The MD simulation of the equation of state of MgO: Application as a pressure calibration standard at high temperature and high pressure

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ABSTRACT

Molecular dynamics (MD) simulation is used to calculate the elastic constants and their temperature and pressure derivatives, and the T-P-V equation of state of MgO. The interionic potential is taken to be the sum of pairwise additive Coulomb, van der Waals attraction, and repulsive interactions. In addition, to account for the observed large Cauchy violation of the elastic constants of MgO, the breathing shell model (BSM) is introduced in MD simulation, in which the repulsive radii of O ions are allowed to deform isotropically under the effects of other ions in the crystal. Quantum correction to the MD pressure is made using the Wigner-Kirkwood expansion of the free energy. Required energy parameters, including oxygen breathing parameters, were derived empirically to reproduce the observed molar volume and elastic constants of MgO, and their measured temperature and pressure derivatives as accurately as possible. The MD simulation with BSM is found to be very successful in reproducing accurately the measured molar volumes and individual elastic constants of MgO over a wide temperature and pressure range. The errors in the simulated molar volumes are within 0.3% over the temperature range between 300 and 3000 K at 0 GPa, and within 0.1% over the pressure range from 0 up to 50 GPa at 300 K. The simulated bulk modulus is found to be correct to within 0.7% between 300 and 1800 K at 0 GPa. Here we present the MD simulated T-P-V equation of state of MgO as an accurate internal pressure calibration standard at high temperatures and high pressures.

INTRODUCTION

In high temperature and high pressure X-ray diffraction experiments, known equations of state of standard materials, such as NaCl (Decker 1971), or the ruby-fluorescence pressure scale (Mao et al. 1986) are usually used to measure the pressure of the system. However, there are some problems inherent in these pressure calibration methods, as cited previously (Jamieson et al. 1982; Heinz and Jeanloz 1984). Namely, NaCl transforms from the B1 to the B2 structure at about 27 GPa and 300 K, and at about 21 GPa and 1000 K (e.g., Li and Jeanloz 1987), and the ruby pressure scale is unsuitable at high temperatures due to the broadening of the ruby R lines, as well as the decreasing of their intensity (Wunder and Schoen 1981).

The equation of state (EOS) of Au, proposed by Anderson et al. (1989), has recently been widely used to estimate pressure at high temperatures (e.g., Mao et al. 1991; Fei et al. 1992; Meng et al. 1994; Funamori et al. 1996; Irfune et al. 1998). However, Anderson et al. (1989) derived the EOS of Au based on the measured elastic and thermodynamic properties of Au at temperatures less than 550 K, where the contribution from the thermal energy due to excited conduction electrons is expected to be very small. Thus their EOS of Au underestimates the pressure especially at high temperatures where the electronic thermal pressure becomes significant. We note, in the case of Fe as a metal for example, the thermal pressure of electrons is estimated to be only 0.2 GPa at 600 K, but it increases to 1 GPa at 1400 K, and reaches 2 GPa at 2000 K, with the pressure values being only weakly dependent on volume, according to the band structure calculations by Bukowinski (1977) and Boness et al. (1986).

Jamieson et al. (1982) have presented the EOS of MgO as an alternate pressure scale at high temperatures. However, their proposed EOS for MgO contains errors resulting from the inaccuracy of key physical properties used in their model, including the bulk modulus and its pressure dependence, and the Grüneisen parameter and its volume dependence. In addition, Jamieson and coworkers derived the EOS based on the harmonic Debye model which results in significant errors at high temperatures where the anharmonic contribution to the thermal energy is important.

Previously (Matsui et al. 1994), we have shown that by combining the molecular dynamics (MD) method with quantum corrections to the MD values, it is possible to simulate accurately the structural and thermodynamic properties of crystals over a wide temperature and pressure range. The exception is at very low temperatures where quantum effects are dominant. This paper shows how accurately the MD simula-

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