

# Quasi-hydrostatic compression of magnesium oxide to 52 GPa: Implications for the pressure-volume-temperature equation of state

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**Abstract.** Room temperature static compression of MgO (periclase) was performed under nearly hydrostatic conditions using energy dispersive synchrotron X-ray diffraction in a diamond anvil cell with methanol-ethanol (to 10 GPa) or helium (to 52 GPa) as a pressure-transmitting medium. Highly precise cell parameters were determined with an average relative standard deviation  $\langle \Delta a/a \rangle = 0.0003$  over all the experimental pressure range. Fixing the bulk modulus  $K_{0T} = 160.2$  GPa, a fit of the data to the third-order Birch-Murnaghan equation of state yields:  $V_0 = 74.71 \pm 0.01 \text{ \AA}^3$ ,  $(\partial K_{0T} / \partial P)_T = 3.99 \pm 0.01$ . A fit of different P-V-T datasets, ranging to 53 GPa and 2500 K, to a Birch-Murnaghan-Debye thermal equation of state constrained the Grüneisen parameter  $\gamma = 1.49 \pm 0.03$ , but not its volume dependence  $q$ , which was constrained to  $1.65 \pm 0.4$  by thermodynamic theory. A model based on a constant value of  $q$  cannot explain the ultrahigh pressure ( $P = 174\text{--}203$  GPa) shock compression data. We developed a model in which  $q$  decreases with compression from 1.65 at 0.1 MPa to 0.01 at 200 GPa. This model, within the framework of the Mie-Grüneisen-Debye assumptions, satisfactorily describes the low-pressure static data ( $\langle \Delta V/V \rangle = 0.4\%$  to 53 GPa) and the high-pressure Hugoniot data ( $\langle \Delta V/V \rangle < 1\%$  to 203 GPa). Average values of the thermal expansion coefficient  $\alpha$  range between  $14.1 \pm 2.8$  and  $16.3 \pm 2.7 \times 10^{-6} \text{ K}^{-1}$  at  $P = 174\text{--}203$  GPa. The pressure dependence of the melting temperature yields an initial pressure derivative  $\partial T_m / \partial P = 98 \text{ K/GPa}$ . Our analysis shows that it is possible to develop a simple model of the volume dependence of the Grüneisen parameter that can successfully describe the P-V-T equation of state of MgO from ambient conditions to 203 GPa and 3663 K.

## 1. Introduction

Periclase (MgO) is a simple oxide with a cubic NaCl structure stable to megabar pressures [Vassiliou and Ahrens, 1981; Mehl et al., 1988; Duffy et al., 1995] and has been the subject of extensive experimental and theoretical study. Static compression experiments [Bridgman, 1948; Mao and Bell, 1979; Duffy et al., 1995; Fiquet et al., 1996; Utsumi et al., 1998; Fei, 1999; Dewaele et al., 2000], acoustic resonance and ultrasonic interferometry studies [Anderson and Andreatch, 1966; Chang and Barsch, 1969; Spetzler, 1970; Jackson and Niesler, 1982; Sumino et al., 1983; Isaak et al., 1989; Chen et al., 1998], shock wave experiments [Carter et al., 1971; Vassiliou and Ahrens, 1981; Svendsen and Ahrens, 1987; Duffy and Ahrens, 1995], calorimetric measurements [Robie et al., 1978; Watanabe, 1982], vibrational spectroscopy [Chopelas, 1996] and Brillouin scattering

studies [Sinogeikin and Bass, 1999; Sinogeikin et al., 2000; Zha et al., 1998], thermal expansion measurements [Suzuki, 1975; Dubrovinsky and Saxena, 1997; Fiquet et al., 1999; Zhang, 2000] have improved our knowledge of the thermal and elastic properties of this simple oxide (Figure 1). This vast amount of experimental data is also a reference for different first principles models which predict MgO properties [e.g. Hemley et al., 1985; Wolf and Bukowinski, 1988; Mehl et al., 1988; Isaak et al., 1990; Agnon and Bukowinski, 1990; Inbar and Cohen, 1995; Karki et al., 2000; Matsui et al., 2000].

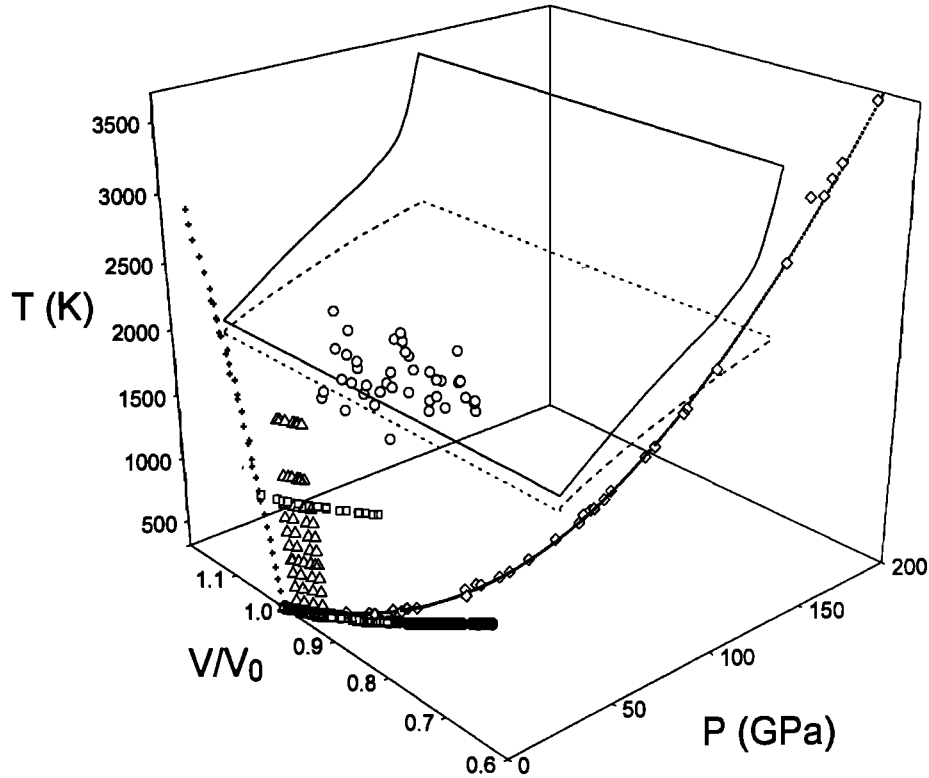
The importance of MgO arises also from its structural simplicity and its geophysical relevance as the end member of magnesiowüstite (Mg,Fe)O, a mineral which is expected to be a major constituent of the Earth's lower mantle [Stixrude et al., 1992; Jackson, 1998]. An accurate knowledge of the P-V-T properties of MgO (and FeO) is necessary to formulate those of magnesiowüstite along its compositional range.

Despite the wealth of experimental studies on MgO, there is no study that has successfully integrated all these data into a single framework that can describe the compression behavior over the entire experimental range (0–200 GPa, 300–3663 K). Two recent studies [Hama and Suito, 2000; Jacobs and Oonk, 2000] have attempted such a formulation, but as we discuss below, both use a fundamental parameter (the pressure derivative of the bulk modulus) that is inconsistent with experimental results from this and other studies. We show here that a wide-ranging thermal equation of state can

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**Figure 1.** Pressure–volume–temperature data for MgO. Solid circles, this study; pluses, *Fiquet et al.* [1999]; open triangles, *Utsumi et al.* [1998]; open squares, *Fei* [1999]; open circles, *Dewaele et al.* [2000]; open diamonds, shock compression data [*Carter et al.*, 1971; *Vassiliou and Ahrens*, 1981; *Svensen and Ahrens*, 1987; *Duffy and Ahrens*, 1995]; The dashed line is the P-V-T Hugoniot curve. The dashed and the solid surfaces are the model adiabatic P-T profiles of *Brown and Shankland* [1981] and *Stacey* [1977], respectively, for the Earth's lower mantle extended over the experimental compression range.

be developed by a modification of the Debye-Grüneisen model and that the equation of state derived is qualitatively consistent with the results of first principles studies. Such a thermal equation of state describing all the available experimental data makes MgO a candidate to become a standard for high-pressure/high-temperature experiments.

## 2. Pressure–Volume–Temperature Equations of State

### 2.1. Static Equation of State

The equation of state of crystalline materials is necessary to describe their properties over the range of pressure and temperature encountered in the earth and is relevant to the interpretation of the structure of terrestrial planetary interiors.

It can be assumed that the pressure,  $P$ , in a solid is the summation of static ( $T = 0$  K), vibrational and electronic (both temperature-dependent) terms. The electronic term is generally negligible in insulators such as MgO in the pressure-temperature range of geophysical interest. The P-V-T equation of state can then be written

$$P(V,T) = P(V,T_0) + \Delta P_{th}(V,T), \quad (1)$$

where  $P(V,T_0)$  is the pressure component at a reference temperature  $T_0$ , generally fixed at 300 K, and  $\Delta P_{th}$  is the thermal pressure (the pressure produced by the change of temperature from  $T_0$  at constant volume).

The formulation of the isothermal equation of state,  $P(V,T_0)$ , adopted in our model is the Eulerian Birch-Murnaghan equation, derived through an expansion of free energy  $F$  in Taylor series in strain  $f$  [*Birch*, 1947]. The thermal pressure term ( $\Delta P_{th}$ ) is expressed by the Mie-Grüneisen equation [*Grüneisen*, 1926]

$$P_{th}(V,T) - P_{th}(V,T_0) = [\gamma(V)/V] [E_{th}(V,T) - E_{th}(V,T_0)], \quad (2)$$

where the subscript 0 refers to the principal isotherm (300 K). The Grüneisen parameter  $\gamma$  defined as:  $\gamma = -V(\partial P/\partial E)_v$ , is assumed to be independent of temperature and its volume dependence  $q = (\partial \ln \gamma / \partial \ln V)_T$ , is generally fixed with values between 0.5 and 1.5 for metals and minerals [*Carter et al.*, 1971; *Boehler and Ramakrishnan*, 1980, *Duffy and Ahrens*, 1995].

The Debye model gives a simple form for the characterization of the vibrational spectrum and the thermal free energy,  $E_{th}$ , of a crystal. All the vibration modes are described as a unique acoustic phonon branch such that [*Debye*, 1912]

$$E_{th} = \frac{9nRT}{(\theta/T)^3} \int_0^{\theta/T} \frac{\xi^3}{e^\xi - 1} d\xi, \quad (3)$$

$$\theta = \theta_0 \exp[(\gamma_0 - \gamma)/q], \quad (4)$$

where  $n$  is the number of atoms per formula unit,  $R$  is the gas constant and  $\theta$  is the Debye temperature.

## 2.2. Shock Compression

Shock wave propagation is a powerful method to investigate extreme P-V-T conditions [McQueen *et al.*, 1970; Ahrens, 1980]. In this technique, a shock wave is generated by a fast impact of a flyer plate with a stationary target. A one-dimensional shock pulse propagates through the two plates at a shock velocity,  $U_S$ , relative to the uncompressed material while the velocity of the material behind the shock front is  $u_p$  (particle velocity). The mass, momentum, and energy conservation along the shock front give the Rankine-Hugoniot equations which relate  $U_S$  and  $u_p$  to thermodynamic variables  $P$ ,  $V$  and specific internal energy,  $E$  [McQueen *et al.*, 1970].

The  $U_S$  and  $u_p$  velocities are linearly related, in many materials, over large ranges of compression. This empirical relation is called the shock wave equation of state

$$U_S = c_0 + s u_p, \quad (5)$$

where  $c_0$  is equal to the bulk sound velocity at zero compression. Shock temperature is deduced from the thermodynamic law [McQueen *et al.*, 1970]

$$dU = T\delta S - P\delta V = C_V dT + TC_V dV/V - PdV, \quad (6)$$

which can be solved for  $T$ . The Grüneisen parameter ( $\gamma$ ) is considered independent of temperature and its volume dependence ( $q$ ) is generally considered constant and equal to 1.  $C_V$  is taken constant and equal to  $3R$  (Dulong-Petit limit), or it is calculated using Debye theory. The 300 K isotherm can be calculated following the model used by Jamieson *et al.* [1982] as

$$P_{300K}(V) = P_{0K}(V) + P_{th300K}(V), \quad (7)$$

where  $P_{th300K}(V)$  is the thermal pressure along the 300 K isotherm and  $P_{0K}$ , the 0 K isotherm, is calculated as the difference between the Hugoniot pressure and the thermal pressure contribution along the Hugoniot

$$P_{th} = \gamma E_{th}/V, \quad (8)$$

where  $E_{th}$  is the thermal energy calculated applying the Debye model.

## 3. Experimental Method

Pure MgO powder was compressed to 52 GPa at room temperature using a symmetric diamond anvil cell with 350  $\mu\text{m}$  culets. Two experiments were carried out under quasi-hydrostatic conditions. The first run used a mixture of methanol and ethanol and the second run used helium as a pressure transmitting medium. Energy dispersive synchrotron X-ray diffraction was performed at the X17C beam line of the National Synchrotron Light Source.

In both the experiments MgO was loaded in a rhenium gasket drilled with a 150  $\mu\text{m}$  hole. In the first experiment, MgO, loaded with a mixture of ethanol and methanol, was compressed to a final pressure of 10 GPa. The helium-medium experiment was carried out to a maximum pressure of 52 GPa. Pressure was determined by ruby fluorescence measurements before and after each run. The precision of pressure measurement is  $\pm 0.1$  GPa along the entire experimental pressure range. Experimental data are summarized in Table 1. The experimental data reported here

**Table 1. X-ray Diffraction Data for MgO<sup>a</sup>**

Pressure, GPa	$V$ , Å <sup>3</sup>	Pressure Medium
0.8	74.442 (22)	ME
1.3	74.032 (20)	ME
3.1	73.267 (13)	ME
4.5	72.649 (19)	ME
5.7	72.165 (18)	ME
6.6	71.729 (28)	ME
7.6	71.336 (12)	ME
8.3	71.153 (15)	ME
9.5	70.727 (18)	ME
10.0	70.699 (19)	ME
5.7	72.188 (43)	He
8.7	71.212 (22)	He
10.6	70.459 (15)	He
12.5	69.849 ( 7)	He
16.0	68.719 (12)	He
18.1	67.937 (16)	He
20.1	67.479 (12)	He
21.9	67.038 (98)	He
24.0	66.398 (19)	He
26.4	65.851 (17)	He
29.1	65.133 (19)	He
31.2	64.626 (30)	He
33.2	64.200 ( 2)	He
35.2	63.780 (15)	He
37.1	63.353 (12)	He
39.4	62.884 ( 9)	He
41.7	62.393 (11)	He
43.3	61.985 (26)	He
46.8	61.349 ( 9)	He
48.3	61.053 (21)	He
50.4	60.625 (13)	He
52.2	60.301 (16)	He

<sup>a</sup>Numbers in parentheses are 1 standard deviation uncertainty in the last digits. ME, methanol-ethanol mixture.

were also used in a related Brillouin scattering study of MgO [Zha *et al.*, 1998].

## 4. Results

### 4.1. Experimental Results

In both experiments, the (111), (200), (220), (311), (222), (400), (420), (442) diffraction peaks were resolved for MgO and used to determine the unit cell parameter. Figure 2 shows representative X-ray diffraction patterns from the two experiments. It has been shown that uniaxial compression in diamond anvil cell could result in a deviatoric stress in the sample [e.g., Kinsland and Bassett, 1976]. The shear stress that is produced can be related to the difference in the lattice parameters from different diffraction lines [Singh, 1993; Duffy *et al.*, 1995].

In both the experiments, lattice parameters measured using single lines show a random deviation from the average values obtained by fitting all the lines (Figure 3). An exception is the (111) line whose fitting suffers the effect of a rising background. The average deviation for all the measurements is  $0.03 \pm 0.03\%$  of the fit value. This result confirms that nearly hydrostatic conditions are obtained when using helium as a pressure transmitting medium [Bell and Mao, 1981] and that very high precision values of lattice parameters can be obtained using energy dispersive diffraction under such conditions. The deviation in a nonhydrostatic compression experiment for MgO is monotonically increasing to 0.3% or more in the same pressure range (Figure 4).

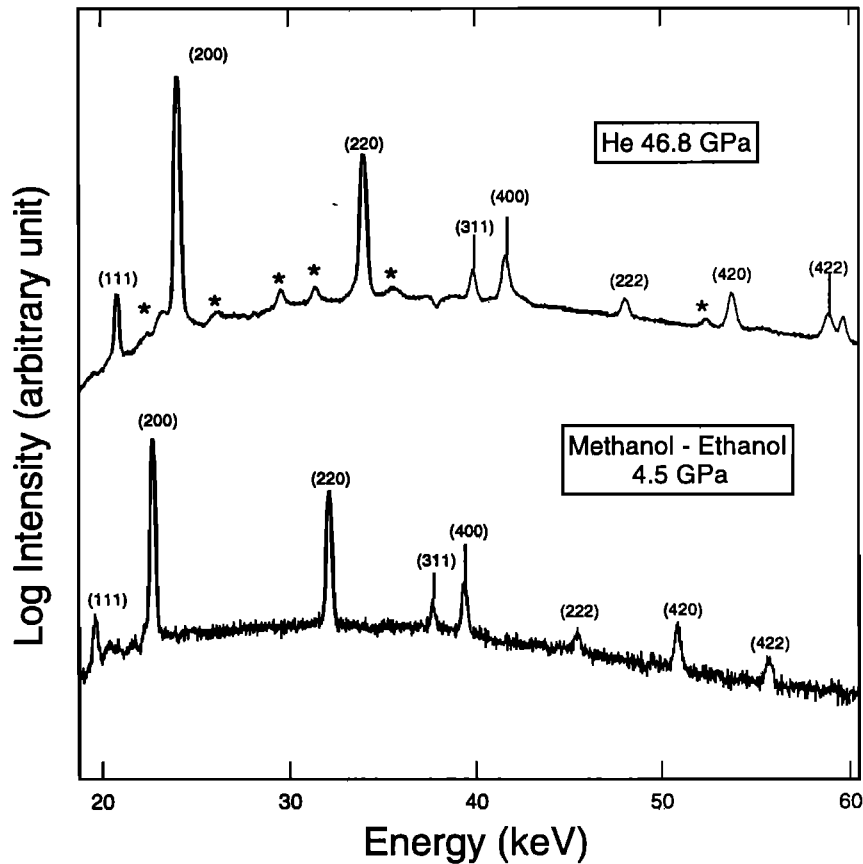


Figure 2. Examples of X-ray diffraction patterns. MgO lines are labeled with (hkl) value. The asterisks indicate diffraction lines of the rhenium gasket.

#### 4.2. Fit Parameters for the Principal Isotherm

A fit of the experimental data to the third-order Birch-Murnaghan equation yields:  $K_{0T} = 170 \pm 1$  GPa,  $K_{0T}' = 3.59 \pm 0.04$ , with a fit  $V_0 = 74.53 \pm 0.02$ , where  $K_{0T}$  is the isothermal bulk modulus ( $-V(\partial P/\partial V)_T$ ),  $K_{0T}' = (\partial K_{0T}/\partial P)_T$ , and  $V_0$  is the unit cell volume, all defined at standard conditions. By fixing  $K_{0T} = 160.2 \pm 0.2$  GPa from high-precision sound velocity measurements (Table 2) we can obtain:  $K_{0T}' = 3.99 \pm 0.01$  and  $V_0 = 74.71 \pm 0.01$ . The result of this second fit is compared to other equations of state from different techniques in Figure 5. Our fitting is in good agreement with the other models except for the *Utsumi et al.* [1998] 300 K isotherm, for which an anomalously low bulk modulus is obtained (Table 2).

### 5. Discussion

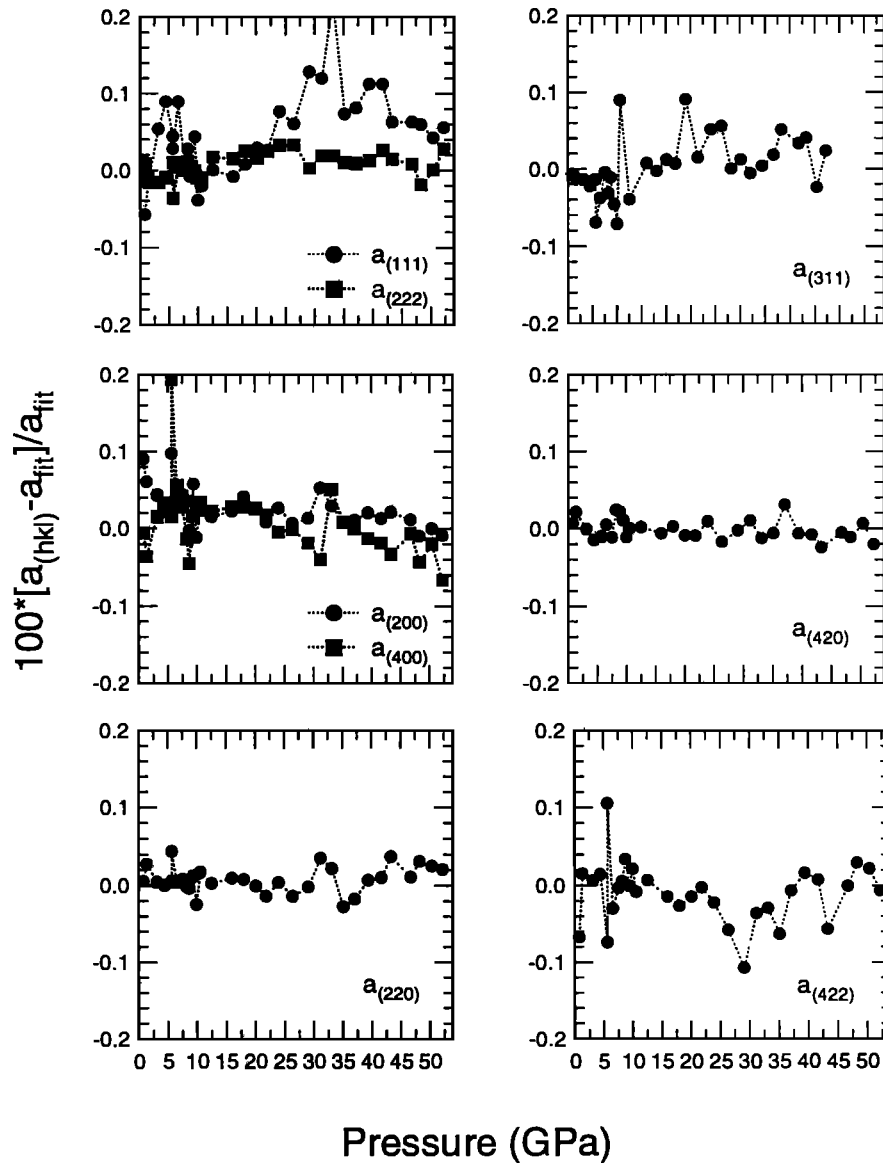
#### 5.1. Fit of Thermal Equation of State

Three high-temperature static compression data sets ranging to 53 GPa and 2500 K [*Utsumi et al.*, 1998; *Fei*, 1999; *Dewaele et al.*, 2000] and thermal expansion data at 0.1 MPa of *Fiquet et al.* [1999], which are in substantial agreement with *Suzuki* [1975] but cover a wider temperature range (300-3000 K), have been fit to a Birch-Murnaghan-Debye equation of state where  $q$  is assumed constant (Table 3). *Fei* [1999] reported high-temperature data using two different pressure standards (NaCl and Au), which have a significant disagreement (6% at 24 GPa and 1100 K). This highlights the fundamental importance of pressure calibration

at in situ high P-T conditions. The adoption of the Au pressures produces negative values of  $q$  (Table 3).

We fixed the parameters determined from the room temperature isotherm [ $V_0$ ,  $K_{0T}$ ,  $(\partial K_{0T}/\partial P)_T$ ] and the Debye temperature ( $\theta_0$ ) was fixed to 773 K [*Watanabe*, 1982] (heat capacity measurement). The average fit values of the Grüneisen parameter  $\gamma_0$  and its volume dependence  $q$  are  $1.49 \pm 0.03$  and  $0.8 \pm 0.6$ . The value of  $\gamma_0$  is in excellent agreement with the value of  $1.524 \pm 0.025$ , calculated using the thermodynamic identity  $\gamma_0 = \alpha_0 K_{0T} / \rho_0 C_P$  ( $\alpha_0 = 31.2 \pm 0.6 \times 10^{-6} \text{ K}^{-1}$  from *Suzuki* [1975];  $C_P = 928 \text{ J Kg}^{-1} \text{ K}^{-1}$  from *Garvin et al.* [1987]). For this reason, we fixed the value of the Grüneisen parameter to 1.524. *Utsumi et al.*'s [1998] data are incompatible with the data of *Fei* (NaCl pressure scale), *Dewaele et al.* [2000] and *Fiquet et al.* [1999] in that fixing  $\gamma_0$  and the parameters determined from our room temperature isotherm, the former constrain  $q$  to  $5.8 \pm 2.2$ , while the latter constrain  $q$  to  $2.1 \pm 1.0$ ,  $1.3 \pm 0.5$  and  $1.0 \pm 0.4$ , respectively (Table 3). A combined fit to the *Dewaele et al.* [2000], *Fiquet et al.* [1999] and *Fei*'s [1999] data sets yields  $q = 1.3 \pm 0.5$ .

To reduce the uncertainty in the  $q$  fit value, it is necessary to apply the fitting to a dataset covering a wide pressure-temperature range [*Shim and Duffy*, 2000]. Shock wave data cover a wide pressure-volume range but the calculated temperature on the Hugoniot depends mainly on the value of specific heat at constant volume ( $C_V$ ). *Svendsen and Ahrens* [1987] report four P-V-T shock data where temperature is directly measured by recording the spectrum of shock-induced thermal radiation. We used the *Svendsen and Ahrens* data in



**Figure 3.** MgO lattice parameter calculated using a single line ( $a_{(hkl)}$ ) normalized to the average value obtained by fitting all the lines ( $a_{fit}$ ).

combination with *Fei's* [1999] and *Suzuki's* [1975] data to constrain  $q$  in the fit to Birch-Murnaghan-Debye equation. The result of the combined fit is unreasonable as it produces a negative  $q$  (Table 3).

A rigorous constraint on  $q$  along an isotherm is derived by *Bassett et al.* [1968]

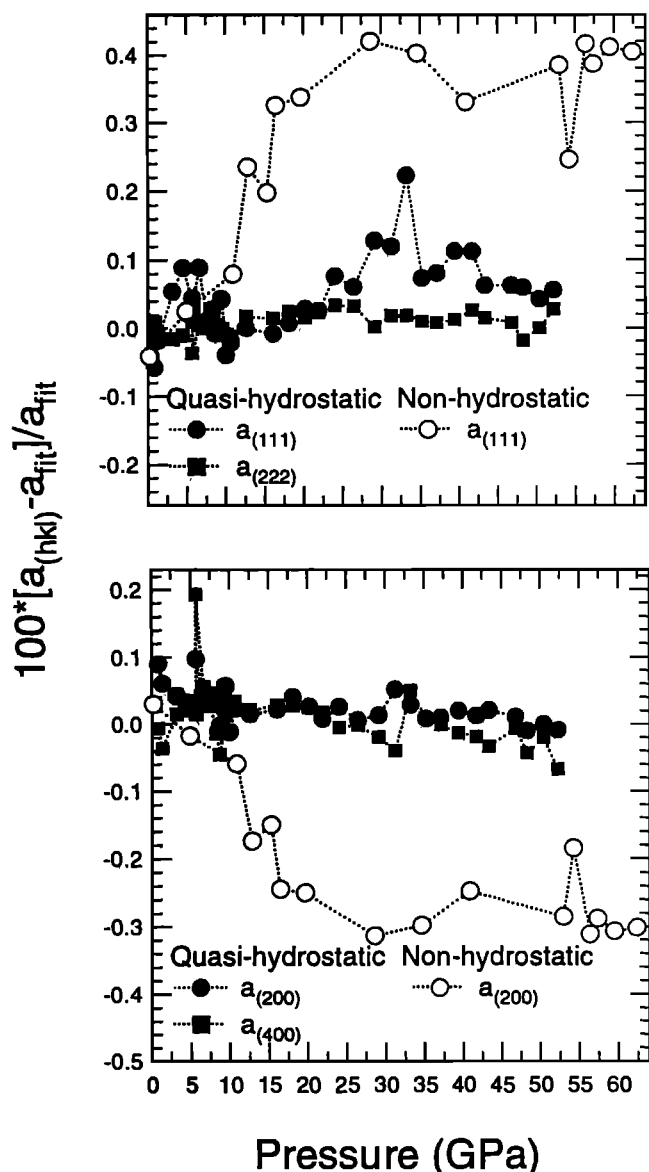
$$q = (\partial \ln \gamma / \partial \ln V)_T = (\partial \ln \alpha / \partial \ln V)_T + (\partial \ln K_T / \partial \ln V)_T + 1 - (\partial \ln C_V / \partial \ln V)_T, \quad (9)$$

and the thermodynamic theory of the Grüneisen parameter developed by *Anderson et al.* [1993]. The value of  $q$  consistent with the parameters of our 300 K equation of state is  $1.65 \pm 0.4$  ( $(\partial \ln \alpha / \partial \ln V)_T = 5.48 \pm 0.12$ ,  $K_{0T} = 160.2 \pm 0.3$  GPa;  $(\partial \ln K_T / \partial \ln V)_T = -3.99 \pm 0.01$ ;  $(\partial \ln C_V / \partial \ln V)_T = 0.846 \pm 0.034$ ; see *Anderson et al.* [1993] for details on the derivation). This value of  $q$  is also consistent with the fit results of the static compression data (Table 3). It is also in

reasonable agreement with the value of  $q = 1.3$  proposed by *Jackson* [1998], constrained by the high temperature acoustic data at room pressure [*Sumino et al.*, 1983; *Isaak et al.*, 1989]. Selected isotherms calculated with the Birch-Murnaghan-Debye equation, which fit data to 24 GPa and 1100 K, using our model parameters, are plotted in Figure 6. The calculated isotherms using  $q = 1.65$  are inconsistent with the shock wave data ( $T = 3071$ - $3663$  K at  $P = 174$ - $203$  GPa), as shown in the inset of Figure 6.

## 5.2. Using Hugoniot Equation of State to Constrain $\gamma$ and $q$

The Birch-Murnaghan-Debye equation of state well describes the static compression data (to 53 GPa and 2500 K) when the thermoelastic parameters  $\gamma$  and  $q$  are fixed to their thermodynamic values. Yet it fails in describing the available high-pressure, high-temperature shock wave data ( $\Delta V/V = 2.6$ - $2.9\%$  at  $P = 174$ - $203$  GPa,  $T = 3071$ - $3663$  K). It is



**Figure 4.** Comparison between single line lattice parameter measured under quasi-hydrostatic (this study) and nonhydrostatic experimental conditions (S.-H. Shim and T.S. Duffy, unpublished data, 1999).

important to analyze the high-pressure region explored by shock wave experiments to test the validity of a unique equation of state for the entire stability field of MgO.

A constraint on  $q$  can be obtained using the relation between Hugoniot and the principal isentrope through the Mie-Grüneisen theory. The resulting best fit theoretical Hugoniot calculated by *Duffy and Ahrens* [1993] using the definition of the Grüneisen parameter requires  $q = 0.3 \pm 0.7$ .

In this study we perform a more straightforward comparison of our fit 300 K isotherm with the 300 K isotherm reduced from the available shock wave data [*Carter et al.*, 1971; *Vassiliou and Ahrens*, 1981; *Svendsen and Ahrens*, 1987; *Duffy and Ahrens*, 1995] under the assumption that  $\gamma(V) = \gamma_0(V/V_0)^q$  with  $q$  constant under compression. Due to the intrinsic uncertainty of the Hugoniot volume data, the estimated volume uncertainty on the reduced 300 K isotherm is  $\Delta V/V \cong 1.0\%$  at  $P = 200$  GPa. Thus we adopt  $\Delta V/V = 1\%$  as our criterion for agreement of shock data to the extrapolated 300 K Birch-Murnaghan isotherm. The high-pressure extrapolation of our Birch-Murnaghan 300 K isotherm is inconsistent with that reduced from shock waves for  $q = 1.65$  ( $\Delta V/V = 3.0\%$  at  $P = 200$  GPa), but the agreement is excellent if  $q$  is fixed to the value of 0 ( $\Delta V/V = 0.2\%$  at  $P = 200$  GPa; Figure 7). These results are evidence that the  $q$  value affects the P-V Hugoniot curve at high pressure and strong compression. In fact, the fitting to the Debye model thermal equation of state describes all the static compression data to 53 GPa and 2500 K with a  $q$  value of 1.65, but it is not in agreement with Svendsen and Ahrens shock wave temperatures unless  $q = 0$  is used (inset of Figure 6). The assumption of  $q = 0$  implies that  $\gamma$  is in disagreement with the theoretical high compression limit for the Thomas-Fermi free electron gas,  $\gamma = 2/3$  [*Zharkov and Kalinin*, 1971] and the limit values calculated in the same approximation for bcc and fcc crystal lattices (0.543 and 0.547, respectively [*Kopyshv*, 1965]).

### 5.3. Comparison of Different Equations of State

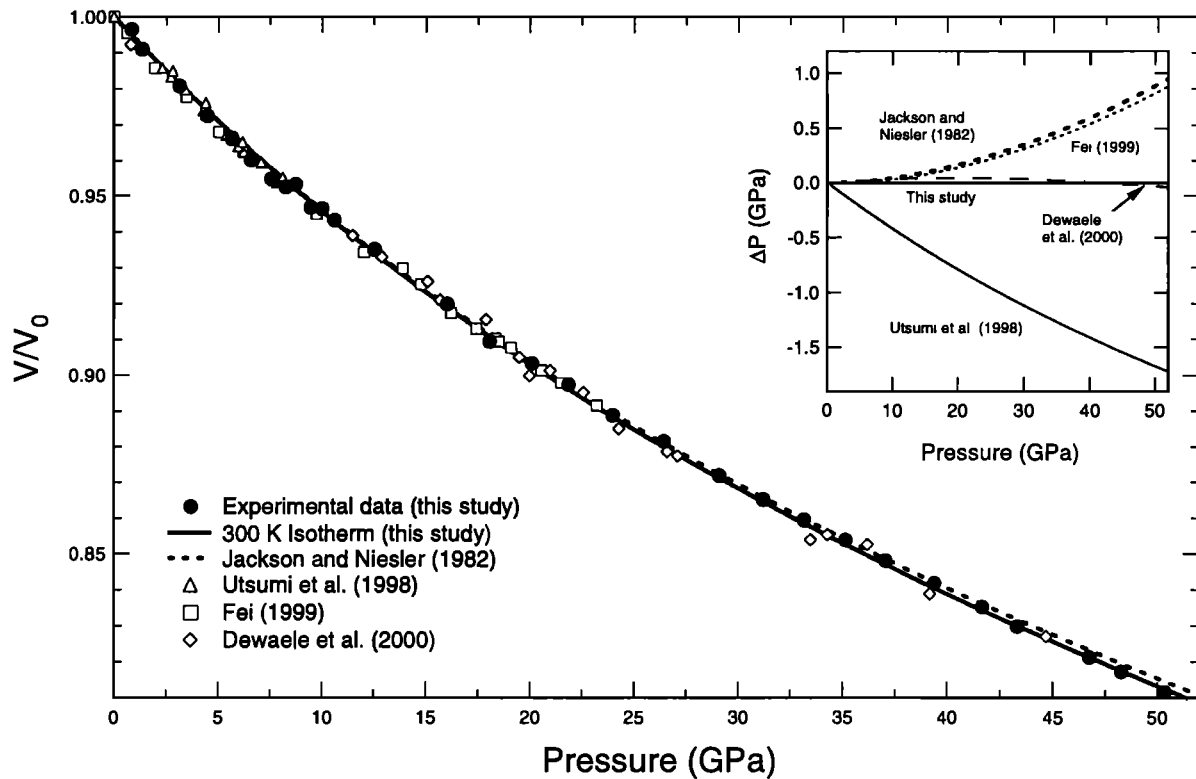
A possible explanation for the discrepancy between static and shock data might be the error introduced in the extrapolation of the third-order Birch-Murnaghan equation from 52 to 200 GPa, therefore other phenomenological equation of state functions were tested on our data set. A fit to the Vinet universal equation [*Vinet et al.*, 1986; 1989] yielded

**Table 2.** Elastic Parameters of MgO

Study	$V_0, \text{\AA}^3$	$K_{0r}, \text{GPa}$	$(\partial K_{0r} / \partial P)_T$
This study	74.71 (1)	160.2 <sup>a</sup>	3.99 (1)
<i>Anderson and Andreatch</i> [1966]	74.71	159.8 <sup>b</sup>	4.52 <sup>b</sup>
<i>Spetzler</i> [1970]	74.71	160.5 <sup>b</sup>	3.89 <sup>b</sup>
<i>Vassiliou and Ahrens</i> [1981]	74.74	161.4 <sup>a</sup>	4.29 (3)
<i>Jackson and Niesler</i> [1982]	74.70	160.2 (2) <sup>b</sup>	4.15 (9) <sup>b</sup>
<i>Sumino et al.</i> [1983]	74.61	161 (1)	
<i>Isaak et al.</i> [1989]	74.7 (1)	161.6 (6)	
<i>Yoneda</i> [1990]		160.4 (2) <sup>b</sup>	4.15/4.26 <sup>b</sup>
<i>Utsumi et al.</i> [1998]	74.71	153 (3)	4.1 (11)
<i>Fei</i> [1999]	74.78	160 (2)	4.15 <sup>a</sup>
<i>Sinogeikin and Bass</i> [1999]		160.9 (10) <sup>b</sup>	4.02 (10) <sup>b</sup>
<i>Dewaele et al.</i> [2000]	74.71	161 <sup>a</sup>	3.94 (20)

<sup>a</sup>Fixed parameter.

<sup>b</sup>Converted to isothermal conditions.



**Figure 5.** The 300 K third-order Birch-Murnaghan equation ( $V_0 = 74.71 \pm 0.01 \text{ \AA}^3$ ,  $K_{0T} = 160.2 \pm 0.2 \text{ GPa}$ ,  $K'_{0T} = 3.99 \pm 0.01$ ) fit to present data plotted with other 300 K static compression data. The uncertainties on the data points are smaller than the symbols. The inset shows the difference between 300 K isotherms from the literature and our model ( $\Delta P$ ).

$K_{0T} = 160.2 \pm 0.1 \text{ GPa}$ ,  $K'_{0T} = 4.12 \pm 0.06$ , a fit to Poirier's logarithmic equation [Poirier and Tarantola, 1998] gave  $K_{0T} = 160.2 \pm 0.6 \text{ GPa}$ ,  $K'_{0T} = 4.21 \pm 0.05$ . We have also calculated the 300 K isotherm applying the two parameter Holzappel's [1991] equation of state with the assumption that MgO behaves at high pressure as a "simple" solid characterized by an average atomic number  $\langle Z \rangle = 10$  and mean atomic volume at zero pressure  $\langle V_0 \rangle = 9.338 \pm 0.001 \text{ \AA}^3$ . All of these calculated and fitted isotherms show good agreement with our preferred model to 52 GPa, but their extrapolations to higher pressure regimes fail to reproduce the reduced shock wave isotherm (Figure 8). Both the logarithmic and the Vinet equations, when extrapolated to 200 GPa, yield an equation of state more compressible than

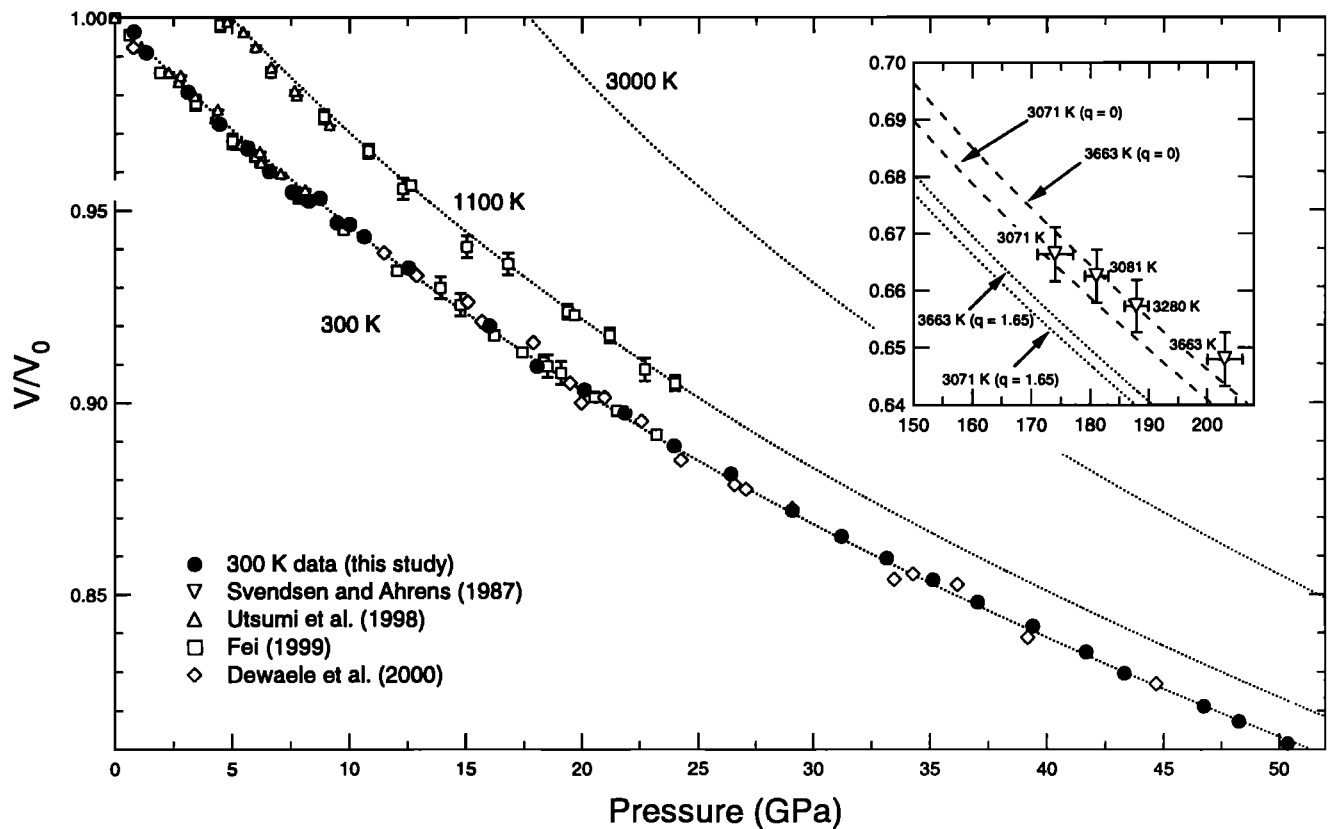
the Birch-Murnaghan and increase the discrepancy with the reduced shock isotherm. The Holzappel equation is slightly less compressible than the Birch-Murnaghan, and marginally improves the fit (Figure 8).

The only other studies that attempted to formulate a wide range P-V-T equation of state for MgO were the work of Hama and Suito [1999] and the work of Jacobs and Oonk [2000]. The former model is almost successful in describing the P-V relationship of the shock wave derived isotherm, but it is inconsistent with the experimental dataset presented in this study (8% difference in pressure at 52 GPa; inset in Figure 8) because of the value  $(\partial K_{0T} / \partial P)_T = 4.52$  used by the two authors, which is inconsistent with the most recent experimental results (Table 2). Similar comment apply to the

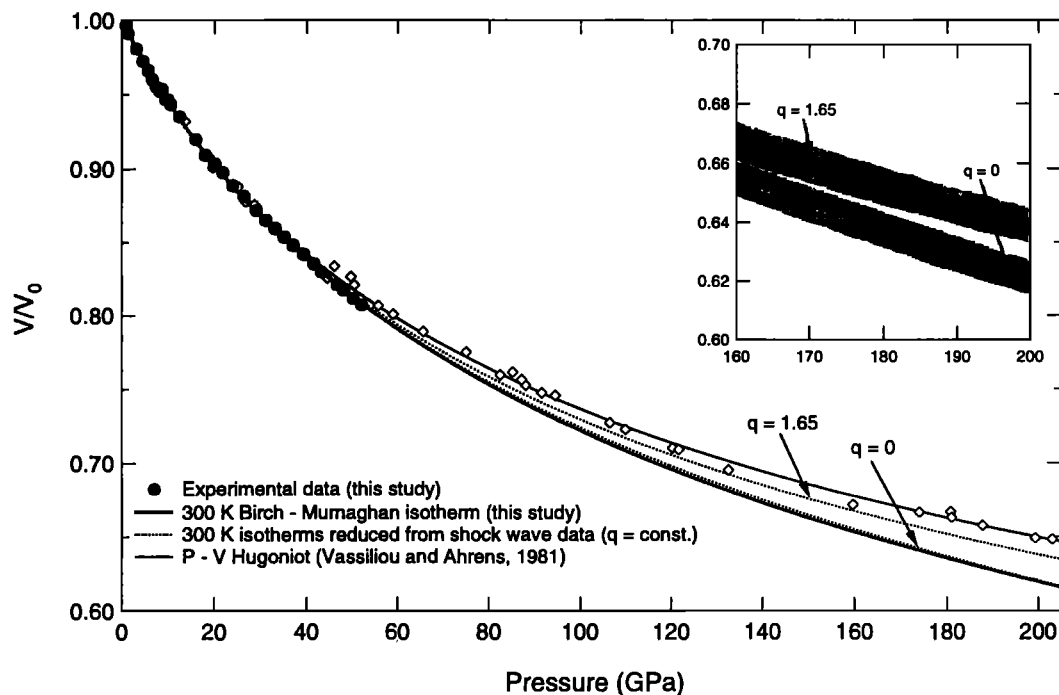
**Table 3.** Results of Fits to the Birch-Murnaghan-Debye Equation of State for MgO<sup>a</sup>

Data Sets	$P_{\max}$ , GPa	$q$
UT	(10)	5.8 (22)
FI	(10 <sup>-4</sup> )	1.0 (4)
DE	(53)	1.3 (5)
FE (NaCl P standard)	(24)	2.1 (10)
FE (Au P standard)	(25)	-1.2 (8)
FI + DE + FE	(10 <sup>-4</sup> ) - (53) - (25)	1.3 (5)
SA + DE + FE + FI	(203) - (53) - (25) - (10 <sup>-4</sup> )	-0.32 (4)

<sup>a</sup>SA, Svendsen and Ahrens [1987]; UT, Utsumi et al. [1998]; FE, Fei [1999]; FI, Fiquet et al. [1999]; DE, Dewaele et al. [2000]. Fixed parameters:  $V_0 = 74.71 \text{ \AA}^3$ ,  $K_{0T} = 160.2 \text{ GPa}$ ,  $(\partial K_{0T} / \partial P)_T = 3.99$ ,  $\theta_0 = 773 \text{ K}$ ,  $\gamma_0 = 1.524$ .

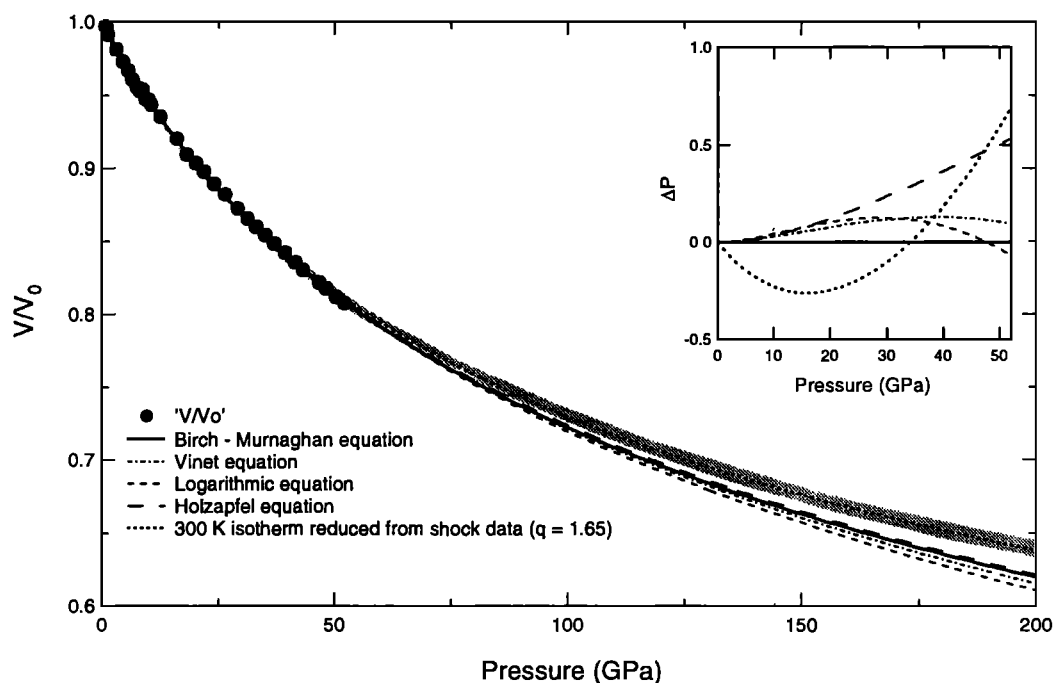


**Figure 6.** Isotherms calculated using Birch-Murnaghan-Debye model. Parameters are  $V_0 = 74.71 \pm 0.01 \text{ \AA}^3$ ,  $K_{0T} = 160.2 \pm 0.2 \text{ GPa}$ ,  $K_{0T} = 3.99 \pm 0.01$ ,  $\gamma_0 = 1.524 \pm 0.025$ ,  $q_0 = 1.65 \pm 0.3$ ,  $\theta_0 = 773 \text{ K}$ . The inset compares the extrapolated model to shock compression data [Svendsen and Ahrens, 1987] for different values of  $q$ . The error bars are  $1\sigma$  uncertainties.



**Figure 7.** Comparison of the 300 K isotherm from our model with the calculated 300 K isotherms reduced from shock wave data for different values of  $q$ . The shaded areas represent  $1\sigma$  volume uncertainties on the associated curves. The open diamonds are the experimental pressure-volume shock states for MgO (see references in the text).





**Figure 8.** The 300 K isotherms from different equations of state, extrapolated to multi megabar pressure in comparison with the 300 K isotherm reduced from the shock compression data. The inset shows the difference between the different models and our preferred fit to the third-order Birch-Murnaghan equation over the experimental static pressure range.

work of *Jacobs and Oonk* [2000] who present a value of  $(\partial K_{0T}/\partial P)_T = 4.769$ .

#### 5.4. Relevance of the Grüneisen Parameter

A correct expression of the volume dependence of  $\gamma$  is crucial to reconcile the experimental data from static compression and shock waves. Amongst theoretical models which describe the volume dependence of  $\gamma$ , the relationship  $\gamma(V) = \gamma_0(V/V_0)^q$  with constant  $q$  is not general [*Boehler*, 1983; *Shaner*, 1988; *Anderson et al.*, 1993]. In addition, in this commonly accepted formulation of its volume dependence, the infinite-pressure limit of the Grüneisen parameter is forced to be 0 for every nonzero constant, positive value of  $q$ , in contrast with the theory. One possible solution is that  $q$  itself varies with volume as it has been suggested in theoretical studies [*Anderson et al.*, 1993; *Inbar and Cohen*, 1995; *Karki et al.*, 2000].

*Anderson et al.* [1993] proposed a thermodynamic model for the Grüneisen parameter, calculated  $\gamma$  and  $q$  variation along some isotherms for MgO and suggested that  $(\partial C_V/\partial V)_T$  is near zero in the conditions relevant for lower mantle models. It should be noted that their results are completely dependent on a description of  $(\partial K_T/\partial T)_V$  that they derive from a theoretical model [*Isaak et al.*, 1990].

Quasi-harmonic lattice dynamics calculations using nonempirical potentials [*Isaak et al.*, 1990; *Inbar and Cohen*, 1995] predict the behavior of  $q$  with compression and with temperature. *Isaak et al.* found that at 300 K,  $q$  decreases from 1.4 to 0.9 from 0 to 60 GPa ( $V/V_0$  from 1 to 0.8) and then it remains constant till 150 GPa. They also estimated a steeper variation at 2000 K, from 1.6 to 0.8 over the pressure range 0-50 GPa ( $V/V_0$  from 1 to 0.85) and to 0.6 at  $P = 100$  GPa ( $V/V_0 = 0.75$ ). *Inbar and Cohen's* [1995] model (see also *Cohen*,

[2000]) predicts, at 1000 K, a decrease of  $q$  from 1 to 0 from  $V/V_0 = 1$  to  $V/V_0 = 0.6$  (Figure 9).

We developed a model for the description of the volume dependence of the Grüneisen parameter in analogy with *Jeanloz* [1989]

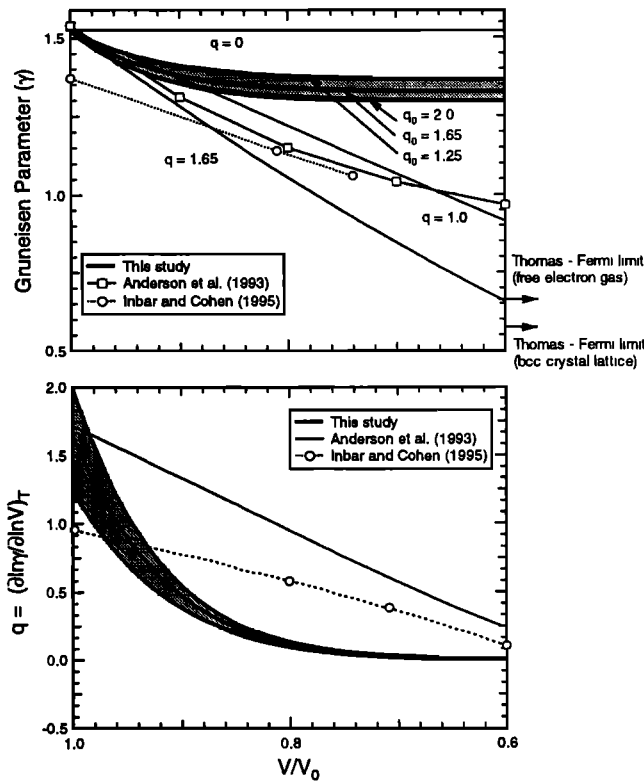
$$q = q_0 \left( \frac{V}{V_0} \right)^{q_1}, \quad (10)$$

from which

$$\gamma = \gamma_0 \exp \left\{ \frac{q_0}{q_1} \left[ \left( \frac{V}{V_0} \right)^{q_1} - 1 \right] \right\}, \quad (11)$$

where  $q_0$  and  $q_1$  are constant. The value of  $q_0$  (standard conditions) is constrained by the thermodynamic theory to  $1.65 \pm 0.4$  while the value of  $q_1$  is constrained at  $11.8 \pm 0.2$  by the value of  $q(V_{200}) = 0.01$  (where  $V_{200}$  is the specific volume at  $P = 200$  GPa) which gives the best approximation of the Birch-Murnaghan-Debye equation to *Svendsen and Ahrens'* [1987] Hugoniot data, with a tolerance of 6 GPa (or  $\Delta V/V = 1\%$ ).

The 300 K isotherm calculated reducing the shock data shows  $\Delta V/V = 0.1\%$  at 10 GPa, 1.1% at 200 GPa from the best fit to the static data (Figure 10). The model presents an average  $\langle \Delta V/V \rangle = 0.4\%$  from the experimental data of *Fei* [1999] and *Dewaele et al.* [2000], in the range 0-53 GPa, 300-2500 K. In this model the Grüneisen parameter decreases monotonically from 1.524 to 1.33, and  $q$  decreases from 1.65 to 0.01 in the pressure range between 0 and 200 GPa (Figure 9). This result confirms that the different constant  $q$  fits are representative of bulk averages of the pressure dependence of



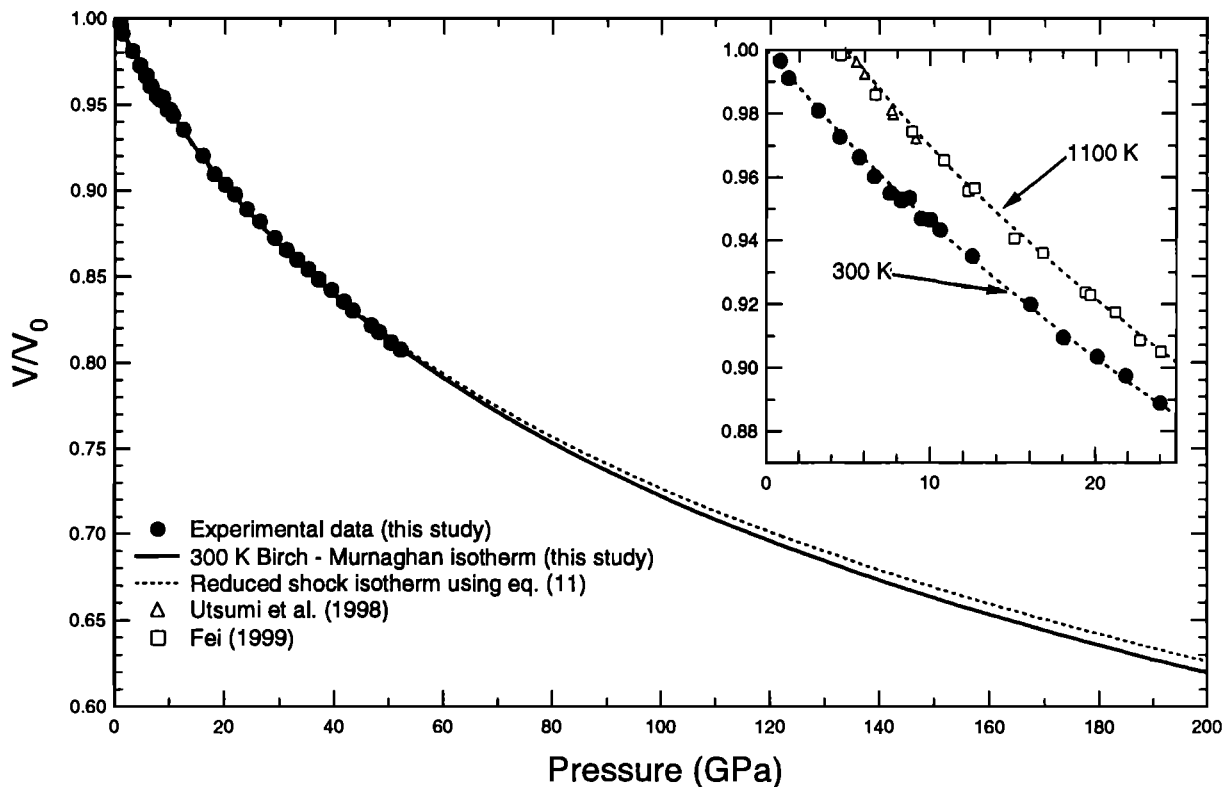
**Figure 9.** Variation with compression of the Grüneisen parameter ( $\gamma$ ) and its volume dependence ( $q$ ) using the model presented in this study, compared with different theoretical models and with three values of constant  $q$ . The shaded area represents the range of possible model values expressing the uncertainty on the best model  $q_0$  parameter.

the Grüneisen parameter restricted to the fitted pressure range (Table 2).

The model for the volume dependence of  $\gamma$  proposed by Anderson *et al.* [1993] was tested reducing the shock data to the 300 K isotherm. We also tested Inbar and Cohen's [1995] model calculating the Grüneisen parameter from  $q(V)$  [Cohen, 2000]. Both the models do not satisfy the criterion for agreement with the fit 300 K ( $\Delta V/V \leq 1\%$ ) that we fixed before. The first model shows a volume difference ( $\Delta V/V$ ) from our best fit 300 K Birch-Murnaghan isotherm equal to 2.7% at 200 GPa. Inbar and Cohen's model gives a similar result ( $\Delta V/V = 2.6\%$  at 200 GPa). Both these models allow a variation of  $q$  with volume ( $q = 1.7$  at  $V = V_0$ ,  $q = 0.24$  at  $V/V_0 = 0.6$  in Anderson *et al.*'s model,  $q = 1 - 0.1$  in Inbar and Cohen's model) and describe a smooth monotonic decrease of the Grüneisen parameter ( $\gamma = 1.53 - 0.98$  in Anderson *et al.*'s model,  $1.37 - 1.02$  in Inbar and Cohen's model) within the compression range analyzed in this work. While our results are consistent with these studies in that  $q$  decreases with compression, a much stronger decrease of  $q$  is required to satisfy both the ambient pressure thermodynamic data and the high-pressure shock data.

## 6. Melting Curve of MgO

Knowing the melting temperature of MgO at high pressure is important for understanding the thermal environment of the lower mantle. The experimental results of Zerr and Boehler [1994] strongly differ from thermodynamic estimations [Jackson, 1977; Ohtani, 1983] and from theoretical simulations [Belonoshko and Dubrovinsky, 1996; Vocadlo and Price, 1996; Cohen and Weitz, 1998]. The experimentally



**Figure 10.** Comparison of the 300 K isotherm from our model with the calculated 300 K isotherm from shock wave data adopting the volume dependence of the Grüneisen parameter expressed by equation (11) (see text). In the inset the 1100 K isotherm from the model is compared with the existing experimental data.

observed initial  $\partial T_m / \partial P$  (36 K/GPa [Zerr and Boehler, 1994]) is lower than the calculated values (80 K/GPa [Ohtani, 1983; Belonoshko and Dubrovinsky, 1996], 114 K/GPa, Jackson, 1977, and 110 K/GPa [Cohen and Weitz, 1998]).

The extrapolation of the melting curve of minerals to high pressures and temperatures is based on empirical equations like the Simon equation [Simon and Glatzel, 1929] and the Kraut and Kennedy's [1966] equation, hereafter cited as Kraut-Kennedy equation, or on theoretical models (shear instability model [Born, 1939] and vibrational instability [Lindemann, 1910]). Lindemann's [1910] theory of vibrational frequency in a solid at the melting point was later developed by Gilvarry [1956] as a model of melting as vibrational instability of the solid state. In the Lindemann-Gilvarry approach, melting occurs when the root-mean-square amplitude of atomic vibrations  $\langle u \rangle$  reaches a critical fraction  $f$  of the interatomic distance  $r_m$ . The empirical Simon and Kraut-Kennedy equations can be derived as special cases of Lindemann model [Gilvarry, 1966; Ross, 1969]. Even though the Lindemann-Gilvarry model is not based on the thermodynamic criterion of equilibrium between the liquid and solid state, it proves to be a satisfactory semi-empirical scaling law when used with an equation of state [Mulargia and Quarenì, 1988].

We have calculated MgO melting temperatures using Lindemann's [1910] relation in the form [Gilvarry, 1956]

$$\frac{d \ln T_m}{d \ln V} = -2\gamma + \frac{2}{3}, \quad (12)$$

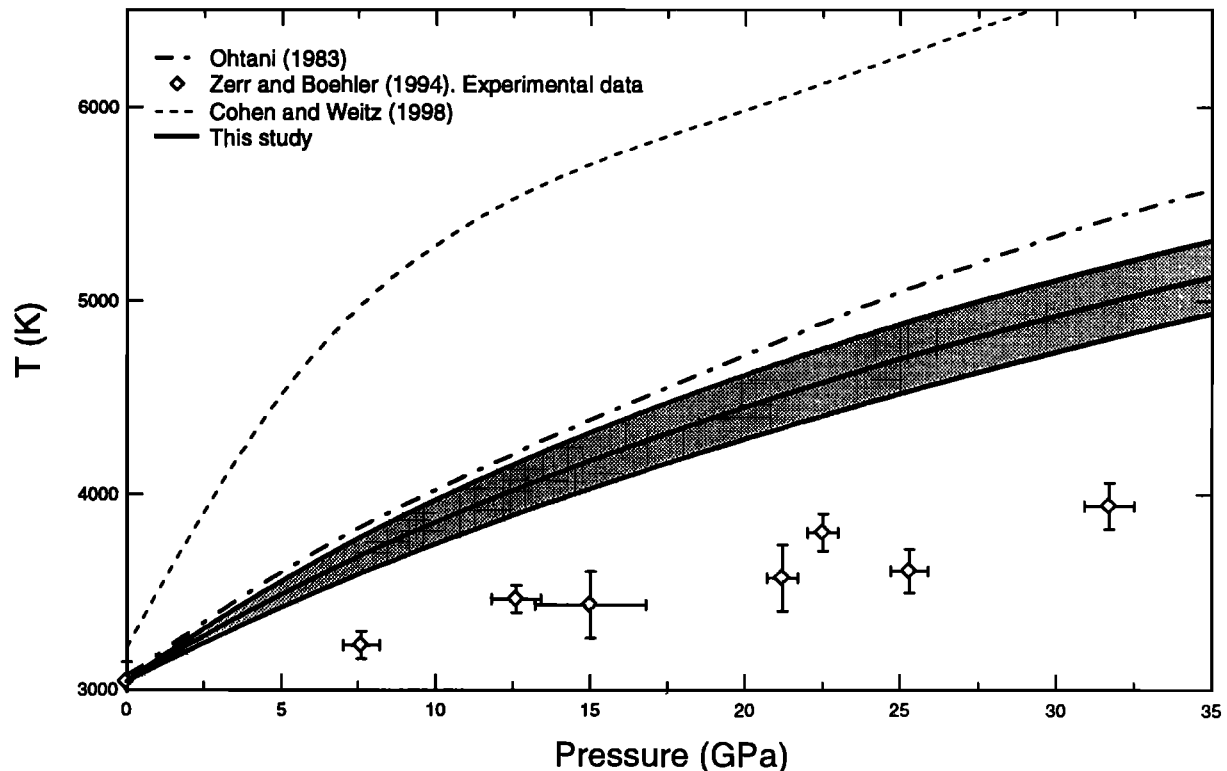
where  $T_m$  is the melting temperature and  $\gamma$  and  $V$  are the Grüneisen parameter and the specific volume at the melting temperature. The value  $\partial T_m / \partial P$  at ambient pressure, calculated applying our model for the volume dependence of the Grüneisen parameter, is 98 K/GPa. It is much higher than the Zerr and Boehler [1994] results. The behavior of the melting curve is sensitive to the value of  $q$  ( $\partial T_m / \partial P = 73.1$  and 53.8 K/GPa for constant  $q = 1.65$  and  $q = 0$ , respectively). Our model of volume dependence of the Grüneisen parameter combined with the Lindemann's melting law cannot reproduce the experimental melting temperatures of Zerr and Boehler [1994], unless  $q$  has unreasonable negative values. The model melting curve is in good agreement with the melting curve of Ohtani [1983] at  $P < 15$  GPa, while it is significantly lower than the theoretical model of Cohen and Weitz [1998], calculated by integration of the Clapeyron equation (Figure 11).

### 7. Thermal Expansion Coefficient

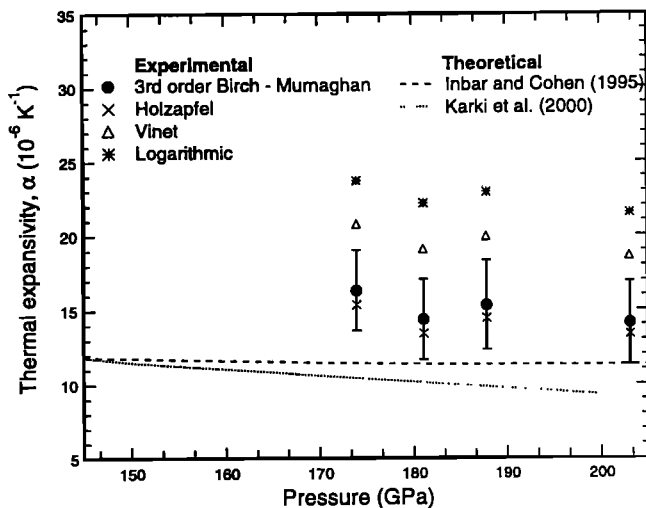
Average values of the thermal expansion coefficient were calculated from density along the P-V Hugoniot curve and the 300 K isotherm as

$$\alpha = \frac{\ln \left( \frac{\rho_{300K}}{\rho_H} \right)}{T_H - 300}, \quad (13)$$

where  $\rho_{300K}$  and  $\rho_H$  are the densities along the 300 K isotherm and the Hugoniot P-V curve and  $T_H$  is the measured shock



**Figure 11.** Melting curve for MgO calculated using Lindemann's [1910] relation and the parameters of the model proposed in this study. Melting curves from experimental data and theoretical calculations are also presented for comparison. The shaded area represents the range of possible model values expressing 1 $\sigma$  uncertainty on the best model value of  $q_0$  parameter. The error bars represent the uncertainty on the experimental results of Zerr and Boehler [1994].



**Figure 12.** Average thermal expansivity from shock wave temperature data. The error bars indicate  $1\sigma$  uncertainty on the values calculated using the best fit to the third-order Birch-Murnaghan equation.

temperature. The thermal expansion coefficients calculated using our best fit third order Birch–Murnaghan 300 K isotherm range between  $14.1 \pm 2.8$  and  $16.3 \pm 2.7 \times 10^{-6} \text{ K}^{-1}$ . They are 35% higher than those calculated by *Duffy and Ahrens* [1993] and the theoretical predictions [*Inbar and Cohen*, 1995; *Karki et al.*, 2000]. We have also calculated thermal expansion coefficients using the fit of our data to other isothermal equations of state (logarithmic, Vinet, Holzapfel and Hama and Suito model). The results scatter as a function of the “stiffness” of the equation of state (Figure 12). The Holzapfel equation, which best fits the shock data, yields values ranging between  $13.3 \pm 2.8$  and  $15.4 \pm 2.7 \times 10^{-6} \text{ K}^{-1}$ . Yet, due to the large uncertainties both in our and in *Duffy and Ahrens* values, it remains unclear if we can generalize the discrepancy between the results in terms of geodynamic modeling.

## 8. Summary

New MgO static compression experiments were carried out at 300 K under quasi-hydrostatic conditions to 52 GPa using helium as a pressure transmitting medium. The new data set allows a precise determination of the cell parameter ( $\langle \Delta a/a \rangle = 0.03 \pm 0.03\%$ ) and an improved equation of state of MgO. A model that describes all the experimental data from ambient pressure and temperature to 203 GPa and 3663 K is presented. The model is based on the third-order Birch-Murnaghan equation for the 300 K isotherm and on the Debye approximation for the thermal pressure contribution. The parameters for the 300 K isotherm are  $K_{0T} = 3.99 \pm 0.01$  and  $V_0 = 74.70 \pm 0.01$ ;  $K_{0T} = 160.2$  GPa was fixed. The low-pressure thermodynamic and static compression data and shock wave data are incompatible with the common description of the volume dependence of  $\gamma$ ,  $\gamma(V) = \gamma_0(V/V_0)^q$ , with constant, positive  $q$ . They instead suggest that  $q$  decreases with compression in qualitative agreement with the theoretical predictions. In our model, the value of the Grüneisen parameter and its volume dependence are constrained by thermodynamic theory and by the experimental

observations. The parameters for the thermal pressure contribution are  $\gamma_0 = 1.524$ ,  $q_0 = 1.65$ ,  $\theta = 773$  K, at standard conditions, and  $\gamma = 1.33$ ,  $q = 0.01$  at 200 GPa. The Birch-Murnaghan isotherm appears superior in the high pressure extrapolation than the Vinet and Logarithmic equations, and substantially equivalent to the Holzapfel equation. Existing theoretical models for MgO show only a marginal agreement with the shock wave data. The thermodynamic models of *Hama and Suito* [1999] and *Jacobs and Oonk* [2000] are largely inconsistent with the static compression data, because of the choice of an unreasonably high value for the pressure derivative of the bulk modulus at ambient conditions. The average thermal expansion coefficient, calculated between the 300 K isotherm and the Hugoniot P-T results range between  $14.1$  and  $16.3 \times 10^{-6} \text{ K}^{-1}$ . They are higher than previous determinations [*Duffy and Ahrens*, 1993]. The melting curve of MgO, calculated by using the Lindemann’s relation, yields  $\partial T_m / \partial P = 98 \text{ K/GPa}$  at ambient pressure. The melting temperatures are higher than the experimental results [*Zerr and Bohler*, 1994], and in relatively good agreement with the thermodynamic model of *Ohtani* [1983]. The results show that it is possible to define a thermal equation of state for MgO which coherently describes data from differing techniques ranging to high pressure-temperature conditions within the framework of the Mie-Grüneisen theory, taking into account a plausible decrease in the volume dependence of  $\gamma$  which can be described in terms of a simple monotonic function of compression.

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