High Pressure Effects on Thermal Properties of MgO

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Abstract.
Using the non-empirical Variational Induced Breathing (VIB) model, the thermal properties of periclase (MgO) under high pressures and temperatures are investigated using molecular dynamics, which includes all anharmonic effects. Equations of state for temperatures up to 3000K and pressures up to 310 GPa were calculated. Bulk modulus, thermal expansivity, Anderson-Grüneisen parameter, thermal pressure, Grüneisen parameter and their pressure and temperature dependencies are studied in order to better understand high pressure effects on thermal properties. The results agree very well with experiments and show that the thermal expansivity decreases with pressure up to about 100 GPa ($\gamma=0.73$), and is almost pressure and temperature independent above this compression. It is also affected by anharmonicity at zero pressure and temperatures above 2500K. The thermal pressure changes very little with increasing pressures and temperatures, and the Grüneisen parameter is temperature independent and decreases slightly with pressure.

Introduction

The density of lower mantle minerals at high pressures and temperatures is crucial for interpreting seismological data in terms of mineral constituents. For the first time all anharmonic effects up to extreme pressures and temperatures are being addressed using a non-empirical, first principles ionic model. We study MgO here since 1) We have an extremely well characterized and accurate potential for MgO; 2) it is an end member of magnesiowüstite (Mg,Fe)O thought to be a major constituent of the lower mantle; 3) MgO has no phase transitions or soft modes in the region of interest and therefore should show generic oxide character; and 4) MgO is the simplest oxide; other dense minerals whose compression is homogeneous should behave similarly.

Previous studies using non-empirical potentials [Isaak
et al., 1990; Wolf and Bukowski, 1988], empirical potentials [Agnon and Bukowski, 1990, Reynard and Price, 1990] and thermodynamic models [Anderson et al. 1992, 1993] all concluded that the thermal expansivity becomes temperature independent at high pressures. All studies are consistent with an Anderson-Grüneisen parameter $\delta_T = \left( \frac{\partial \ln \alpha}{\partial \ln V} \right)_T$ equal to about 5.0 at zero pressure which decreases with pressure. How anharmonicity might affect these results and how $\delta_T$ behaves with pressure and temperature, as well as other thermal quantities like $K_T$, $\gamma$ and $P_{TH}$ is addressed here.

**Method**

We have developed a massively parallel molecular dynamics code for the connection machine CM-5, using the VIB model [Wolf and Bukowski, 1988] and periodic boundary conditions. We have used supercells of 64 and 216 atoms, and performed constant $E$, $N$ and $V$ simulations; no scaling was used after equilibration. Results of $P$ and $T$ were obtained by averaging over 4-10 ps after the system has equilibrated, which took 1-2 ps. The runs were sufficiently long so that statistical errors were smaller than the size of the symbol. The Variational Induced Breathing (VIB) potential is based on density functional theory which states that all the ground state properties are determined by the charge density alone, which is modeled here by overlapping ionic charge densities. Since oxygen ions are unstable in the free state, they are surrounded by a Watson sphere of charge +2. The Watson spheres are allowed to relax spherically at each time step to minimize the total energy. In the related PIB model the Watson sphere radius is chosen to give the Madelung potential at the ion site. The Local Density Approximation (LDA) is used to calculate the total energy which is written as the sum of the self-energy of each ion, the electrostatic energies, the overlap kinetic energy (calculated using the local Thomas-Fermi electron gas functional) and exchange and correlation energies, which are all functionals of the charge density. Further discussion of the method can be found in Cohen and Gong [1994], who studied the melting of MgO using PIB rather than VIB, and a finite cluster rather than periodic boundary conditions.

**Results and Discussion**

We find excellent agreement between our equation of state parameters and experimental values (Table 1). The temperature variation of the thermal expansivity is shown in Fig. 1a at pressures up to 310 GPa. Since
we use classical MD, and quantum thermal and zero point corrections are neglected, we expect the results to be accurate at temperatures above the Debye temperature ($\Theta_D=945$K for MgO). Above the Debye temperature the thermal expansivity agrees well with experimental data. Previous non-empirical studies have never included all effects of anharmonicity; here at high temperatures and zero pressure we find a nearly linear thermal expansivity with temperature compared with the diverging form found by Isaak et al. [1990] which employed the quasi-harmonic approximation. At higher pressures (100 GPa) and high temperatures we do not find significant differences between our results and the quasi-harmonic results implying therefore that at high pressures anharmonicity does not play a major role. At high pressures (Fig. 1b) we also find excellent agreement between the results of this study and experimental data. Duffy and Ahrens [1993] measured the thermal expansivity at $T=1800$K and pressures ranging between 160 and 200 GPa to be a constant within experimental errors. These results agree extremely well with our values for the T=1880 K isotherm at these pressures. We further predict the thermal expansivity to be pressure and also temperature independent at higher pressures and at higher temperatures as previous non-empirical studies have not studied the effects of such extreme pressures, up to 310 GPa on $\alpha$. The thermal expansivity decreases with pressure up to about 100-150 GPa ($\eta=0.73-0.65$) at which point it becomes pressure and temperature independent.

Shown in Fig. 2 as a function of pressure is the Anderson-Grüneisen parameter, $\delta_T = (\partial \ln \alpha / \partial \ln V)_T$. For $\delta_T$ at ambient conditions, we obtain $\delta_T=4.8$, in excellent agreement with experiment [Chopelas and Boehler, 1989]. With increasing pressure the value of the Anderson-Grüneisen parameter decreases and becomes temperature independent, much like Agnon and Bukowskii’s [1990] empirical model. Anderson and Isaak [1993] have suggested that $\delta_T = \delta_T^0 \eta^\kappa$, with $\kappa = 1.4$ and independent of $T$ and $\eta$. We find that this is correct only up to about $\eta=0.8$ (50 GPa), at which point this begins to diverge from our results (Fig. 2).

The quantity $\alpha K_T$ is important in determining other thermodynamic properties. The bulk modulus $K_T$ is also almost temperature independent at high pressures (Fig 3) and is consistent with the above results as $\left( \frac{\partial \alpha}{\partial P} \right)_T = \frac{1}{K_T^0} \left( \frac{\partial K_T^0}{\partial P} \right)_T$. At zero pressure we get very good agreement with experiment and at high temperatures there is no difference between our results and the quasi-harmonic results implying anharmonicity does not effect $K_T$. 

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The Grüneisen parameter $\gamma$ depends on $aK_T$ via $\gamma = \frac{\partial aK_T}{\partial V}$, and its temperature and pressure dependence are shown in Fig 4a and b, respectively. We find that the Grüneisen parameter is temperature independent in accord with experimental results and decreases slightly as a function of pressure, which is similar to other theoretical models [Agnon and Bukowinski, 1990] and calculations [Isaak et al., 1990a]. Here too, the effects of not including anharmonicity are shown by the diverging form of the dashed line corresponding to the results of Isaak et al. who used the quasi-harmonic approximation.

The thermal pressure along an isochore is defined as $P_{TH} = \int_0^T (\frac{\partial P}{\partial T})_V dt = \text{Const.} + aK_T T$. We calculated the pressure dependence of the thermal pressure at different temperatures above the Debye temperature. As pressure increases, the thermal pressure increases, up to about 100 GPa ($\eta=0.73$), at which point the thermal pressure becomes pressure independent. In order to understand this phenomenon we can look at $(\frac{\partial (\alpha K_T)}{\partial P})_T = \alpha (K_T' - \delta_T)$. Our results show that while $K_T'$ is slightly smaller than $\delta_T$ at zero pressure ($K_T = 4.68$, $\delta_T = 4.8$ and $K_T' = \delta_T$ at 20 GPa), $\delta_T$ decreases much faster than $K_T$, at pressures up to 150 GPa ($\delta_T$ decreases exponentially and $K_T'$ decreases linearly). At this point $\delta_T$ becomes almost pressure independent while $K_T'$ continuously decreases until at 250 GPa $K = \delta_T$.

Conclusions

These $ab$ initio calculations yield values for the thermal expansivity which are in very good agreement with available experimental data and show that with increasing pressure the thermal expansivity decreases, up to about 120 GPa ($\eta=0.7$) at which pressure it becomes pressure and temperature independent. Anharmonicity effects are shown to be important only at zero pressure and temperatures above 2500K. The Anderson-Grüneisen parameter $\delta_T$ follows the same behavior; it decreases with increasing pressure and becomes temperature independent at high pressures. The bulk modulus is found to be temperature independent at high pressures and unaffected by anharmonicity. The Grüneisen parameter $\gamma$ and the thermal pressure are also calculated at various pressures and temperatures and are also found to be almost temperature and pressure independent, which is consistent with the assumption made by Birch [1952] that $aK_T$ is independent of density in the deep earth. Previous non-empirical studies have never found such good agreement with experiment.
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Figure 1. a). Temperature variation of the thermal expansivity at pressures up to 310 GPa. Lines for 0, 100, 200 and 310 GPa are results from this study, dashed line is from Isaak et al. [1990] +’s are data from Touloukian et al., and *’s are data from Anderson et al. [1993a] at 100 GPa. b). Pressure variation of the thermal expansivity at different temperatures above the Debye temperature. Lines are results of this study, •’s are data from Duffy and Ahrens at 1800K, x’s are from Chopelas and Boehler [1992] at 2000K.
Figure 2. Pressure Variation of $\delta_T$ at different temperatures. The $\circ$'s are $T=940$K, $+$'s are $T=1880$K and *'s are $T=2830$K. $\delta_T$ decreases with pressure and becomes temperature independent at high pressures. $\times$'s represent Anderson-Isaak proposed fit of $\delta_T = \delta_{T_0} \eta^{1.4}$.

Figure 3. The temperature variation of the Bulk modulus for different pressures. The +'s are data from Anderson et al. [1992], and the solid line is from Isaak et al. [1999] using the PIB model and the quasi-harmonic approximation.

Figure 4. a). The temperature dependence of the Gr"uneisen parameter at zero pressure. The solid line represents results of this study, the dashed line is from calculations by Isaak et al. [1990] and the +'s are experimental results from Sumino, Isaak and Garvin. b). Pressure variation of the Gr"uneisen parameter at 1000K. Results from this study are shown by $\circ$'s, +'s represent results from calculations by Isaak et al. [1990] and *'s are calculations from a model by Anderson et al. [1993a].

Table 1. Calculated Equation-of-state Parameters for MgO at zero pressure.

|        | T = 300 K | This Study | QH PIB$^a$ | QH VIB$^b$ | EM$^c$ | EM$^d$ | 940K   | 1880K   | 2830K   |
|--------|-----------|------------|------------|------------|--------|--------|--------|---------|---------|
| $V$ [Å$^3$] | 18.66$^+$ | 18.70      | 18.66      | 18.69      | 18.73  | -      | 19.29  | 20.29   | 21.38   |
| $K_T$ [GPa] | 160.1$^+$ | 153.11     | 180.1      | 177.2      | 232.1  | 161.3  | 132.09 | 104.15  | 83.93   |
| $K'_{T}$ | 4.22$^+$  | 4.68       | 4.15       | -          | -      | -      | 5.04   | 5.44    | 5.66    |
| $\alpha \times 10^{-5}$ [K$^{-1}$] | 32.0$^b$  | 38.79      | 23.9       | 19.4       | 31     | 44.56  | 52.41  | 58.75   |

a) QH-Quasi-harmonic, Isaak et al. [1990], b) Wolf and Bukowski [1988], c) EM:Empirical model, Reynard and Price [1990], d) Agnon and Bukowski [1990], e) Mao and Bell [1973], f) Sumino et al. [1988], g) Chang and Barsch [1969], h) Touloukian et al. [1977]
