Molecular dynamics simulation of phase transitions and melting in MgSiO₃ with the perovskite structure

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Abstract

The high pressure phase transitions and melting of the mantle mineral MgSiO₃ with the perovskite structure were investigated using molecular dynamics (MD) simulations of a large system of atoms on a parallel computer. The simulations reveal an orthorhombic to cubic transition accompanied by a sharp increase in diffusion of the O atoms. The phase transition and melting temperature depend sensitively on the level of defects in the solid. At pressures of the Earth's lower mantle, the transition is found to occur at temperatures substantially higher than the mantle temperatures. Therefore, any seismic discontinuity in the lower mantle may not be related to a phase transition of the perovskite structure, but instead may be due to chemical changes at that depth, in contrast to currently accepted mineralogical models assuming chemical homogeneity of the lower mantle.

Introduction

The perovskite with composition $Mg_{1-x}Fe_xSiO_3$, ($x =$ almost 0.1), in the orthorhombic crystal structure is believed to be the principal constituent of the Earth's lower mantle that extends from a depth of 660 km to about 2700 km. The stability of the orthorhombic perovskite structure and its possible phase transitions are therefore of great importance to geophysics. A seismic discontinuity at a depth of 920 km has been reported (Kawakatsu and Niu 1994) that could be due to a phase transition of the perovskite structure or a change in the chemical composition at this depth (Jeanloz and Thompson 1983). X-ray diffraction (XRD) studies reveal that the orthorhombic phase is stable up to high pressures and temperatures (Funamori and Yagi 1993; Knittle and Jeanloz 1987); however, recent synchrotron XRD experiments (Meade et al. 1995) indicate an orthorhombic to cubic phase transition on heating at 70 GPa. There is a continuing debate on the value of the melting temperature of MgSiO₃ perovskite (Brown 1993; Zerr and Boehler 1993) because large variations exist in the data reported from different sources.

It is of considerable importance to provide a theory that addresses the microscopic behavior of the phase stability and melting and the atomic mechanism of these transitions. First-principles MD simulations and total energy calculations (Wentzcovitch et al. 1993, 1995; Stixrude and Cohen 1993; Karki et al. 1997) have been carried out as a function of pressure that predict stability of the orthorhombic phase up to high pressures of 150 GPa. However, these calculations are computationally very intensive and therefore were restricted to zero temperature and systems of only about 100 atoms. Finite temperature sim-

ulations on a large system are needed to predict precisely the changes in the orthorhombic distortion and transition to a tetragonal or a cubic phase because the inherent fluctuations of the characteristics, such as the volume in a constant pressure simulation, of a small system of size N are proportional to $N^{-1/2}$. Previous MD simulation (Matsui and Price 1991; Kaputsa and Guillope 1993) on systems of a few hundred atoms revealed phase transitions from orthorhombic to cubic, pseudocubic, or tetragonal phases, however these involved considerable fluctuations.

Methods

We carried out MD simulations at high temperatures and pressures using empirical potentials on a system size of 12 000 atoms, which allow us to estimate distortions in the crystal-structure parameters of <1 part in 1000. This is quite adequate because the orthorhombic distortion under ambient conditions is about 1 part in 100.

Although one is constrained to use empirical potentials (Rao et al. 1987; Choudhury et al. 1989; Matsui and Price 1991; Kaputsa and Guillope 1993) for simulation of large systems (Chaplot et al. 1986; Allen and Tildesley 1987), there is a need for caution in selecting the potentials. We have chosen an interatomic potential (Ghose et al. 1992) consisting of the long-range Coulomb and short-range repulsive terms that lead to an overall good agreement with a wide variety of known structural and thermodynamical properties. The results on the crystal structure and the equation of state are in good agreement with experimental data, and also with recent results (Wentzcovitch et al. 1995) calculated by first-principles local density approximation (LDA) technique up to 150 GPa (Fig. 1). The model also predicts fairly well the lattice dynamics over the entire range of the vibrational spectrum as revealed

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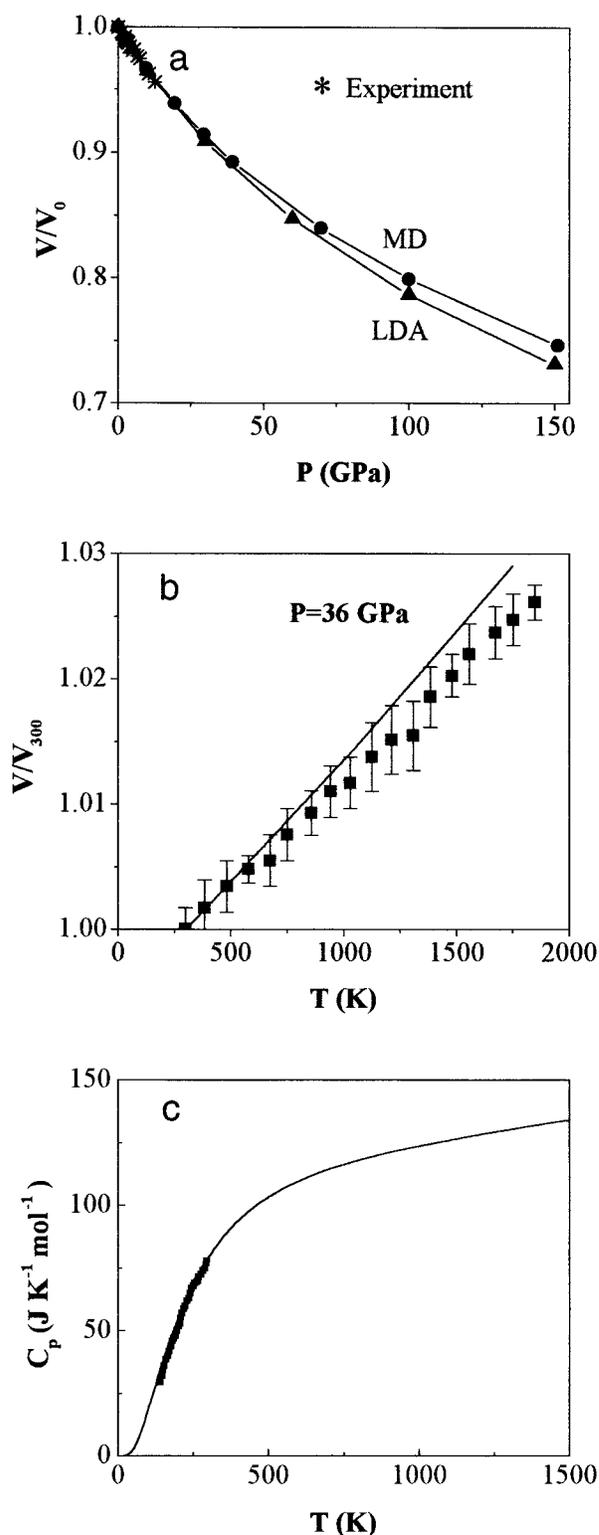
FIGURE 1. (**a**) The equation of state at $T = 300$ K as observed in the MD simulation, which shows a good agreement with the experimental data (Mao et al. 1991) and results from the first-principles simulation at $T = 0$ K based on the LDA (Wentzcovitch et al. 1993). (**b**) The simulated thermal expansion at 36 GPa (full line) and its comparison with the high pressure-temperature experimental data (squares) of Funamori and Yagi (1993). At 36 GPa and $T = 300$ K, the calculated and experimental volumes are, respectively, 147.70 and 145.55 Å^3. (**c**) The specific heat at ambient pressure as calculated from the present model (line) showing an excellent agreement with the experimental data (squares from Akaogi et al. 1993). Because the present theory is able to reproduce the above thermodynamical experimental data very satisfactorily, we may have confidence in using the theory in making predictions at high pressures and temperatures where experimental data are not yet available.
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from the excellent description of the specific heat (Fig. 1c), which has very important implications in the prediction of the high temperature thermodynamical properties. Our calculations (unpublished) of the Raman and infrared modes are also found to be in satisfactory agreement with experiments (Lu et al. 1994; Durben and Wolf 1992).

The MD simulations have been performed as a function of P and T using a computer program developed by one of us and previously used for the simulation of pressure-induced amorphization of quartz and other materials (Chaplot and Sikka 1993), and the simulation of order-disorder transitions in high-temperature superconducting oxides (Chaplot 1990) and fullerene (Pintschovius et al. 1995). The MD program has been adapted on the parallel computer ANUPAM developed at Bhabha Atomic Research Center, which has up to 64 nodes. A typical simulation of a system of 12 000 atoms interacting by long range forces for 40 000 time steps performed on a 32-node system needed about one week of CPU time, which adds up to several months for the work reported here. Simulation time steps of 1 and 2 fs are used to cross check the results. Besides the average structure, we have monitored the mean square displacements of atoms, diffusion, pair correlation functions, and the vibrational spectra.

Results

The simulation under ambient conditions of pressure ($P = 0.1$ MPa) and temperature ($T = 300$ K) reproduces the orthorhombic phase (space group *Pnma*, calculated $a = 4.931$ Å, $b = 6.914$ Å, $c = 4.810$ Å; experimental (Mao et al. 1991) $a = 4.930$ Å, $b = 6.898$ Å, $c = 4.778$ Å). At $P = 0.1$ MPa and $T = 2300$ K, we observe a phase transition of the system to a tetragonal phase with $a/c = 1.021$ (Fig. 2). Calculations at higher temperature indicate complete melting at 2600 K. At a higher pressure of 40 GPa, the tetragonal transition occurs at a higher temperature of 4600 K with a smaller $a/c = 1.005$. However, with a further small increase of temperature, the tetragonal distortion becomes negligible. We therefore
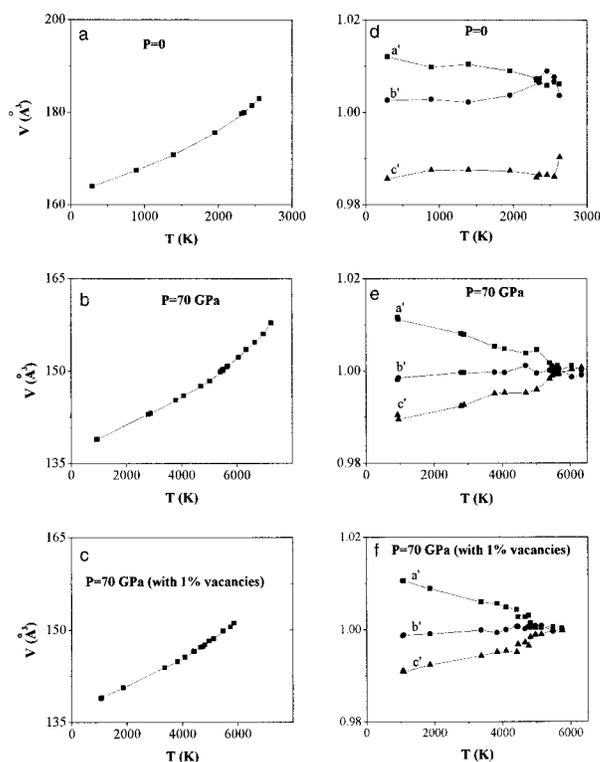
FIGURE 2. Results of the molecular dynamics simulation of the phase transition from the orthorhombic to tetragonal or cubic forms of perovskite in **a–f**. The volume and normalized pseudocubic lattice parameters [$a' = a/V^{1/3}, b' = b/(2^{1/2}V^{1/3})$ and $c' = c/V^{1/3}$] are shown as a function of temperature at $P = 0$ and 70 GPa. Compared to the perfect lattice system, the system with 1% vacancies shows a significantly lower transition temperature.

FIGURE 3. The variation of the calculated diffusion coefficient of various atoms with temperature in the MD simulations at 70 GPa indicating partial melting (diffusion) of the O sublattices accompanying the orthorhombic to cubic phase transition in perovskite and the full melting on further heating. (**a**) defect-free initial system. (**b**) 1% vacancies.

consider the transformation as from orthorhombic to the cubic symmetry. The transition temperature further increases to 5400 K at 70 GPa (Fig. 2) and to 6000 K at 135 GPa. We thus observe that the orthorhombic to tetragonal transition temperature increases with pressure. The tetragonal distortion after the transition is significantly lower with increasing pressure so that at high pressures, the transition practically occurs to a cubic phase at a typical resolution of 1 part in 1000 as in usual diffraction experiments. The transition does not accompany any significant volume change and therefore may be described as only a weakly first-order transition.

The phase transition temperatures observed in the above simulations on perfect systems appear to be rather high compared to those observed in experiments (Meade et al. 1995). We therefore carried out further simulations incorporating disorder and lattice defects. Perovskite, in the lower mantle, is expected to have about 10% of Mg atoms replaced by Fe atoms. In our simulation we introduced this substitutional disorder. The simulated transition behavior is rather insensitive to the substitutional disorder up to 50%. We then considered whether possible defects in the lattice might have a significant influence.

A certain amount of defects would naturally exist at any finite temperature at equilibrium. We estimate from defect energies that about 1% vacancy defects may exist at 5000 K at 70 GPa in the perovskite. However, in MD simulation starting with a perfect lattice, defects are not easily created in a short time of only a few ps. We therefore introduced defects in the form of vacancies in the starting system itself. In order to maintain the charge neutrality of the system as a whole, equal number of defects were introduced in all the ionic sublattices.

As the simulation proceeded, the system equilibrated with relaxation of atoms around the vacancies and a lower average cell volume compared to the perfect lattice. A small amount of vacancy diffusion was also observed that increased with temperature. With 1% vacancies, the transition temperature is significantly lower (by as much as
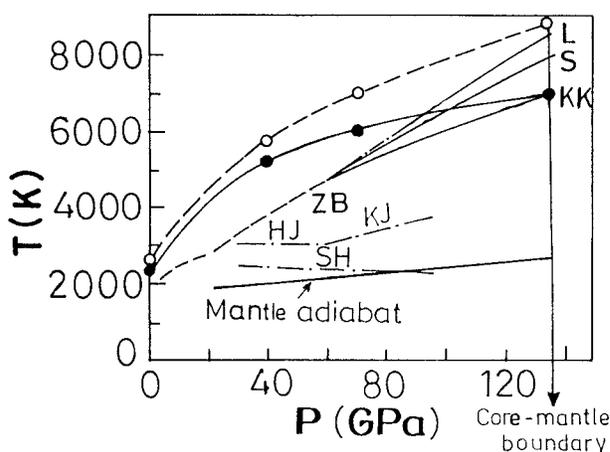
Figure 4. The simulated melting temperature as a function of pressure. The melting temperatures are significantly lower for the system with 1% vacancies (filled circles) than that for the perfect lattice system (open circles). Comparison is made with the experimental data (ZB = Zerr and Boehler 1993) up to 62.5 GPa and its extrapolations (L, S, and KK) to higher pressures using different melting relations as reported in ZB and also with earlier laser heating experiments [HZ = Heinz and Jeanloz 1987; KJ = Knittle and Jeanloz 1989; SH = Sweeney and Heinz 1993 (SH indicates a lower bound only)]. The data below 25 GPa are from Ito and Katsura (1992) and Kato and Kumazawa (1985). The various experimental data and the differences among them have been discussed by Brown (1993). In a perovskite sample at equilibrium, about 1% vacancy defects are estimated to occur at 5000 K and 70 GPa. Real samples at high temperature and pressure are likely to have a high defect level depending on the sample history. The agreement between the simulated and the observed melting temperatures is therefore considered satisfactory although the shape of the curve is somewhat different. [Part of the figure has been adapted from Zerr and Boehler (1993)].

15%) than that of the perfect lattice system (Fig. 2). In a real sample, depending on its history, the defect concentration may be even more and that would at least partly account for the smaller observed transition temperatures at high pressures. The effect is much less dramatic at ambient pressure.

An interesting property of the orthorhombic to cubic transition as observed in the MD simulation is that it is accompanied by melting of the O sublattices (Fig. 3). The cubic phase is thus a superionic conductor in which certain ions have an almost liquid-like diffusion in a rigid framework provided by other species of ions. Fairly large electrical conductivity in the lower mantle has been reported that increases continuously as a function of depth by several orders of magnitude (Peyronneau and Poirier 1989). It has been suggested (Keeffe and Bovin 1979) that the conductivity is ionic rather than electronic and that MgSiO$_3$ perovskite may behave as a superionic conductor in the lower mantle. Our MD simulations do not appear to support this suggestion because the insulator to superionic conductor phase transition at mantle pressures is predicted at temperatures much above the mantle tem-

peratures. Further heating of the superionic conducting phase led to the melting of all the sublattices.

The melting temperature in MD simulation may be somewhat higher than those in experiments because overheating may be required to achieve melting at the small time scale of 100 ps in the simulation. Our observed melting temperature in simulation at 70 GPa was about 7000 K in the perfect lattice but is significantly lower, 5800 K, in the system with only 1% vacancy defects. Because real samples may have a larger and varying concentration of defects, our simulated melting temperature compares very well with the observed values (Zerr and Boehler 1993) in the range of 5000 K at 62.5 GPa (Fig. 4).

In summary, whereas our MD simulations reproduce the stability of the orthorhombic perovskite phase up to high pressures of 150 GPa at ambient temperature consistent with the predictions of first-principles calculations, we also observe its transformation to the cubic phase (Meade et al. 1995) and melting (Zerr and Boehler 1993) at high pressures and high temperatures in agreement with recent experiments. The simulations further provide a microscopic understanding of the nature of the phase transitions involving partial and total melting, and the important influence of lattice defects on the transition temperatures. At lower mantle pressures, the transitions are found to occur at temperatures substantially higher than the mantle temperatures. Therefore, it would appear that the 920 km seismic discontinuity (Kawakatsu and Niu 1994) may not be related to any phase transition of the perovskite structure. This strengthens the suggestion of possible chemical changes (Kawakatsu and Niu 1994; Saxena et al. 1996) at that depth, which would have far reaching consequences as it is in contrast to currently accepted mineralogical models assuming chemical homogeneity of the lower mantle.

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