Bulk Modulus and Equation of State under the Effect of High Temperature and High Pressure for MgO

Quan Liu

Department of Physics, Anhui University, Hefei 230039, China

Reprint requests to Q. L.; E-mail: quanliu@ah172.com.cn

Z. Naturforsch. **63a,** 53 – 56 (2008); received July 2, 2007

A new method for the determination of the equation of state is investigated and applied for MgO crystals. The method is developed by using the Hildebrand approximation and an analytical potential form for the overlap repulsive energy derived by Harrison from quantum mechanical considerations. The bulk modulus is also evaluated for MgO in the temperature range 300 – 200 K and down to a compression of $V/V_0 = 0.6$ using an expression based on the Chopelas-Boehler approximation. The results obtained agree well with the ab-initio values determined by Isaak et al.

Key words: Bulk Modulus; Equation of State; Harrison's Model.
PACS numbers: 64.30. +t; 62.20.Dc

1. Introduction

The thermoelastic properties and equation of state of minerals are of substantial physical and geological interest [1]. Magnesiowustite (MgO) is a major mineral in the earth's lower mantel and is therefore an oxide of considerable geophysical interest. Although iron can appreciably affect the elastic moduli of MgO, the elastic moduli of pure MgO are more amenable to study, both experimentally and theoretically. Many theoretical studies [1 – 5] have been undertaken in order to better understand the pressure and temperature dependence of its elastic properties and to define the equation of state of MgO.

Isaak et al. [6] calculated the thermoelastic properties of MgO at high temperatures and high pressures using the potential-induced breathing (PIB) electron gas model based on the first principles approach. The ab-initio method of [6] is based on detailed calculations of the Helmholtz energy F versus volume V at constant temperature T at selected temperatures. By taking the appropriate derivatives of F, values of the pressure P and the isothermal bulk modulus B_T are numerically determined. The results thus obtained compare well with recent experimental data on MgO [7, 8].

The purpose of the present paper is to develop a simple method for the determination of the equation of state and bulk modulus under the effect of high temperature and high pressure. The calculations are performed within the framework of the Hildebrand approximation [9] for the equation of state. The potential model considers the overlap repulsive energy by Harrison [10] from a quantum mechanical treatment along with van der Waals interactions. For calculating the bulk modulus we use a formulation based on the Chopelas-Boehler approximation [11], which considers a linear relationship of the volume dependence with the Anderson-Gruneisen parameter δ_T. The results obtained are compared with those derived by the PIB model in case of MgO.

2. Equation of State

The equation of state for a solid can be derived from the Hildebrand approximation [9], which is expressed as

$$P = -\frac{\mathrm{d}\phi}{\mathrm{d}V} + T\alpha B_T, \tag{1}$$

where ϕ is the lattice potential energy and V the volume. T is the temperature, α the coefficient of volume thermal expansion and B_T the isothermal bulk modulus. In (1) the first term of the right-hand side is the pressure due to volume dependence of the electronic ground state energy (static pressure) and the second term is the pressure due to vibration of nuclei (thermal pressure). P is the externally applied pressure. For MgO $V = 2r^3$, and therefore we can rewrite (1) as fol-

lows:

$$P = -\frac{1}{6r^2}\frac{\mathrm{d}\phi}{\mathrm{d}r} + T\alpha B_T, \tag{2}$$

where r is the nearest neighbour separation.

The total lattice potential energy ϕ for ionic solids contains the main contributions

$$\phi = -\frac{a_{\mathrm{M}}Z^2e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + \phi_{\mathrm{rep}}, \tag{3}$$

where the first term on the right-hand side is the electrostatic Coulomb energy with the Madelung's constant a_{M}, the charge of the electron e, and the valency Z. The second and third terms are the van der Waals (vdW) dipole-dipole and dipole-quadrupole energies. C and D are the constants related to the dipole-dipole c_{ij} and dipole-quadrupole d_{ij} interaction coefficients as follows [12]:

$$C = S_{+-}c_{+-} + S_{++}c_{++} + S_{--}c_{--}, \tag{4}$$

$$D = T_{+-}d_{+-} + T_{++}d_{++} + T_{--}d_{--}, \tag{5}$$

where S_{ij} and T_{ij} are lattice sums which have been given by Tosi [13]. The subscripts $+-$, $++$, $--$ represent the cation-anion, cation-cation, and anion-anion interactions, respectively. The values of c_{ij} and d_{ij} are obtained from the Kirkwood-Muller formulas [13]

$$c_{ij} = -\frac{6mc^2}{N}\chi_i\chi_j\left(\frac{\chi_i}{\alpha_i} + \frac{\chi_j}{\alpha_j}\right)^{-1}, \tag{6}$$

$$d_{ij} = -\frac{9mc^2}{Ne^2}c_{ij}\left(\frac{\chi_i}{n_i} + \frac{\chi_i}{n_j}\right)^{-1}, \tag{7}$$

where c is the velocity of light, α and χ are the polarizabilities and molar susceptibilities, respectively. N is Avogadro's number. n_i and n_j are the numbers of outmost electrons. The values of C and D calculated from (4) – (7) are used in the present work.

For the overlap repulsive energy, we use the analytical form proposed by Harrison [10]. The normalized charge density, as used by Harrison from quantum mechanical consideration, is

$$n(r) = \frac{6\mu^3}{\pi}\exp(-2\pi r), \tag{8}$$

where μ is related to the valence p and the state energy (ε_p):

$$\varepsilon_p = -\frac{\hbar^2\mu^2}{2m}, \tag{9}$$

where $\hbar$ is Planck's constant h divided by 2π. The total overlap interaction has been considered as arising from three contributions, viz., (i) the kinetic energy ϕ^{ke}, (ii) the exchange energy ϕ^{ex}, and (iii) the Coulombian energy ϕ^{coul} of electrons in the overlap region. These contributions to the overlap repulsive potential are given:

$$\phi^{\mathrm{ke}} = 70.8\varepsilon_p\mu r\exp\left(-\frac{5\mu r}{3}\right), \tag{10}$$

$$\phi^{\mathrm{ex}} = -2.728e^2\mu^2 r\exp\left(-\frac{4\mu r}{3}\right), \tag{11}$$

$$\phi^{\mathrm{coul}} = -6e^2\mu^3 r^2\exp(-2\mu r). \tag{12}$$

Harrison [10] assumed that the total overlap interaction has the form of the kinetic energy term and can be expressed by an equation similar to (10). Following the previous work [14] on Harrison's potential for ionic crystals, we can write the overlap repulsive potential as follows:

$$\begin{aligned}\phi_{\mathrm{rep}} = \frac{6n_0\hbar^2}{2m}\Big[&\bar{\mu}^3 r\exp(k\bar{\mu}r)\\ &+\sqrt{2}{\mu_1}^3 r\exp(-\sqrt{2}k\mu_1 r)\\ &+\sqrt{2}{\mu_2}^3 r\exp(-\sqrt{2}k\mu_2 r')\Big],\end{aligned} \tag{13}$$

where m is the mass of the electron. The values of μ_1 and μ_2 are calculated using the valence p state energy (ε_p) given by (9), and $\bar{\mu}$ is the arithmetic average of μ_1 and μ_2 of the cation and anion.

In order to calculate the lattice potential energy ϕ from (3), there remain only two unknown parameters, viz., n_0 and k, which are obtained from the equilibrium condition and the following relations:

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}r}\right)_{r=r(T_0,0)} = 0, \tag{14}$$

$$\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}r^2}\right)_{r=r(T_0,0)} = 18r(T_0,0)B_T/T_0,0). \tag{15}$$

The potential parameters thus calculated are assumed to be independent of the pressure.

The values of $\mathrm{d}\phi/\mathrm{d}r$, the first derivative of the lattice potential energy, can be calculated using (3) for any value of r, and finally the pressure P is obtained from (2). The method is repeated along different isotherms from room temperature up to higher temperature. The input data required are given in Table 1. The results obtained are reported in Table 2 along with the ab-initio values [6].

Table 1. Values of input parameters used in the present work.

$r(T_0,0)$ (Å)	δ_{T_0}	αB_T (MPa deg^{-1})	μ_1 (10 nm^{-1})	μ_2 (10 nm^{-1})	C (10^{-60} erg cm^6)	D (10^{-76} erg cm^8)	n_0	k
2.105 [1]	4.78 [1]	5.042 [1]	3.838 [14]	1.923 [14]	170	79	7.0	1.2

Table 2. Values of the pressure P (GPa) and the bulk modulus B_T (GPa) for MgO crystals at different interatomic separation r (Å). The ab-initio values [6] are given within parentheses.

— 300 K —			— 500 K —			— 1000 K —			— 1500 K —			— 2000 K —		
r	P	B_T	r	P	B_T	r	P	B_T	r	P	B_T	r	P	B_T
2.105	0	180.1	2.110	0	174.5	2.125	0	159.7	2.141	0	144.1	2.160	0	127.6
	(0)	(180.1)		(0)	(174.5)		(0)	(159.7)		(0)	(144.1)		(0)	(127.6)
2.069	10.28	228.4	2.074	10.01	221.3	2.089	9.17	202.6	2.105	8.29	182.8	2.123	7.41	161.8
	(10.3)	(221.5)		(9.97)	(215.3)		(9.16)	(198.5)		(8.30)	(180.5)		(7.39)	(161.4)
2.032	23.61	288.8	2.037	22.96	279.9	2.051	21.24	256.2	2.068	19.21	231.2	2.085	17.37	204.7
	(23.6)	(272.6)		(22.94)	(265.6)		(21.15)	(246.4)		(19.25)	(225.8)		(17.22)	(203.7)
1.994	40.83	364.2	1.999	39.82	353.0	2.013	36.91	323.0	2.029	33.67	291.5	2.046	30.46	258.1
	(40.9)	(336.0)		(39.9)	(328.1)		(36.9)	(306.2)		(33.7)	(282.5)		(30.3)	(256.9)
1.954	63.22	457.6	1.959	61.83	443.5	1.972	57.42	405.9	1.988	52.73	366.3	2.005	47.93	324.3
	(63.6)	(415.2)		(62.0)	(406.3)		(57.7)	(381.2)		(53.0)	(353.8)		(47.9)	(324.1)
1.913	92.47	572.8	1.917	90.67	555.2	1.930	84.67	508.1	1.946	77.98	458.4	1.962	71.32	405.9
	(93.6)	(515.2)		(91.4)	(505.0)		(85.2)	(476.1)		(78.6)	(444.4)		(71.5)	(409.7)
1.869	131.02	713.8	1.874	128.15	691.8	1.887	120.01	633.1	1.901	112.24	571.3	1.918	103.07	505.8
	(133.4)	(642.5)		(130.4)	(630.8)		(122.1)	(597.1)		(113.2)	(560.1)		(103.4)	(519.5)
1.823	182.73	884.9	1.828	179.48	857.6	1.841	168.48	784.9	1.855	157.35	708.2	1.871	146.09	627.1
	(186.9)	(806.2)		(183.0)	(792.4)		(172.0)	(752.6)		(160.0)	(708.9)		(147.0)	(661.0)
1.775	250.58	1090.5	1.780	246.64	1056.9	1.792	233.22	967.3	1.806	218.37	872.8	1.822	204.34	772.8
	(259.6)	(1018.6)		(254.5)	(1001.9)		(240.0)	(953.8)		(224.2)	(901.4)		(207.0)	(814.4)

3. Pressure Dependence of the Bulk Modulus at Different Temperature

The thermal expansion and compression data discussed in Section 2 can be used to investigate the pressure dependence of the bulk modulus at different temperatures. For this purpose one can start from the well-known thermodynamic approximation [15]

$$\alpha B_T = K, \tag{16}$$

where K is a constant for a given solid. Equation (16) represents only an approximation, i. e., it does not hold strictly. However, it is useful for deriving a number of thermodynamic relations of sufficiently wide applicability and simplicity. The product αB_T remains nearly constant under the effect of high pressure and high temperature [1].

Equation (16) gives

$$\alpha \left(\frac{\mathrm{d}B_T}{\mathrm{d}V}\right)_T + B_T \left(\frac{\mathrm{d}\alpha}{\mathrm{d}V}\right)_T = 0, \tag{17}$$

which yields

$$\delta_T = \frac{V}{\alpha}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}V}\right)_T = -\frac{V}{B_T}\left(\frac{\mathrm{d}B_T}{\mathrm{d}V}\right)_T. \tag{18}$$

At constant temperature we get

$$\frac{\mathrm{d}B_T}{B_T} = -\delta_T \frac{\mathrm{d}V}{V}. \tag{19}$$

On the basis of an analysis of experimental data, Chopelas and Boehler [11] investigated the following relationship for the isothermal variation of the Anderson-Gruneisen parameter δ_T with the volume:

$$\delta_T + 1 = A\frac{V(T,P)}{V(T,0)}, \tag{20}$$

where A is a constant for a given crystal, i. e., $A = \delta_{T_0} + 1$. By using (19) and (20) and considering $V = 2r^3$, we get the following expression after doing some calculation work:

$$\frac{B_T(T,P)}{B_T(T,0)} = \left(\frac{r(T,P)}{r(T,0)}\right)^3 \exp\left[A\left\{1 - \left(\frac{r(T,P)}{r(T,0)}\right)^3\right\}\right]. \tag{21}$$

4. Results and Discussion

We have proposed a simple method to investigate the properties of solids at high temperature and high pressure, based on the interionic potential model which

incorporates the quantum mechanical form of the overlap repulsive energy proposed by Harrison [10]. The results for r vs. p obtained in the present work agree well with the ab-initio values [6] based on the PIB model, supporting the validity of the potential model. The results of the bulk modulus as a function of pressure and temperature are also included in Table 2. It may be noted that the calculated values present close agreement with the ab-initio values.

For estimating the values of $\mathrm{d}\phi/\mathrm{d}r$ at r, we have used the potential energy expression given in the form of (3). Within the framework of this model, we have considered van der Waals dipole-dipole and dipole-quadrupole interactions. The dipole-dipole energy term, which arises from the interaction between induced dipole moments of different atoms, is actually the first term in an infinite series of rapidly converging terms. The dipole-quadrupole term is interpreted as arising from the interaction of a dipole on one atom with a quadrupole on the other. Actually, there exists a third term, which varies inversely as the tenth power of interatomic distance, which is called the quadrupole-quadrupole term. In the present article we discuss only the dipole-dipole and dipole-quadrupole interactions because the quadrupole-quadrupole term is negligible in ionic crystals.

It should be mentioned that the overlap potential forms, as given by (13), are based on Harrison's quantum mechanical formulation and differ from the traditional Born-Mayer exponential forms [16] in some important aspects. First, the pre-exponential factors appearing in (13) also depend directly on the interionic separation, whereas in the Born-Mayer exponential forms, only the exponential factors depend on r. Secondly, ionic radii have been introduced arbitrarily as adjustable parameters in the Born-Mayer exponential forms. On the other hand, in (13) the pre-exponential as well as the exponential factors depend on fundamental factors like Planck's constant, electronic mass, and energy values. Moreover, the exponential factors are different in different pair interactions, whereas in the Born-Mayer potential a common value of hardness parameters has been taken for the cation-anion, cation-cation, and anion-anion interactions. This is not justified for the reasons discussed by Shanker and Kumar [17]. If one takes unequal values of hardness parameters for the crystal, then the number of parameters becomes too large to be determined from the input data for the lattice parameter and bulk modulus. Thus, the Harrison potential form is superior to the Born-Mayer exponential forms.

Finally, it should also be mentioned that the equation of state and the expression of the bulk modulus proposed in the present study is of general nature, and therefore its application may be extended to different classes of solids. The results of the present investigation also lead to the understanding of the equation of state based on the microscopic details of the theory of interionic potentials.

Acknowledgements

This work has been financially supported by the Key Laboratory of Opto-electronic Information Acquisition and Manipulation of the Ministry of Education of China (No. 9603).

[1] O. L. Anderson, Equation of State of Solids for Geophysics and Ceramic Science, Oxford University Press, Oxford 1995.
[2] B. B. Karki, R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni, Science **286**, 1705 (1999).
[3] S. Gaurav, B. S. Sharma, S. B. Sharma, and S. C. Upadhyaya, J. Phys. Chem. Solids **65**, 1635 (2004).
[4] K. Sushil, Physica B **367**, 114 (2005).
[5] S. K. Srivastava and S. K Sharma, Physica B **373**, 258 (2006).
[6] D. G. Isaak, R. E. Cohen, and M. J. Mehl, J. Geophys. Res. **95**, 7055 (1990).
[7] S. Speziale, C. Zha, T. Duffy, R. Hemley, and H. K. Mao, J. Geophys. Res. **106**, 515 (2001).
[8] Y. W. Fei, J. Li, K. Hirose, W. Minarik, J. V. Orman, C. Sanloup, W. v. Westrenen, T. Komabayashi, and K. Funakoshi, Phys. Earth Planet. Inter. **143 – 144**, 515 (2004).
[9] J. H. Hildebrand, Z. Phys. A, Hadrons and Nuclei **67**, 127 (1931).
[10] W. A. Harrison, Phys. Rev. B **23**, 5230 (1981).
[11] A. Chopelas and R. Boehler, Geophys. Res. Lett. **19**, 1983 (1992).
[12] J. Shanker and G. G. Agrawal, Phys. Status Solidi (b) **123**, 11 (1984).
[13] M. P. Tosi, Cohesion of Ionic Solids in the Born Model, in: Solid State Physics (Eds. F. Seitz and D. Turnbull), Academic Press, New York 1964.
[14] S. D. Chaturvedi, S. B. Sharma, P. Paliwal, and M. Kumar, Phys. Status Solidi (b) **156**, 171 (1989).
[15] J. Shanker and M. Kumar, Phys. Status Solidi (b) **179**, 351 (1993).
[16] X. Q. Deng and Z. T. Yan, High Temp. High Pressures **34**, 387 (2002).
[17] J. Shanker and M. Kumar, Phys. Status Solidi **142**, 325 (1987).