Vol 18 No 11, November 2009
1674-1056/2009/18(11)/5001-07

Chinese Physics B

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Effect of pressure on the thermal expansion of MgO up to 200 GPa*

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(Received 14 February 2009; revised manuscript received 4 May 2009)

Constant temperature and pressure molecular dynamics (MD) simulations are performed to investigate the thermal expansivity of MgO at high pressure, by using effective pair-wise potentials which consist of Coulomb, dispersion, and repulsion interactions that include polarization effects through the shell model (SM). In order to take into account non-central forces in crystals, the breathing shell model (BSM) is also introduced into the MD simulation. We present a comparison between the volume thermal expansion coefficient α dependences of pressure P at 300 and 2000 K that are obtained from the SM and BSM potentials and those derived from other experimental and theoretical methods in the case of MgO. Compared with the results obtained by using the SM potentials, the MD results obtained by using BSM potentials are more compressible. In an extended pressure and temperature range, the α value is also predicted. The properties of MgO in a pressure range of 0–200 GPa at temperatures up to 3500 K are summarized.

Keywords: molecular dynamics simulation, volume thermal expansion coefficient, MgO, high pressure

PACC: 7115Q, 6740K, 6570, 6250

1. Introduction

MgO with NaCl-type structure has been extensively investigated over the past three decades. On the one hand, MgO is structurally simple and therefore suitable for detailed experimental and theoretical studies.[1,2] On the other hand, it represents an end member of magnesiowüstite, (Mg, Fe)O, an important constituent of the Earth's lower mantle whose thermal and elastic properties are crucial to developing accurate mineralogical and compositional models of the Earth's interior.[3] Furthermore, its stability over a wide range of pressures and temperatures has prompted its use as an internal pressure standard in high-pressure and temperature x-ray diffraction experiments.[4]

A number of static, ultrasonic, and shock compression experiments and theoretical methods have been previously conducted to determine the thermal expansitivity of MgO. The effect of pressure on the thermal expansitivity of MgO, however, has been less emphasized in previous investigations, even though such an effect can be derived from currently available volume measurements at high pressures. Thermal expansivity is a very important parametric quantity for interpreting the thermodynamic and the thermoelastic behaviours of solids at high temperatures because it has been emphasized that most of the serious errors in calculations of thermodynamic functions arise due to the uncertainty of thermal expansivity at high temperatures.[5] The coefficient of volume thermal expansion $\alpha_{\rm P}$ is defined as

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \tag{1}$$

where V is the specific volume, T is the temperature, and P is the pressure. It is well known that α_P enters into many formulas for the thermodynamical coefficients. At present great attention is paid to investigations of α_P at high pressures and high temperatures. It is, therefore, desirable to develop a model

*Project supported by the National Natural Science Foundation of China (Grant Nos 10674120 and 10774121), the 'Qing Lan' Talent Engineering Funds by Lanzhou Jiaotong University of China (Grant No QL-06-22A), and the Research Foundation from Ministry of Education of China (Grant No 209127).

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for evaluating and predicting thermal expansivity at high temperatures. Various attempts have been made to study the temperature dependence of thermal expansivity by considering its linear dependence as well as its non-linear dependence.[6−8] We believe that the application of molecular dynamics (MD) tools to the calculation of thermal expansivity properties is a viable strategy for obtaining some of the available information. MD is a technique that enables us to use the description of interatomic interactions to predict the physical properties of matter. The advantage of the computational approach is that it can provide a much clear atomic and electronic picture of the materials and their influence on the structures, properties, synthesis and performances. Empirical interatomic potentials for oxides, like MgO, have been applied to dynamic treatments, such as the MD method of simulating complex systems with a large number of atoms, where the application of the first-principles method is currently limited by the large computational effort.

In the polarizable-ion model developed by Wilson and Madden,[9] polarization effects in classical MD simulations of ionic systems are accurately represented by the inclusion of ion dipoles as additional degrees of freedom in an extended Lagrangian, and the simultaneous propagation of these additional variables together with the ionic positions is analogous to the Car–Parrinello method. Another simple and consistent way to go beyond rigid-ion models and to approximately include polarization effects in an empirical potential is the shell model (SM) given by Dick and Overhauser[10] which can be efficiently implemented in classical MD simulations.[11] In this work, constant temperature and pressure MD simulations were performed to investigate the thermal expansivity of MgO at high pressures using a potential that is very similar to the Lewis–Catlow (LC)[12] and Stoneham–Sangster (SS)[13] potentials which consist of the Coulomb, dispersion, and repulsion interactions that include polarization effects through the SM. For centrosymmetric cubic crystals at zero stress, the calculated elastic constants, based on simple pair-wise additive rigid-ion models, must obey the Cauchy relation $C_{12} = C_{44}$.[14] However, for MgO with a centrosymmetric cubic NaCl-type structure, the measured elastic constants deviate severely from this relation.[15] In order to account for the observed large departures from the Cauchy relation of the elastic constants of the MgO, the breathing shell model (BSM) is also introduced into the MD simulation, in which the repulsive radii of oxygen ions are allowed to deform isotropically under the effects of other ions in the crystal, with each core and breathing shell linked by a harmonic spring with force constant k.

The rest of the present paper is organized in the following way. In Section 2, we describe the interatomic potential model and some details of the simulation method. In Section 3, we present the test calculations, i.e. the dependences of volume thermal expansion coefficient α of MgO on pressure at 300 and 2000 K, in order to demonstrate that our potential is transferable. The reliable potential model is solid ground for prediction of the properties of MgO at extreme $P - T$ conditions where experimental data are scarce. Finally, in Section 4, we summarize the main conclusions.

2. Potential model and simulation method

Molecular dynamics is a technique that enables us to use the description of interatomic interactions, given in the previous section, to predict the physical properties of matters. The essence of MD calculations is to solve Newton laws of motion over a finite time period for a simulation box containing N ions, calculating the dynamic properties iteratively as the system evolves. Normally, a periodic boundary condition applied to the ensemble generates a required infinite system. The ions have initially assigned positions and velocities within the simulation box; their initial coordinates are usually chosen to be at the crystallographically determined sites, whilst their velocities, v_i, are chosen such that they concur at a temperature of the required system and both energy and momentum are conserved as well, i.e.

$$\sum_i m_i v_i(0) = 0, \tag{2}$$

$$\sum_i m_i [v_i(0)]^2 = 3Nk_{\mathrm{B}}T, \tag{3}$$

where m_i is the atomic masses, k_{B} is the Boltzmann constant and T is the chosen initial simulation temperature.

In order to calculate subsequent positions and velocities, the forces acting on any individual ion must be calculated from the first derivative of the potential function, and the new position and velocity of each ion may then be calculated at each timestep by solving the Newton equation of motion:

$$F_i = -\frac{\partial U}{\partial r_i} = m_i a_i(t) = m_i \frac{\mathrm{d}^2 r_i}{\mathrm{d}t^2}, \tag{4}$$

where the terms have their usual meanings. Equation (4) may be numerically integrated to generate a set of positions, $r_i(t+\Delta t)$, and velocities, $v_i(t+\Delta t)$, as the system evolves. For an infinitesimally small timestep the updating equations are

$$r_i(t+\Delta t) = r_i(t) + v_i(t)\Delta t, \tag{5}$$

$$v_i(t+\Delta t) = v_i(t) + \frac{F_i(t)}{m_1}\Delta t. \tag{6}$$

For a finite timestep, the above equations lose their accuracy and higher powers of Δt are required; in our calculations the equations of motion are solved by using the Gear predictor corrector algorithm, therefore a fourth order Taylor series expansion of the displacements with respect to time generates predicted evolving positions which are then corrected iteratively until a convergent solution to the trajectories and velocities is obtained.[16]

The instantaneous temperatures are calculated at each timestep for a system of N particles from the equation and expressed as

$$T = \frac{2}{3Nk_\mathrm{B}} E_\mathrm{kin}, \tag{7}$$

where

$$E_\mathrm{kin} = \frac{1}{2}\sum_{i=1}^{N} m_i v_i^2. \tag{8}$$

The pressure of the simulated system is calculated from the Virial Theorem to be

$$P = \frac{Nk_\mathrm{B}T}{V} - \frac{Nk_\mathrm{B}T}{6V}\left(\sum_{i=1}^{N}\sum_{j>1}^{N} r_{ij}\frac{\partial \psi_{ij}}{\partial r_{ij}}\right), \tag{9}$$

where N is the number of particles within the system, V is the volume, r_{ij} is the distance between ions i and j, $\dfrac{\partial \psi_{ij}}{\partial r_{ij}}$ is the first derivative of the potential energy of ion i with respect to ion j, and k_B is the Boltzmann constant.

Conventional MD involves a purely classical simulation, though the work of Matsui included quantum corrections to order h^2.[17] However, in this model the ionic polarizability was not included, thereby radically affecting many properties, particularly vibrational frequencies. The dipolar SM[18] opens the way for the study of ionic materials without the limitations imposed by the use of either the rigid-ion model or the quasi-harmonic approximation. Here the polarizability of the oxygen ions is incorporated through the SM: the total charge Z of the ion is distributed between a core (of charge $Z-Y$) and a shell (of charge Y), which are coupled by a harmonic spring k_cs,

$$E_\mathrm{cs}(r) = \frac{1}{2}k_\mathrm{cs}r^2. \tag{10}$$

Short-range forces only act on the shells, whereas Coulomb forces act on both shells and cores. The shells are then polarized by the field of the surrounding ions and in this way the local environment of each ion affects its charge distribution: with the further inclusion of three-body interactions, partial covalence effects are approximately accounted for.

In the 'ideal' SM the shells are regarded as being massless and relax instantaneously to minimum energy (zero force) positions. In our MD procedure the adiabatic shell method is used.[11] In this approach, a small fraction of the core mass is assigned to the shells, and their motion, controlled by conventional equations of motion, follows the ionic motion adiabatically. Starting from a configuration where all the shells have been relaxed, with no vibrational energy in the core–shell springs, the small mass allows shells to respond quickly to the changing environment so that (almost) no net force acts on them: this is a necessary condition in order to accurately calculate the forces on the ion cores. Ideally, due to the low shell mass, no energy exchange between the core–shell spring and the other degrees of freedom should occur as the frequency of the spring is well above the ionic frequencies. If ions are polarizable they may also be made compressible by means of the BSM.

In the present study, we use the very similar SM potentials of LC[12] and SS.[13] The interatomic potentials have the usual form as shown in Ref.[19] and in both cases $A_{++} = C_{++} = C_{+-} = 0$, $A_{--} = 22764.4$ eV, $\rho_{--} = 0.1490$ Å and $C_{--} = 20.37$ eV·Å^6. The potential models differ in Mg–O interaction, the SS has $A_{+-} = 1346.6$ eV and $\rho_{+-} = 0.2984$ Å, while LC has $A_{+-} = 821.6$ eV and $\rho_{+-} = 0.3242$ Å. In both models the Mg^{2+} ion is non-polarizable, but the shell charge Y and spring constant k for the O^{2-} ion differ between the two models. In the SS potential, $Y = -2.9345e$ and $k = 51.71$ eV·Å^{-2}, while in the LC

potential $Y = 2.0000e$ and $k = 15.74$ eV·Å^{-2}. This leads the LC model to have a larger polarizability than the SS model. The potential models that are used here reproduce the *ab initio* static equation of state calculations given by Isaak *et al*,[20] and the experimental data were summarized by Knittle.[21] Fincham *et al*[22] studied the $P-V-T$ relations for MgO at high pressures and temperatures, and the obtained results were compared with those of other studies, and they were in agreement with each other. In order to take into account non-central forces in crystals, the BSM is also introduced into the MD simulation. The pair-wise interactions are still represented by the combination of the Coulomb energy, repulsive exponential and attractive dispersion terms. The main change is related to the description of the oxygen polarization. In the BSM, the ion shell has a finite radius, R_0, which is allowed to deform isotropically under the influence of the other ions. Here, the ion size is coupled to the environment through the short-range repulsive potential acting on the radius of the shell, rather than on its centre. The contribution to the energy from each core–shell pair $V_i = k_i r_i^2/2$ in SM is still valid to treat the core–shell dipolar contribution, but an additional potential, which has been chosen to be harmonic, describes the breathing shell:

$$V_i = \frac{1}{2} K_i (R_i - R_0)^2, \tag{11}$$

where K_i is the spring constant and $(R_i - R_0)$ is the distance from the finite shell radius of the ion i. The most significant consequence of the introduction of a BSM is that introducing non-central forces can reproduce the Cauchy violation ($C_{44} \neq C_{12}$).

All of the simulations are performed in an NPT (constant N is the number of particles, T is the temperature, and P is pressure) ensemble in conjunction with a Nose–Hoover[23] thermostat and the Parrinello–Rahman[24] constant pressure algorithm. Simulation runs are carried out with 512 particles (256 Mg^{2+} and 256 O^{2-} ions) initially arranged in the NaCl-type crystal structure, which is sufficient for high accuracy of results.[19] The system is allowed to evolve for 10 picoseconds, the first 5 picoseconds of which are used for equilibration but not included in the calculation of thermodynamic averages. A timestep of 1.0 fs is used for integrating equations of motion. Coulombic interaction is calculated by using the Ewald method.[25]

3. Results and discussion

Figure 1 shows a comparison of the thermal expansivities of MgO obtained with SM- and BSM-MD simulations versus pressure, with the available experimental data and the latest theoretical results[1,4,26–29] at 300 K. Our calculations of the volume thermal expansion coefficients by using the SM-LC, SM-SS, BSM potentials at 300 K are 2.487×10^{-5}, 2.533×10^{-5}, 2.746×10^{-5} K^{-1}, respectively. The data are close to the value 3.12×10^{-5} K^{-1} of Anderson's x-ray diffraction experiment.[1] Isobaric volume measurements for MgO were carried out by Zhang at 2.6, 5.4, and 8.2 GPa in the temperature range 300–1073 K using a DIA-type, large-volume apparatus in conjunction with synchrotron x-ray powder diffraction.[4] Linear fitting to the thermal expansion data over the experimental pressure range yields the pressure derivative, $(\partial\alpha/\partial P)_T$, of $-1.04(6) \times 10^{-6}$ GPa$^{-1}\cdot$ K^{-1} and the mean zero-pressure thermal expansion $\alpha_{0,T} = 4.09(4) \times 10^{-5}$ K^{-1}. The $\alpha_{0,T}$ value is in good agreement with results of Suzuki[26] and Utsumi *et al*[27] over the same temperature range, whereas $(\partial\alpha/\partial P)_T$ is determined for the first time on MgO by direct measurements. The unit-cell volumes measured under various pressure and temperature conditions are obtained by Zhang,[4] and these data show that thermal expansivity of MgO, as expected, decreases with increasing pressure. At each pressure, the thermal expansion coefficient, $\alpha_{P,T}$, is obtained from the relation

$$V_{P,T} = V_{P,300} \exp \int \alpha_{P,T} \mathrm{d}T, \tag{12}$$

where $V_{P,300}$ and $V_{P,T}$ are the unit-cell volumes at room and high temperatures, respectively, for a given pressure. Zhang has given two different approaches to analyse the data: $\alpha_{P,T}$ in expression (12) is treated as a constant, representing an average thermal expansion over the range 300–1073 K; and $\alpha_{P,T}$ is considered to be temperature-dependent, in the form of $\alpha_{P,T} = \alpha_1 + \alpha_2 T$, with α_1 and α_2 being constants. In both approaches, $V_{P,300}$ in expression (12) is regarded as a fitting parameter. Results of the least-square fit are given in Fig.1. Our simulations are in good agreement with both the results of Zhang in which $\alpha_{P,T}$ was considered to be temperature-dependent[4] and the calculations from Sushil's equation of state.[28] Meanwhile, the results calculated by using the BSM potential are in excellent agreement with the data obtained from Zharkov's data[29] under high pressures.

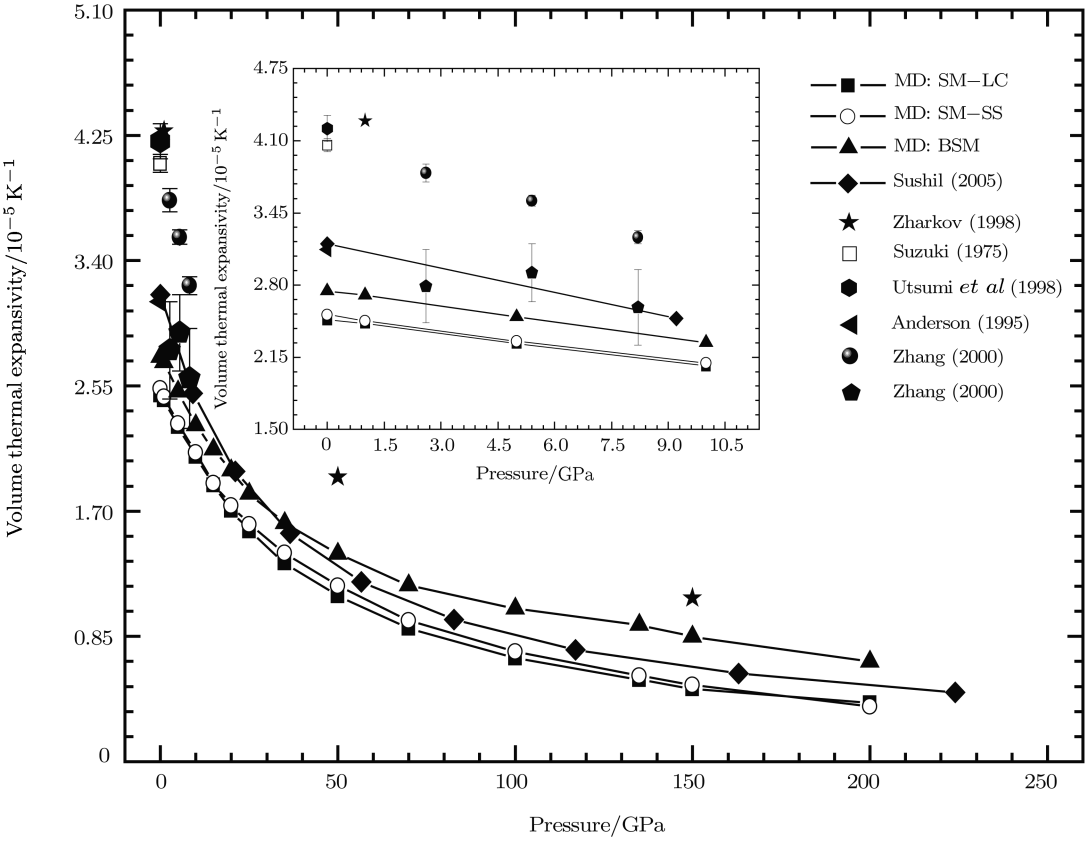


Fig.1. MD-calculated volume thermal expansivities of MgO as a function of pressure up to 200 GPa at 300 K.

In Fig.2, the available experimental data[30,31] and the theoretical results[28,32] for the volume thermal expansion coefficient of MgO are compared with the isotherms calculated by using the SM- and BSM MD at 2000 K. Though scattered due to the uncertainty in the measured volumes, these results give an idea of the actual thermal expansion coefficient, and our calculations favour the experimental data given by Chopelas and Boehler,[30] and Duffy and Ahrens.[31] The calculated thermal expansivity reproduces all known features: the values of α are nearly constant at high pressures and high temperatures. The results for thermal expansivity are in agreement with the calculations from the equation of state[28] and *ab initio* results[32] as shown in Fig.2. It has been emphasized that most of the serious errors in the calculations of thermodynamic functions arise due to the uncertainty of thermal expansivities at high temperatures.[5] Each calculation method also has its own limitations related to the basic material parameters, basis sets, and the accuracies used, in addition to the approximations of the method itself, leading to variations in the calculated parameters. Compared with the results obtained by the SM potential, the α dependences of the pressure obtained through the MD simulation by using the BSM potential at high pressures (50–200 GPa) have been found to be close to the results mentioned above, especially the calculations from Sushil's equation of state.[28]

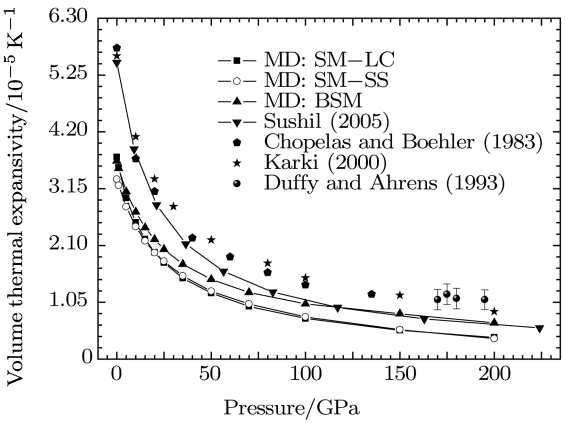


Fig.2. Experimental and theoretical MD-calculated volume thermal expansivities of MgO at 2000 K versus pressure.

In order to study further the influence of pressure on thermal expansivity of MgO, sim-

ulations in the temperature range 500–3500 K and at pressures up to 200 GPa are performed and the obtained results are shown in Fig.3. It can be seen that the volume thermal expansivity

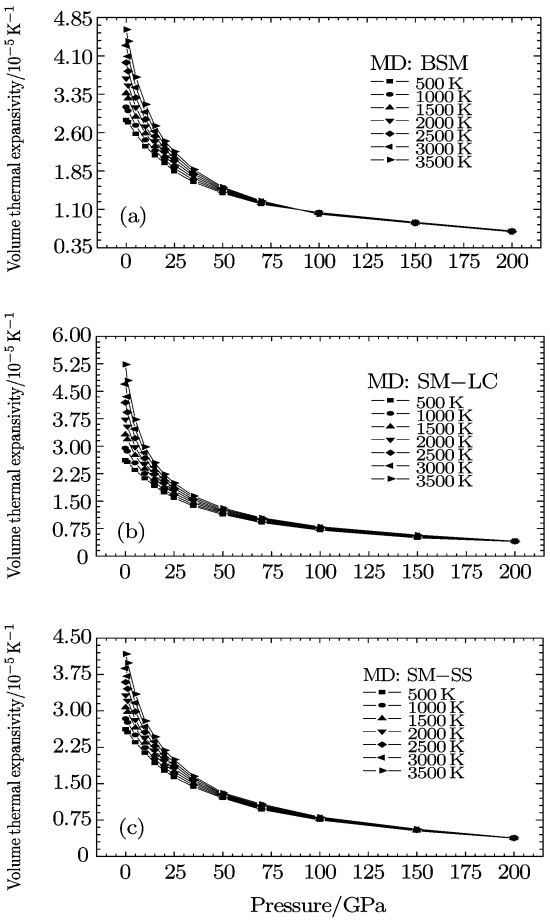


Fig.3. Volume thermal expansivities of MgO as a function of pressure at different temperatures, calculated by (a) BSM-MD; (b) SM-LC-MD; and (c) SM-SS-MD separately.

of MgO decreases with the increase of pressure. The curve of volume thermal expansivity of MgO, rather steep at lower pressures, rapidly flattens with increasing pressure. Note that the influence of temperature on thermal expansion at high pressures is very small and may be neglected above 70 GPa pressure. This is mainly because the anharmonic effect becomes less important at high pressures. With the increase of pressure, the volume of the solid reduces and the atoms come closer to each other, increasing the depth of the potential energy well and reducing the anharmonic nature of the potential energy curve at high temperatures. Since thermal expansivity is a result of anharmonicity in the potential energy, it becomes virtually independent of pressure and temperature in the high pressure and temperature domain. Thus, the thermal expansivity of MgO at high pressures is a weak function of temperature. The knowledge of thermal expansivity can help to constrain other important parameters such as Grüneisen parameters and the Rayleigh number.

4. Conclusions

Volume thermal expansion coefficients under high pressures are obtained by using the MD method with SM and BSM potentials. We can calculate these thermodynamic parameters not only in the normal state, but also at extended temperature and pressure ranges. It can be found that the thermal expansivity of MgO at a low pressure range increases with rising temperature. The influence of temperature on thermal expansivity is very small and may be neglected above 70 GPa pressure. Therefore, the thermal expansivity of MgO at high pressures is a weak function of temperature.

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