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Properties of MgO at high pressures: Shell-model molecular dynamics simulation

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Abstract

Shell-model molecular dynamics (MD) simulation has been performed to investigate the melting of the major Earth-forming mineral: periclase (MgO), at elevated temperatures and high pressures, based on the thermal instability analysis. The interatomic potential is taken to be the sum of pair-wise additive Coulomb, van der Waals attraction, and repulsive interactions. The MD simulation with selected Lewis–Catlow (LC) potential parameters is found to be very successful in describing the melting behavior for MgO, by taking account of the overheating of a crystalline solid at ambient pressure. The thermodynamic melting curve is estimated on the basis of the thermal instability MD simulations and compared with the available experimental data and other theoretical results in the pressure ranges 0–150 GPa. Our simulated melting curve of MgO is consistent with results obtained from Lindemann melting equation and two-phase simulated data at constant pressure by Belonoshko and Dubrovinsky, in the pressure below 20 GPa. The extrapolated melting temperatures in the lower mantle are in good agreement with the results obtained from Wang's empirical model up to 100 GPa. Compared with experimental measurements, our results are substantially higher than that determined by Zerr and Boehler, and the discrepancy between DAC and MD melting temperatures may be well explained with different melting mechanisms. Meanwhile, the radial distribution functions (RDFs) of Mg–Mg, O–Mg, and O–O ion pairs near the melting temperature have been investigated.

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Keywords: MgO; Melting; Thermal instability; Radial distribution function; Molecular dynamics simulation

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1. Introduction

The melting mechanism of solids has attracted the attention of researchers both theoretically and experimentally [1,2]. Of the known first-order phase transitions, melting covers the widest range of pressures and temperatures. Consequently, melting data provide a potentially rich source of information regarding the role played by interatomic forces in determining pressure-induced and temperature-induced changes in solids and liquids. Recent advances, particularly the development of high-temperature diamond anvil cell (DAC) techniques, have led to an order of magnitude increase in the pressure range accessible for study [3,4]. Much of this effort has been motivated by a need for melting data of oxides and silicates for the purpose of understanding the structure and dynamics of the Earth's interior. On the other hand, the determination of the melting curves of materials to very high pressures is of fundamental importance to our understanding of the properties of planetary interiors. However, obtaining such melting curves remains a major challenge to experimentalists and theorists alike. The difficulties in experimental measurement greatly limit the generation of melting data, resulting in a poor understanding of the melting mechanism of solids under high pressures. As for theoretical investigation, molecular dynamics (MD) has been used as a powerful tool to simulate the melting of solids [5]. MD simulation was used because it allows substantial metastable overheating of perfect crystals without suffering from surface or interfaces as heterogeneous nucleation sites for melting [6]. 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 mechanism at the onset of melting.

As a first-order phase transition, melting exhibits discontinuities in the first derivatives of free energy, volume, and entropy. The changes of these physical properties are often used for identification of melting at high pressure, and the temperature at which this happens in a MD simulation is invariably higher than the melting temperature. In fact, the melting point is by definition the temperature at which the solid and the liquid phase coexist (they have the same free energy). However, lacking a liquid seed from where the liquid could nucleate and grow, overheating above melting commonly occurs. In this region the system is in a thermodynamically metastable state; nevertheless, it appears stable within the simulation time. An overheated bulk crystal breaks down when its mechanical instability point is reached. This point may correspond to the vanishing of one of the shear moduli of the material or to similar instabilities, and is typically larger than the conventional melting temperature for the bulk by an amount of the order of 20–30% [7]. Jin et al. [8] examined the validity of the Born criterion with MD simulations. They found that the idealized crystal could be superheated by about 20% (in terms of absolute temperatures); melting occurred when the elastic shear modulus of the crystal lattice came very close to zero. Mechanical melting was identified by a sudden change in the atomic volume.

MgO with the NaCl-type cubic structure has been extensively studied at high pressure because of its simplicity in structure and its geophysical importance. It is an important component of the Earth's lower mantle (660–2890 km depth) existing as magnesiowüstite, (Mg,Fe)O, and its stability up to high pressures makes it useful as a pressure calibration standard for high pressure and temperature experiments [9]. Pressure dependence of the melting temperature of minerals forming the Earth's mantle is necessary to describe the timing and sequence of crystallization from the protomelt [10]. Because MgO is believed to be one of the major constituents of the Earth's mantle, the attention that MgO receives is quite understandable. A large amount of previous theoretical work has been done on MgO, and there are well-established interaction models. The most realistic ones include electronic polarizability of the ions through the shell-model [11], and this is essential if the phonon frequencies of the crystal are to be well reproduced. MD simulations of high-temperature MgO using the less realistic, but simpler, rigid-ion representation have already been reported [12]. Shell-model MD simulation has been used