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Simulation of Melting Behavior of the MgSiO_3 Perovskite Under Lower Mantle Conditions

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The melting curve of MgSiO_3 perovskite was simulated using molecular dynamics method combining with the effective pair potentials under the lower mantle conditions. It was shown that the state equation simulated for MgSiO_3 perovskite is very successful in reproducing accurately the experimental data over a wide range of pressure. The pressure dependence of the simulated melting temperature of MgSiO_3 perovskite is in agreement with the recent experimental data. The melting curve simulated for MgSiO_3 is very steep at pressures below 60 GPa first, then it becomes smooth with increasing pressure. At the core mantle boundary pressure 135 GPa, MgSiO_3 perovskite melts at 6500 K, which is significantly lower than that of the extrapolations of the experimental data from Zerr and Boehler.

Key words: Melting curve, Molecular dynamics, High pressure, MgSiO_3

I. INTRODUCTION

MgSiO_3 perovskite is an important material for Earth sciences and solid-state physics because it is one of the most abundant minerals in the Earth (especially in the lower mantle). Its melting properties in the wide temperature range at high pressure are of great interest to the geophysicist [1-3].

At the early stage of Earth's evolution, a significant part of MgSiO_3 was in the molten state [4,5]. The melting temperature as a function of pressure in the pressure range of the lower mantle is needed to describe the Earth's evolution. The melting temperatures of MgSiO_3 perovskite also play a fundamental role in the chemical differentiation, rheology and geodynamics of the Earth's lower mantle. However, it is difficult to obtain directly through laboratory experiments at high temperature and high pressure [6-8]. Numerical computations are particularly useful and powerful for the problem that may be inaccessible to direct experimental studies, such as the problem at high temperature and pressure. We have taken the advantage of the recent advances in computer technology to perform molecular dynamics simulations of the physical properties of MgSiO_3 perovskite, the major mineral of the lower mantle, at the relevant thermodynamic conditions. Furthermore, the molecular dynamics simulations are used because it allows the substantial metastable overheating of perfect crystals without suffering from surface/interfaces as heterogeneous nucleation sites for melting [9]. Molec-

ular dynamics simulation further allows tracking the physical properties of the atoms not only in a global average state but also in a local state. This capability is indispensable for the exploration of a correction between the theories and the atomic-level mechanisms at the onset of melting. In this work, we simulated the melting curve of MgSiO_3 perovskite by using the molecular dynamics simulation method at constant pressure, and compared the results with the previous ones.

II. METHOD

The condition for the successful molecular dynamics calculations is the availability of the reliable interatomic potentials describing the interaction between atoms in the crystalline lattice [10]. Following our previous studies [11,12], the crystal lattice energy is taken to be the sum of the interaction energies between atoms:

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

where Z_i or Z_j is the effective charge of the i th atom, e the unit of the electronic charge, A_{ij} and B_{ij} are the parameters for the repulsive interactions, and C_{ij} is the van der Waals constants. The first term represents the Coulomb interaction, the second one is due to the overlap repulsion. Here r_{ij} is the interatomic distance between atoms i and j . Because the interparticle interaction is the most important factor in molecular dynamics simulations, a proper choice of interaction potential is necessary for better results. The values of the parameters [13] of potential of MgSiO_3 perovskite used in the simulations are listed in Table I.

All of the simulations are performed by using the interaction potential in Eq.(1). The simulations in *NTP*

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TABLE I Parameters of the potential of MgSiO₃ perovskite used in simulations

Source	A/eV	B/nm^{-1}	$C/10^{-6}\text{eV nm}^6$
Mg–Mg	1309336.700	9.615	
Mg–Si	2325826.600	10.869	
Si–Si	5005903.500	12.500	
Mg–O	8035.120	4.950	
Si–O	7363.450	5.263	
O–O	1621.680	3.333	30.222

(constant N is the number of particles, T is the temperature, and P is the pressure) ensemble [14] are performed with 360 particles (72 Mg atoms, 72 Si atoms and 216 O atoms). The cut-off radius is chosen to be $L/2$, where L is the length of the short edges of the computational box. The time steps are varied from 2 femtoseconds ($1\text{ fs}=10^{-15}\text{ s}$) at low temperature to 1 fs at high temperature. The run durations are varied from 6000 steps to 4000 steps, depending on time step. The Coulombic interaction is calculated using Ewald method [15].

III. RESULTS AND DISCUSSION

The simulated molar volume V_0 ($=24.414\text{ cm}^3/\text{mol}$) agrees well with the results of Yeganeh-Haeri [16] (within 0.1%) under 300 K at zero pressure. In a recent study, Belonoshko used the MAM0K potential to perform the molecular dynamics simulations on MgSiO₃ perovskite concerning the equation of state, structure and melting transition at high pressure. Our simulations are in very good agreement with those of Belonoshko ($\alpha_0=2.37\times 10^{-8}\text{ K}^{-1}$ and $K'_{T_0}=4.92$) at the atmosphere pressure [17]. Knittle and Jeanloz carried out the X-ray diffraction experiments of $(\text{Mg}_{0.88}\text{Fe}_{0.12})\text{SiO}_3$ perovskite at pressures up to 112 GPa and 300 K based on the diamond-anvil cell [18]. Mao *et al.* performed the static compression experiments of MgSiO₃, $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$, and $(\text{Mg}_{0.8}\text{Fe}_{0.2})\text{SiO}_3$ perovskite at pressures up to 28.4 GPa and 300 K, using neon as a pressure-transmitting medium [19]. The results showed that the volume-compression data under the normalized volume conditions for these three perovskite at 300 K are indistinguishable. Fiquet *et al.* also reported the volume-compression data of MgSiO₃ perovskite at 300 K and in the pressure range from 28 to 51 GPa [20]. As shown in Fig.1, simulated pressure-volume relation of perovskite at 300 K is in excellent agreement with that of the experimental data over a wide pressure range larger than 100 GPa. Thereby, we can further study the melting curve of MgSiO₃ perovskite at high pressure and high temperature by using the same potentials.

Melting, a mysterious phenomenon in nature, has attracted much attention for a long time, but a general theory for this phase transformation has not been estab-

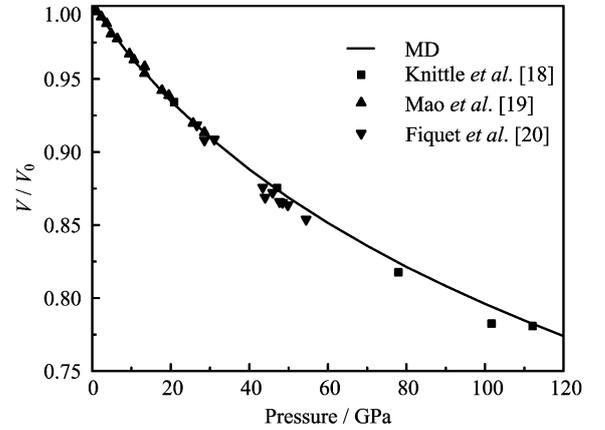


FIG. 1 Pressure-volume relation based on the equations of state of MgSiO₃ perovskite at 300 K. V_0 is the volume at atmosphere pressure. The other data are from Knittle and Jeanloz for $(\text{Mg}_{0.88}\text{Fe}_{0.12})\text{SiO}_3$ perovskite [18], Mao *et al.* for MgSiO₃, $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$, and $(\text{Mg}_{0.8}\text{Fe}_{0.2})\text{SiO}_3$ perovskite [19], and Fiquet *et al.* for MgSiO₃ perovskite. MD values are for MgSiO₃ perovskite [20].

lished. The current studies of the melting of MgSiO₃ perovskite are limited either by the technical problem or by the present state of the theory. To find the melting temperature of MgSiO₃ perovskite is a real challenge. A possible solution is to calculate the temperature of the thermal instability and then estimate the degree of overheating. If one simulated a bulk crystal under periodic boundary conditions, one can find that the crystal will not melt at melting temperature (T_m) with increasing the temperature in a certain range, instead, it will remain the metastable state of the solid state. When the temperature becomes high enough, the crystal will eventually melt. This temperature is called as the thermal instability temperature, also is known as the superheating temperature (T). Calculation of T is a relatively simple task.

It is well known that the MgSiO₃ perovskite melting curve has been studied using a number of methods. Among these methods we choose the one which seems to be the most robust [21]. The first-order melting transition of MgSiO₃ perovskite showed that at certain temperature the mean atom volume underwent a sudden upward jump under different pressures, as marked in Fig.2. The temperature at this jump point is the superheating temperature. 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 overheating. The superheating of a crystalline occurs when the long-range order of the crystalline structure is maintained up to certain temperatures above the equilibrium melting temperature. According to the modern theory of melting, melting temperatures of a crystal can be corrected by certainly melting mechanism [22], corresponding overheating melting of some crystalline solids at atmosphere

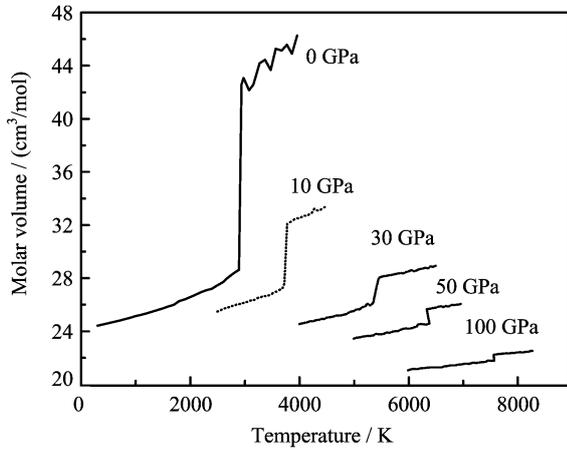


FIG. 2 Volumes of MgSiO₃ perovskite calculated by molecular dynamics at pressures 0, 10, 30, 50, 100 GPa as a function of temperature.

pressure can be concluded as $\theta = T/T_m - 1$, where T_m is the conventional melting temperature for the bulk. This melting process results from temperature increasing rate, and T/T_m is not much dependent on pressure, and will be applied to correct the melting temperatures for overheating of crystal. Luo *et al.* investigated the nucleation energy barrier (β) for elements and compounds [23], and showed that the corresponding overheating (θ) is a function of heating rate (Q). They pointed out that the significant superheating is achievable via ultrafast heating and the degree of superheating can be achieved in shock-wave loading and intense laser irradiation. The Q value of 10^{12} K/s obtained by our molecular dynamics simulations agrees with the established θ - β - Q relation based on the undercooling experiments and the homogeneous nucleation theory. Crystalline solids can be superheated under ultrafast conditions, and the degree of superheating prior to thermal melting is in the range of $(0.1-0.5)T_m$ [23]. The superheating temperature is about 42% higher than the normal equilibrium melting point 2320 ± 100 K at 6.2 GPa. Therefore, we suggest that the superheating temperature of MgSiO₃ perovskite be $0.42T_m$ at the pressure range of the core-mantle boundary. According to this value, we can conclude that the real melting curve of MgSiO₃ perovskite is similar to that shown in Fig.3.

Figure 3 shows that the present melting curve of MgSiO₃ perovskite is in good agreement with the experimental data [7,8]. It is also found that first, the melting curve of MgSiO₃, is very steep at pressures below 60 GPa; then it becomes smooth with increasing pressure. The melting curves fall below the extrapolations of the diamond anvil cell data [7] at high pressures. At 135 GPa, the pressure of the core-mantle boundary, the extrapolations [7] generates the melting temperature higher than 7000 K, while our estimated melting temperature is about 5600 K. The slope of the MgSiO₃

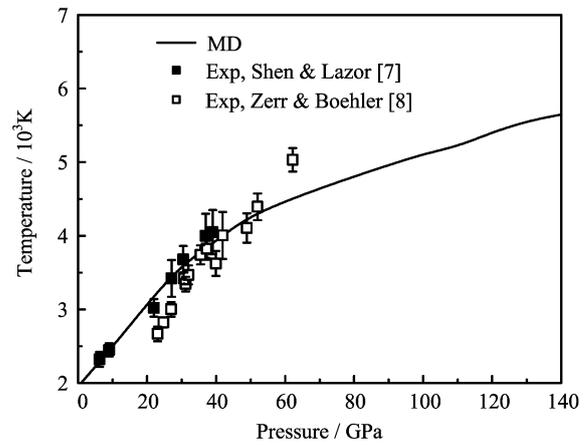


FIG. 3 Melting curve of MgSiO₃ perovskite. The present simulated melting temperatures is indicated by the solid line, the experimental melting data are shown by the solid squares and open squares.

melting curve becomes low at high pressures. A number of theoretical calculations attempted to determine the melting curve of MgSiO₃ up to lower mantle pressure [1,17]. Their calculated results are somewhat scattered, they all predict the temperatures higher than those of the experiments. In the pressure range used in this work the simulated melting curve of MgSiO₃ is higher than the melting curve of iron [24]. Therefore, at the early stage of the Earth's evolution, the Earth is believed to be largely molten, MgSiO₃ will crystallize on cooling first. Since the density of MgSiO₃ at the same pressure is approximately half that of Fe, the MgSiO₃ crystals will float, leading to the fast segregation of the mantle and the core.

IV. CONCLUSION

The predicted melting curve of MgSiO₃ is important for our understanding of the Earth's lower mantle and the history of the Earth's formation. The simulated melting curve of MgSiO₃ perovskite is in good agreement with the recent experimental data. It is found first, that the melting curve of MgSiO₃ perovskite up to lower mantle pressure, is very steep at pressures below 60 GPa; then it becomes smooth with increasing pressure. At the core mantle boundary pressure 135 GPa, the MgSiO₃ perovskite melts at 5600 K, which is significantly lower than that of the extrapolations of the experimental data based on the results of Zerr and Boehler.

V. ACKNOWLEDGEMENTS

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