American Mineralogist, Volume 84, pages 272–276, 1999

Effects of temperature and composition on the bulk modulus of (Mg,Fe)O

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ABSTRACT

Isothermal static compression data for MgO at 300 and 1100 K were obtained by combining synchrotron X-ray diffraction techniques with an externally heated high-temperature diamond-anvil cell that is capable of achieving pressures greater than 125 GPa at temperatures up to 1100 K. The experiments at 300 K were conducted under both hydrostatic and nonhydrostatic conditions. The deviatoric stress in non-hydrostatic environment significantly effects the measured lattice parameters. Fits to the static compression data of MgO at 300 K yield a bulk modulus of 185(7) GPa and 160(2) GPa under nonhydrostatic and hydrostatic conditions, respectively. The deviatoric stress decreases with increasing temperature, and a nearly hydrostatic condition was achieved at temperatures above 900 K when NaCl was used as a pressure-medium. The bulk modulus of MgO was determined to be 135(3) GPa at a temperature of 1100 K, yielding its temperature derivative of −0.030(3) GPa/K. Comparing these results with previous studies in the system MgO-FeO, shows that the bulk modulus of (Mg,Fe)O decreases with increasing FeO content, from 160 GPa for MgO to 146 GPa for FeO.

INTRODUCTION

Experimental measurements of *P-V-T* properties of mantle-related phases are crucial for developing accurate mineralogical and compositional models of the Earth's interior. Magnesiowüstite (Mg,Fe)O is one of the phases that may constitute the Earth's lower mantle. The composition of the lower mantle magnesiowüstite depends on compositional models of the Earth's mantle. Therefore, it is important to provide sufficient experimental measurements that can be used to formulate a function that describes the *P-V-T* properties of magnesiowüstite over its entire composition range. To evaluate the effect of FeO content on the *P-V-T* properties of magnesiowüstite, the *P-V-T* equation of state of MgO, an end-member of magnesiowüstite, must first be determined accurately.

MgO with the NaCl-type cubic structure has been extensively studied at high pressure because of its simplicity in structure and its geophysical importance. Sophisticated theoretical methods have been developed to calculate its thermal and elastic properties at high pressure and temperature (e.g., Isaak et al. 1990; Inbar and Cohen 1995; and references therein). Several static, ultrasonic, and shock compression experiments were conducted to determine the elastic properties of MgO at room temperature (Perez-Albuerne and Drickamer 1965; Chang and Barsch 1969; Carter et al. 1971; Weaver et al. 1971; Mao and Bell 1979; Vassiliou and Ahrens 1981; Bonczar and Graham 1982; Utsumi et al. 1998; Jackson and Niesler 1982; Duffy and Ahrens 1993). Recently, this material was compressed to multimegabar pressures in a diamond-anvil cell (Duffy et al. 1995). The bulk modulus of MgO derived from static compression data under nonhydrostatic stress was 10% larger than the ultrasonic value. To resolve this discrepancy, static compression experiments were made on MgO under nonhydrostatic and hydrostatic conditions at room temperature. Isothermal compression data of MgO is also reported at 1100 K. Finally, previous data on FeO and (Mg,Fe)O solid solutions were utilized with the present results to obtain the isothermal bulk modulus and its temperature derivative as a function of FeO content.

EXPERIMENTAL PROCEDURES

The experimental methods used here are similar to those described by Fei et al. (1992) and Fei (1996). An externally heated high-temperature diamond-anvil cell was used to generate simultaneous high pressure and temperature. In situ measurements of the specific volume of MgO at high pressure and temperature were made by using energy-dispersive X-ray diffraction techniques at x17c beamline, the National Synchrotron Light Source, Brookhaven National Laboratory.

High temperature was achieved by a large sleeve-shaped platinum-wire heater fitted around the protruding portion of the piston-cylinder and a small molybdenum-wire heater positioned around the diamond anvils (Fig. 1). This double-heater high-temperature diamond-anvil cell is capable of achieving pressures greater than 125 GPa at temperatures up to 1100 K in a mildly reducing atmosphere (Ar with 1% H_2) (Fei and Mao 1994). Ex-

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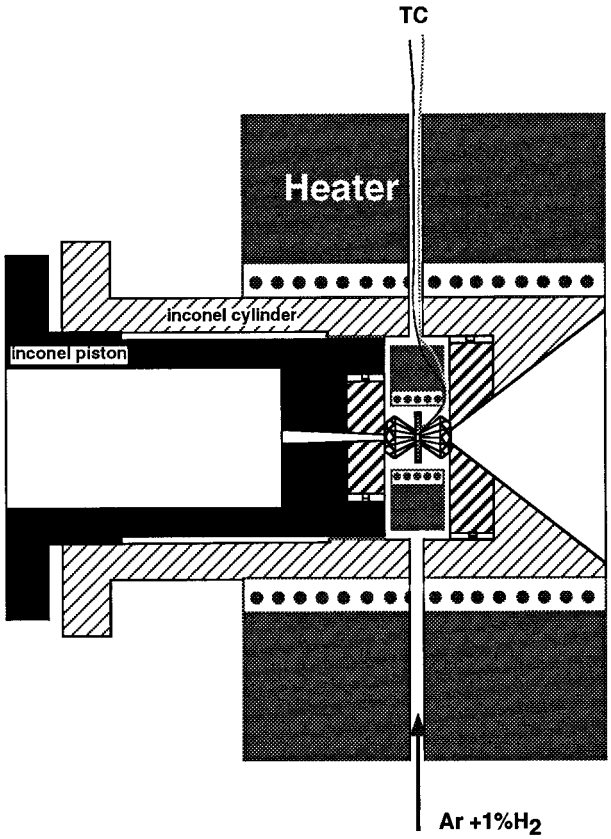

FIGURE 1. Configuration of a high-temperature diamond-anvil cell. High temperatures were achieved by a double-heater system, a large sleeve-shaped platinum-wire heater fitted around the protruding portion of the piston-cylinder, and a small molybdenum-wire heater positioned around the diamond anvils. Piston and cylinder were made of inconel with a double-ring alignment system.

periments on MgO were conducted under both hydrostatic and nonhydrostatic pressure conditions using 600 and 350 μm flat diamond anvils respectively. In the hydrostatic compression experiments up to 23 GPa, neon was used as a pressure-transmitting medium. A quasi-hydrostatic environment was achieved at pressures above 5 GPa, at which neon freezes at room temperature. The powder MgO sample was mixed with NaCl powder in a volume ratio of 4 to 1 and compressed to a thin disk and then loaded into a sample chamber, 200 μm in diameter by 75 μm in thickness, drilled from a preindented rhenium gasket. Only one-third of the chamber volume was filled with sample. Small ruby grains were placed in the sample chamber as pressure calibrants. The sample chamber was then filled with neon gas at 200 MPa in a high-pressure gas-loading device (Jephcoat et al. 1987) and subsequently sealed at a pressure of 0.61 GPa.

In the nonhydrostatic compression experiment up to 65 GPa, the powder MgO sample mixed with NaCl powder in a volume ratio of 4 to 1 and compacted in a sample chamber, 150 μm in diameter by 35 μm in thickness,

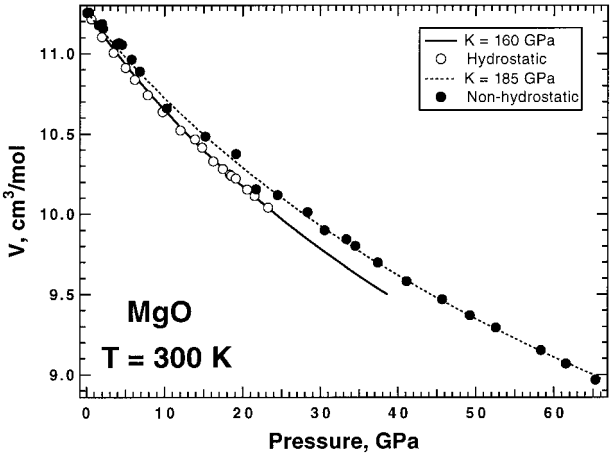

FIGURE 2. Comparison of hydrostatic and nonhydrostatic compression data of MgO at 300 K. The solid and dashed curves are least-squares fits of the hydrostatic (open circles) and nonhydrostatic (solid circles) compression data, respectively.

drilled from a preindented rhenium gasket. Thin Au foil was also placed in the sample chamber as a pressure calibrant.

The sample temperatures were measured with a Pt-Pt13%Rh thermocouple placed near the sample chamber (Fig. 1). Pressures at high temperature were determined from the measured lattice parameters of NaCl and gold, based on the *P-V-T* equations of state of NaCl and gold proposed by Birch (1978) and Anderson et al. (1989). The B1-B2 transition in NaCl occurs at about 29 GPa. At higher pressures, pressures were calculated from the lattice parameters of Au only.

Polychromatic (white) wiggler synchrotron X-radiation was used for energy-dispersive X-ray diffraction measurements. A highly collimated X-ray beam, regulated by two mutually perpendicular slits, was aligned with the detection system and the center of the sample chamber in the diamond-anvil cell. A 30 μm beam spot was used in diffraction measurements. The diffraction data were collected with an intrinsic germanium 4096 channel solid-state detector at a fixed 2θ angle. Diffraction peak positions were determined by using a peak-fitting program.

RESULTS AND DISCUSSION

Static compression data for MgO under nonhydrostatic stress at 300 K

The compression data derived from the X-ray diffraction data are listed in Table 1. A least-squares fit to a Birch-Murnahan equation of state to the compression data yielded a bulk modulus $K_{0T} = 185 \pm 7$ GPa and its pressure derivative $K_{0T}' = 4$. (Fig. 2) This result agreed with the compression data of Duffy et al. (1995) who attained pressures up to 227 GPa with no pressure medium. The result was also in an agreement with other compression data for MgO under nonhydrostatic conditions (Perez-Albuerne and Drickamer 1965; Weaver et al. 1971; Mao

TABLE 1. Static compression data of MgO at 300 K and 1100 K

T = 300 K, Ne medium		T = 1100 K, NaCl medium			T = 300 K, NaCl medium		
P_{NaCl}, GPa	V_{MgO}, cm³/mol	P_{NaCl}, GPa	P_{Au}, GPa	V_{MgO}, cm³/mol	P_{NaCl}, GPa	P_{Au}, GPa	V_{MgO}, cm³/mol
0	11.26	0	0	11.63	0.09(5)	0.03(5)	11.25(1)
0.61(6)	11.21(1)	2.81(9)	3.79(8)	11.39(1)	0.08(2)	0.26(8)	11.26(1)
1.92(4)	11.10(1)	3.55(6)	4.99(10)	11.30(1)	1.95(5)	1.55(47)	11.18(1)
3.45(6)	11.01(2)	4.50(3)	5.94(15)	11.24(2)	2.10(18)	1.96(41)	11.19(1)
5.00(6)	10.91(2)	6.63(10)	7.58(12)	11.10(1)	2.05(17)	2.08(20)	11.16(2)
6.18(10)	10.84(1)	8.89(19)	9.79(20)	10.97(2)	4.29(30)	3.85(26)	11.06(2)
7.82(14)	10.74(2)	10.80(27)	11.90(15)	10.87(2)	4.37(27)	4.13(25)	11.07(1)
9.73(6)	10.64(1)	12.29(18)	13.69(21)	10.76(3)	4.76(20)	4.56(30)	11.06(1)
12.03(13)	10.52(1)	12.63(24)	13.97(24)	10.77(1)	6.25(20)	5.76(35)	10.96(2)
13.89(16)	10.47(3)	15.03(26)	16.34(14)	10.59(3)	6.92(30)	6.83(28)	10.89(3)
14.77(18)	10.42(3)	16.79(29)	17.97(12)	10.54(3)	11.03(29)	10.28(30)	10.66(3)
16.21(24)	10.33(1)	19.37(29)	20.77(27)	10.40(2)	15.15(31)	15.22(10)	10.48(2)
17.41(33)	10.28(1)	19.67(30)	20.94(30)	10.39(1)	18.90(28)	19.11(55)	10.37(5)
18.33(33)	10.25(2)	21.20(27)	22.64(29)	10.33(2)	21.88(25)	21.70(40)	10.16(6)
18.50(32)	10.24(3)	22.72(26)	24.03(32)	10.23(3)	23.53(37)	24.47(47)	10.12(1)
19.09(30)	10.22(3)	24.02(30)	25.51(35)	10.19(2)	27.62(61)	28.32(88)	10.01(8)
20.55(25)	10.15(1)				30.40(56)	30.56(36)	9.90(3)
21.51(26)	10.11(1)				32.24(95)	33.35(56)	9.84(4)
23.22(25)	10.04(1)				33.29(107)	34.51(61)	9.80(2)
						37.40(52)	9.70(3)
						41.12(86)	9.58(4)
						45.68(112)	9.47(5)
						49.24(55)	9.37(4)
						52.55(123)	9.29(3)
						58.33(89)	9.15(5)
						61.53(102)	9.07(5)
						65.32(128)	8.97(5)

and Bell 1979). The calculated shear strength as a function of pressure, based on the difference in the measured lattice parameters of the hkl = 200 and 220 diffraction lines, was compatible with that calculated by Duffy et al. (1995).

Static compression data for MgO under hydrostatic conditions at 300 K

Table 1 lists the compression data for MgO under quasi-hydrostatic conditions. A least-squares fit to these data yielded K_{0T} = 160 ± 2 GPa with fixed K_{0T}' = 4.15 (Fig. 2). The bulk modulus derived from compression data under nearly hydrostatic conditions was consistent with the ultrasonic value (Jackson and Niesler 1982) but about 15% smaller than that from nonhydrostatic compression data obtained under current experimental configuration in which the incident X-ray beam is the same direction of the applied force (Meng et al. 1993). The effect of shear strength on the measured bulk modulus was discussed in detail by Duffy et al. (1995). The difference in the measured lattice parameters of the 200 and 220 diffraction lines was a good indicator for sample stress conditions. Under highly nonhydrostatic conditions in the diamond-anvil cell, the lattice parameter calculated from the 220 diffraction line was larger than that from the 200 diffraction line. In contrast, the measured lattice parameter of the 220 diffraction line in the experiment with neon as a pressure transmitting medium was close to or slightly smaller than that of the 200 diffraction line.

Static compression data for MgO at 1100 K

The temperature dependence of the bulk modulus can be determined by comparing the isothermal compression data at 300 K and at high temperatures. First the sample was compressed (MgO+NaCl powder mix with thin Au foil) to about 27 GPa at 300 K, then heated to 600 K using the large Pt-wire heater (cf. Fig. 1). Higher temperature was achieved by turning on the small Mo-wire heater. Relatively large deviatoric stress was observed at 300 K even with slightly high volume ratio of NaCl to MgO (1:1), as indicated by the difference in the lattice parameters of the 200 and 220 diffraction lines and by

TABLE 2. Bulk moduli of (Mg,Fe)O derived from hydrostatic compression data

$Mg_xFe_{1-x}O$	T (K)	K_T (GPa)	$(\partial K_T/\partial P)_T$	Medium	P_{max} (GPa)	References
MgO	1100	135(3)	4.2	NaCl	24	This study
MgO	300	160(2)	4.15	Ne	23	This study
$Mg_{0.6}Fe_{0.4}O$	300	157(2)	4.0	Ne	28	Fei et al. (1992)
$Mg_{0.4}Fe_{0.6}O$	300	149(4)	4.0	Ar	49	Richet et al. (1989)
$Mg_{0.2}Fe_{0.8}O$	300	148(10)	4.0	Ar	48	Richet et al. (1989)
FeO	300	146(2)	4.0	Ne	16	Fei (1996)

Note: $(\partial K_T/\partial T)_P$ = −0.030(3) GPa/K for MgO, this study; $(\delta K_T/\delta T)_P$ = −0.027(3) GPa/K for $Mg_{0.6}Fe_{0.4}O$, Fei et al. (1992). The $(\delta K_T/\delta P)_T$ values were fixed.

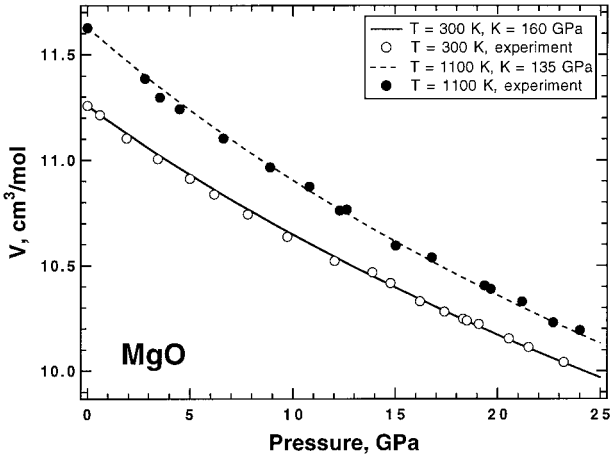

FIGURE 3. Least-square fits to compression of MgO at 300 K (solid curve) and 1100 K (dashed curve). Experimental data were represented by open circles (300 K) and solid circles (1100 K).

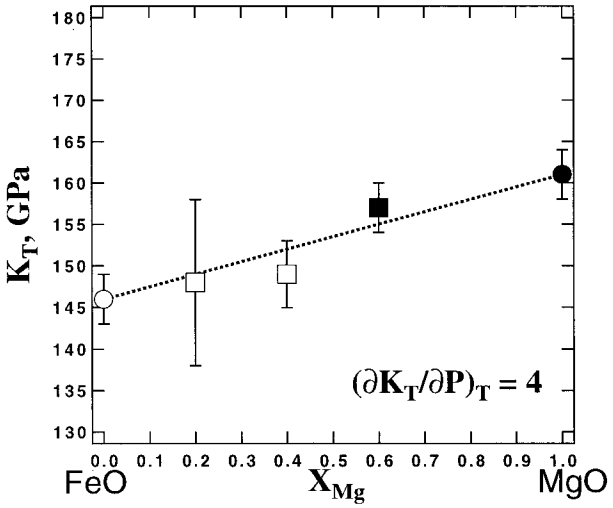

FIGURE 4. Isothermal bulk moduli of $(Mg_{1-x}Fe_x)O$ as a function of FeO content. Solid circle = this study; open circle = Fei (1996); solid square = Fei (1992) and Rosenhauer et al. (1976); and open squares = Richet et al. (1989)

the calculated bulk modulus of MgO. With increasing temperature, the deviatoric stress decreased (Meng et al. 1993). At temperatures above 900 K, the deviatoric stress effect on measured lattice parameter was negligible. We began to collect high-temperature compression data at 24 GPa and 1100 K. Upon decompression, isothermal compression data at 1100 K were obtained (Table 1). A least-squares fit to these high-temperature data yielded K_T = 135 ± 3 GPa and K_T' = 4.2 at T = 1100 K (Fig. 3). By linear interpolation, the temperature derivative of bulk modulus $(\partial K_T/\partial T)_P = -0.030(3)$ GPa/K) was obtained.

Effect of FeO content on bulk modulus and its temperature derivative

The large scattering of the measured bulk moduli of FeO was previously attributed to the use of different pressure-medium conditions (Fei 1996). Therefore, the effect of FeO content on isothermal bulk modulus of (Mg,Fe)O can only be evaluated by comparing compression data for different compositions obtained under similar pressure-medium environments. Hydrostatic compression data (neon as a pressure medium) at 300 K yielded bulk moduli of 146 GPa and 161 GPa for FeO (Fei 1996) and MgO respectively, assuming the pressure derivative $K_{0T}' = 4$. By linear interpolation, the bulk modulus of $(Mg_{1-x}Fe_x)O$ as a function of FeO content can be expressed by K_{0T} (GPa) = 161 − $15X_{FeO}$ (Fig. 4). The linear interpolation also explains the hydrostatic compression data for intermediate compositions including $(Mg_{0.6}Fe_{0.4})O$ (Rosenhauer et al. 1976; Fei et al. 1992), $(Mg_{0.4}Fe_{0.6})O$, and $(Mg_{0.2}Fe_{0.8})O$ (Richet et al. 1989) (Fig 4). Table 2 summarizes the bulk moduli of (Mg,Fe)O derived from hydrostatic compression data.

The temperature derivative of bulk modulus of MgO is −0.030(3) GPa/K, similar to the value of −0.027(3) GPa/K, determined for $(Mg_{0.6}Fe_{0.4})O$ (Fei et al. 1992). It is difficult to determine the temperature derivative of bulk modulus for end-member FeO because of its non-stoichiometric nature (Fei 1996). The value of −0.030 GPa/K for MgO is also consistent with the measured elastic modulus of single-crystal MgO as a function of temperature (Isaak et al. 1989) and the static experimental result reported by Utsumi et al. (1998).

ACKNOWLEDGMENTS

I am grateful to Jiangzu Hu for assistance with the experiments at X17c beam line, the National Synchrotron Light Source, Brookhaven National Laboratory, and to T. Duffy and H.K. Mao for helpful discussion. This work was supported by the National Science Foundation and by the Carnegie Institution of Washington.

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Manuscript received April 20, 1998
Manuscript accepted October 12, 1998
Paper handled by John Parise