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Molecular dynamics study for the melting curve of MgO at high pressure*

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Shell-model molecular dynamics method is used to study the melting temperatures of MgO at elevated temperatures and high pressures using interaction potentials. Equations of state for MgO simulated by molecular dynamics are in good agreement with available experimental data. The pressure dependence of the melting curve of MgO has been calculated. The surface melting and superheating are considered in the correction of experimental data and the calculated values, respectively. The results of corrections are compared with those of previous work. The corrected melting temperature of MgO is consistent with corrected experimental measurements. The melting temperature of MgO up to 140GPa is calculated.

Keywords: high pressure, bulk transition, melting temperature, molecular dynamics
PACC: 6470D, 9160, 6185

1. Introduction

The melting temperatures of minerals in the Mg–Fe–Si–O system play a fundamental role in the chemical differentiation, rheology and geodynamics of the Earth's lower mantle. Therefore, the properties of MgO (periclase) at elevated temperatures and pressures are of great interest to the geophysicist. Melting temperature of MgO is crucial to describe the Earth's evolution and melting of solids at high pressures. But the measured [1] and calculated [1−6] melting temperatures of MgO at high pressures, obtained by different research groups, are usually different.

There has been significant progress lately in the experimental determination of the pressure dependence of the melting temperature of MgO using a diamond-anvil cell (DAC) with laser heating.[1] Therefore, a theoretical approach can provide independent information to support experimental determinations. In this paper, we simulate the melting curve of MgO by the method of shell-model molecular dynamics (MD) simulation at constant pressure. Molecular dynamics simulation was used because it allows substantial metastable overheating of perfect crystals without suffering from surface/interfaces as heterogeneous nucleation sites for melting.[7] MD further allows tracking the physical properties of the atoms not only as global averages but also locally. This capability is indispensable for exploration of a correction between the theories and the atomic-level mechanisms at the onset of melting. Because MgO is probably the most extensively studied compound, both experimentally [1] and theoretically,[1−6] we are able to compare our results with previous works.

2.Method

MD simulation is a well-established technique in mineralogy. A description of the molecular dynamics method can be found elsewhere,[8,9] especially for studying the effects of high pressures and elevated temperatures on the properties of solid and theirs melts. In short, the molecular dynamics [10,11] method consists in solving numerically equations of atomic motion, by assuming initial coordinates and veloc-

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ities of atoms and a model of interaction between them. Normally, as is also the case in MD calculations, periodic boundary conditions are applied. Periodic boundary condition means that if a particle leaves a computational cell on one side of the cell, then an identical particle enters the cell from the opposite side.

MD simulation in its classical modification is quite suitable for calculation of the thermoelastic properties of a solid or a melt. However, melting is known to be a complex phenomenon. It 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 used to judge the melting, such as two-phase, bulk transition, radial distribution functions (RDF), snapshot and so on; whereas bulk transition is a rather direct view and convenient for considering defects. The two-phase method [12−14] 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. Overheating of a crystal in MD simulation of melting is a well-known phenomenon.[15,16] Overheating is required for several reasons. First, a nucleus of melt is unstable unless it reaches a certain size,[17,18] 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 excess energy, which can be provided only by increasing 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).[2] Therefore, we believe that bulk transition simulation at constant pressure indeed provides a useful tool for studying the melting transition.

We carried out shell-model MD simulations at high pressures and temperatures using an empirical potential on a system size of 216 atoms. We have chosen interatomic potentials which are given in the following form:

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

where Z_i or Z_j is an effective charge of the ith atom, e is the electronic unit charge, A_{ij} is the magnitude of repulsion force, B_{ij} is the softness parameter, and C_{ij} and D_{ij} are the parameters of dipole–dipole and dipole–quadruple dispersion forces. The first term represents the Coulomb interaction, the second one is due to overlap repulsion. Here r is the interatomic distance between atoms i and j. The parameters of Eq.(1) are given in Ref.[18]. V_0 is volume at ambient temperature and pressure. Figure 1 shows a comparison of our simulated results and the experimental data [19] for MgO. The simulated 300K isotherms are in good agreement with the experimental data [19] up to the pressure of more than 100GPa. Therefore, we conclude that our interatomic potential works well.

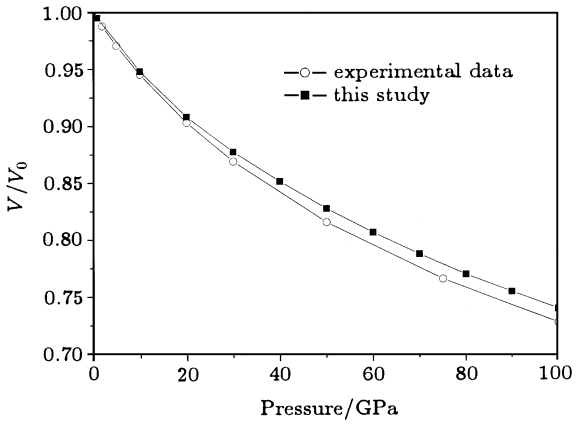


Fig.1. The MD calculated isotherms of MgO at 300K; in comparison with the experimental data.[19] Solid line represents a fit to the MD simulated data for this study.

Simulations in the NTP (constant N: number of particles; T: temperature; and P: pressure) ensemble [20] were performed. The results of shell-model MD simulations in the NTP ensemble with the chosen model of the interatomic interaction depend on, apart from the initial arrangement of particles, the size of time step (Δt), number of particles (N), and temperature of windows (twin). Therefore, the influence of these parameters was carefully studied by carrying out test runs at various temperatures and pressures. It was found that correct results can normally be obtained with Δt=0.001ps, N=216, twin=23. The result might have been affected by the choice of the above parameters, thus we varied them to verify that the final results are stable.

3. Results and discussions

The first-order melting transition manifests itself at 4000K under the pressure of $\sim 10^5$Pa. where the mean atomic volume undergoes a sudden upward jump, as marked in Fig.2. Note that this is higher than normal melting. The reason is that MD simulations in free space are known to exhibit high hysteresis,[3] which prevents us from judging how well the experimental value of melting temperature at 10^5Pa pres-

sure is reproduced. Cohen and Gong [3] noted the high hysteresis at 10^5Pa, which decreases with increasing pressure, and this is also the result of the existence of a substantial metastable overheating. Instable overheating 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. But, according to the modern theory of melting, melting is a dynamic process and melting temperatures of a crystal can be modified by a certain melting mechanism;[21] corresponding overheating melting of MgO at ambient pressure can be concluded as

$$\frac{(T_{\rm m} - T_{\rm mo})}{T_{\rm mo}} = 0.212, \qquad (2)$$

where $T_{\rm mo}$ is the conventional melting temperature for the bulk. This melting process which depends on the temperature increasing rate is hardly dependent on pressure; it will be applied to correct the melting temperatures for overheating of crystals ($T_{\rm m}$ in Eq.(2)) to $T_{\rm mo}$ as a first approximation. Overall, the correction of results from MD simulations performs reasonably well, close to the results of experimental data of corrections at moderate pressures. This suggests that the model might be applied to calculate the melting point of MgO and give us a solid ground for an interpretation of the experimental results.

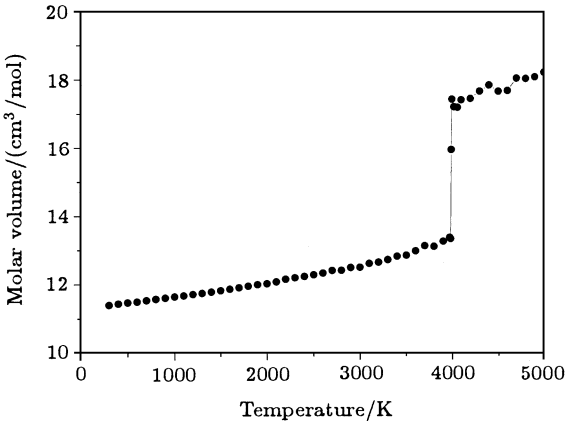


Fig.2. The MD calculated volume of MgO at the pressure of 10^5Pa. The MD calculated points are connected by a solid line for convenience. The volume suddenly changes at a temperature of about 4000K.

The measurement at a pressure $\sim 10^5$Pa and the melting temperature of MgO found in Ref.[22] is 3063±20K. However, the measurement performed outside the diamond cell in air yields a melting temperature $T_{\rm m}$ of 3040±100K.[1] The melting temperature increases with increasing pressure. The melting temperature of MgO up to 31.5GPa is about 4000K, which is considerably lower than all predictions. Moreover, in DAC experiments, the eye-evident surface texture change is usually used as the melting criterion for the melting of samples heated by laser. When a very thin melting layer exists at the sample/DAC interface and the heat balance between this thin layer and the crystal beyond this layer is built, the eye-sighted surface texture is in fact a result of surface melting. In an experiment, large variations might occur, as discussed by Chaplot *et al* [23] due to the sample not being under thermodynamic equilibrium at a uniform temperature and hydrostatic pressure, due to sample history etc. Most of the surface melting temperatures can be related to bulk ones as [24]

$$0.75 < \frac{T_{\rm ms}}{T_{\rm mo}} < 0.90. \qquad (3)$$

As a first approximation, Eq.(3) can be used to correct the melting temperature under static high pressures [$T_{\rm ms}$ in Eq.(3)]] to $T_{\rm mo}$. The corrected melting temperatures of MgO at high pressure are more consistent with each other, as shown in Fig.3. These corrected temperature values (where $T_{\rm mo}$=$T_{\rm ms}$/0.78) is fitted as the melting curve of MgO. Figure 3 compares the calculated pressure dependence of the melting transition of MgO with the corrected experimental results at high pressures. The melting curve of MgO is in agreement with the corrected experimental measurements. Moreover, Fig.3 shows melting temperatures extrapolated to the condition of the core-mantle boundary using MD simulations. For MgO this yields melting temperatures at the bottom of the lower mantle of slightly above 7250K, provided that there are no phase transitions in this pressure range.

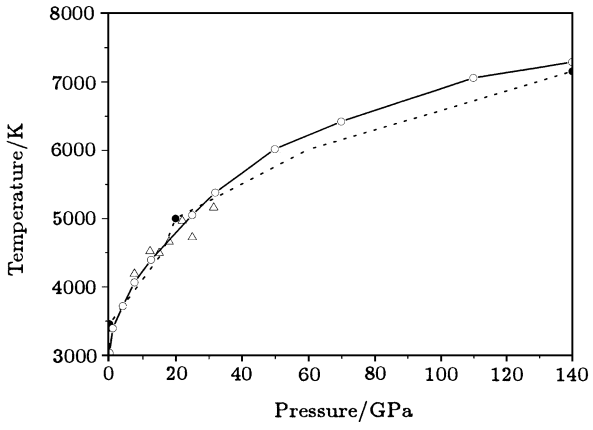


Fig.3. MD simulations of the MgO melting curve. Open circles (○) are from the present study. Open triangles (△) are corrected data of measurements of Zerr *et al.*[1] Solid circles (●) are the theoretical data of MD simulations by Belonoshko *et al.*[2]

4. Conclusions

In summary, our simulated melting temperature of MgO is consistent with corrected values of previously reported experimental results. We extrapolated the melting curves in the lower mantle using MD simulations up to about 7259K at pressure 140GPa. The discrepancy between DAC and MD melting temperatures may be well explained with different melting mechanisms.

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