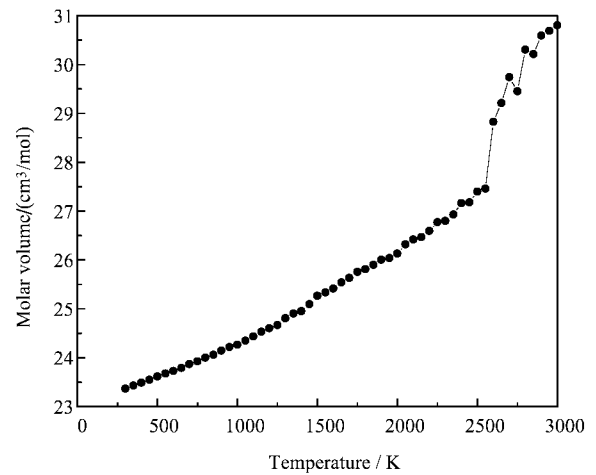


Fig. 2 The calculated volume of CaF₂ at 0.1 kPa versus temperature. The volume is suddenly changed at a temperature of about 2543 K

with increasing pressure^[23]. It was also the result of the existence of a substantial metastable superheating. Instable superheating due to the melting kinetics during the rapid heating is insignificant because of the transient nature of melting at such a high degree of superheating. But, according to the modern theory of melting, melting is a dynamic process and melting temperatures of a crystal can be modified by certain melting mechanism^[24], and corresponding superheating melting of CaF₂ at ambient pressure can be concluded as,

$$\frac{T_m - T_{m0}}{T_{m0}} = 0.212 \quad (2)$$

where T_{m0} is the conventional melting temperature for the bulk. This melting process resulting from the temperature increasing rate, is not much dependent on the pressure. It will be applied to correct the melting tem-

peratures for superheating of crystal (T_m in Eq. (2)) to T_{m0} as a first approximation.

We have ever applied the MD method with the shell model and two-body potential to simulate the melting temperatures of MgO successfully^[20]. Thus, we think that the shell-model MD simulation could be applied to study the process under high pressures over the melting point. In this work, we have extended the model to the calculation of the melting point of CaF₂. In all, the pressure dependence of the melting temperature of CaF₂ was predicted up to 4 GPa. However, to account for the superheating melting of molecular dynamic simulation, the simulated melting temperature of CaF₂ was corrected by the modern theory of melting. Consequently, the melting temperature of CaF₂ was obtained at elevated temperature and high pressure, as shown in figure 3. The corrected melting temperature of CaF₂ was about 2098 K at zero pressure. It is noted that the melting temperatures of CaF₂ increase with increasing the pressure. Moreover, the tendency of the simulated melting temperature curve for CaF₂ is consistent with Liu *et al.*^[20] for MgO and Cheng *et al.*^[21] for NaCl. Therefore, it is believed that the pressure dependence of the melting temperature of CaF₂ is accurately shown in figure 3.

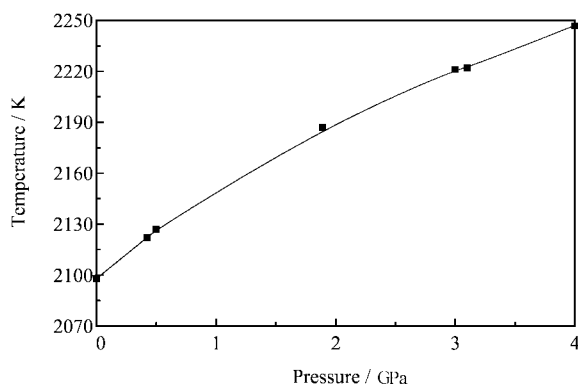


Fig. 3 Molecular dynamics simulated melting temperatures of CaF₂

In summary, on account of the superheating and the hysteresis, we propose to modify our simulation melting temperature. Moreover, the tendency of the simulated melting temperature curve for CaF₂ is consistent with Liu *et al.* for MgO^[20] and Cheng *et al.* for NaCl^[21]. MD simulation further allows tracking the

physical properties of the atoms not only as global but also local average. This capability is indispensable for exploration of a correction between the theories and the atomic level mechanisms at the onset of melting. Therefore, it is shown that shell-model MD simulation at constant pressure indeed provides a useful tool for studying the melting temperatures of other materials under high pressures.

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