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## Thermoelastic properties of minerals

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**Abstract** The simple theory of equation of state recently developed by Kumar is used to investigate the temperature and pressure dependence of elastic moduli of MgO. The results are found to present good agreement with the experimental data. It is concluded that the Kumar formulation is far better than the Suzuki theory of thermal expansivity, and the Shanker formulation is not a new relation.

**Keywords** Minerals · Thermal expansion · Elastic moduli

### Introduction

The knowledge of thermoelastic properties of minerals at high temperature and pressure is required for the understanding of the Earth's deep interior. Considerable efforts have been made to predict the equation of state of minerals under varying conditions of pressures using diamond-anvil cells. However, less efforts have been made under the effect of temperature at room pressure. The following statement was made by Fiquet et al. (1999): "Thermal expansion determination thus remains scarce and extrapolations have to be made at the risk of causing errors affecting strongly the computation of thermodynamic quantities." This inspired the author to the present work. The main purpose of the present paper is to avoid the extrapolation of data. For this, a simple theoretical method is proposed to determine the thermoelastic properties of minerals under varying conditions of temperatures as well as pressures. The simplicity of the method lies in the fact that it is based on the simple theory of equation of state (EOS).

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### Method of analysis

The theoretical attempts made for thermoelastic properties may be categorized in two parts. (1) those which are based on the theory of interionic potentials, either two-body or three-body and (2) those which are entirely free from the use of potentials. It has been discussed (Kumar 1998) that the second one is better as far as simplicity and applicability are concerned. The method used in the present work is based on the theory of high-pressure-high-temperature EOS recently developed by Kumar (1995, 1996, 2000). The EOS has been found to be applicable from room pressure to the structural transition pressure by varying the temperature from room temperature up to melting temperature (Kumar and Bedi 1996). The same EOS has been found more applicable for different classes of solids than the EOS already available (Kumar 1995, 1996). The mathematical form reads as (Kumar and Bedi 1996):

$$\frac{V}{V_0} = 1 - \frac{1}{A} \ln \left[ 1 + \frac{AP}{B_0} - A\alpha_0(T - T_0) \right]. \quad (1)$$

Here  $V$  is the volume,  $P$  pressure,  $T$  temperature,  $\alpha$  the coefficient of volume thermal expansion,  $B$  the isothermal bulk modulus and  $A = (\delta_0 + 1)$ ,  $\delta$  is the Anderson–Grüneisen parameter. 0 refers to their value at room temperature and atmospheric pressure. Differentiation of Eq. (1) gives (Kumar 2002):

$$\frac{B}{B_0} = \left[ 1 - \frac{1}{A} \ln \left\{ 1 + \frac{AP}{B_0} - A\alpha_0(T - T_0) \right\} \right] \left[ 1 + \frac{AP}{B_0} - A\alpha_0(T - T_0) \right]. \quad (2)$$

Combining Eqs. (1) and (2) we obtain:

$$\frac{B}{B_0} = \frac{V}{V_0} \exp A \left( 1 - \frac{V}{V_0} \right). \quad (3)$$

It has been discussed that the relation of bulk modulus may be generalized for the elastic moduli (Tallon 1980). Thus, eq. (3) may be written as:

$$\frac{C_{ij}}{C_{oij}} = \frac{V}{V_0} \exp A_{ij} \left( 1 - \frac{V}{V_0} \right). \quad (4)$$

Here  $A_{ij} = (\delta_{oij} + 1)$  and  $C_{ij}$  are the second-order elastic constants (SOEC),  $\delta_{oij}$  may be determined from the definition of  $\delta$  as given below:

$$\delta_{oij} = - \frac{1}{\alpha_0 C_{oij}} \left( \frac{\partial C_{ij}}{\partial T} \right)_P = - \frac{1}{\alpha_0 C_{oij}} \left[ \frac{C_{ij} - C_{oij}}{T - T_0} \right]. \quad (5)$$

Thus, if the measurements have been made at a temperature close to room temperature for  $C_{ij}$ , the values of  $\delta_{oij}$  may be evaluated using Eq. (5). For MgO,  $\delta_{011} = 6.5$ ,  $\delta_{012} = -2.49$ ,  $\delta_{044} = 2.57$ ,

using the data reported by Anderson and Isaak (1995) for  $C_{ij}$  at 400 K.

Cowley et al. (1990) studied the pressure dependence of SOEC using Monte Carlo simulation and lattice dynamics. The modified Einstein model has been used by Kwon (1995), but these results do not agree with the experimental data. Various other possible methods have been critically reviewed by Karki et al. (2001). In the present paper, I use Eq. (4) to study the pressure dependence of SOEC of MgO. In these calculations  $V/V_0$  is the change in volume under pressure as given by Eq. (1) at  $T = T_0$ . The values of  $A_{ij}$  are evaluated using the relation (Kumar and Bedi 1996):

$$A_{ij} = [(C_{ij}^1)_0 + 1] \text{ and } C_{ij}^1 = (\partial C_{ij} / \partial P) .$$

The experimental values of  $C_{ij}^1$  for MgO are available in the literature (Karki et al. 2001).

Equation(1) may be compared with the Mie–Gruneisen–Debye theory which is widely used in the literature (Shim and Duffy 2000). The theory has been followed by Suzuki (1975), expanding the quantity  $G = PV$ . Suzuki (1975) reported what became widely known as the Suzuki relation of thermal expansivity (Anderson 1995; Helfrich 1999). This reads as follows (Helfrich 1999):

$$\frac{V}{V_0} = \frac{[1 + 2k - (1 - 4kE_{Th}/Q)^{1/2}]}{2k} , \quad (6)$$

where  $k = (B_0^1 - 1)/2$ ,  $Q = B_0 V_0 / \gamma_0$ .  $B_0$  and  $B_0^1$  are the isothermal bulk modulus and its first-order pressure derivative, respectively.  $\gamma_0$  is the Gruneisen ratio. The subscript 0 refers to their value at  $P = 0$  and  $T = 300$  K.  $E_{Th}$  is the thermal energy. In the Mie–Gruneisen EOS,  $P_{Th} = \gamma_0 E_{Th} / V_0$ . Thus, Eq. (6) may be rewritten as follows:

$$\frac{V}{V_0} - 1 = \frac{1 - [1 - 2\left(\frac{B_0^1 - 1}{B_0}\right)P_{Th}]^{1/2}}{(B_0^1 - 1)} , \quad (7)$$

where  $P_{Th}$  is the thermal pressure.

The Gruneisen theory of thermal expansion as formulated by Born and Huang (1954) was advocated by Shanker et al. (1997). These authors included a higher-order term for the change in volume in the expansion of potential energy and claimed to derive a new expression for  $V/V_0$  which reads as follows (Shanker et al. 1997; Kushwah and Shanker 1998):

$$\frac{V}{V_0} - 1 = \frac{1 - [1 - 2\left(\frac{B_0^1 + 1}{B_0}\right)P_{Th}]^{1/2}}{(B_0^1 + 1)} . \quad (8)$$

In terms of  $P_{Th}$  Eq. (1) reads as follows (Kumar and Bedi 1996):

$$\frac{V}{V_0} - 1 = -\frac{1}{(B_0^1 + 1)} \ln \left[ 1 - \frac{(B_0^1 + 1)P_{Th}}{B_0} \right] . \quad (9)$$

By neglecting higher-order terms, it can be shown that

$$-\ln(1 - x) = [1 - (1 - 2x)^{1/2}] . \quad (10)$$

Thus, Eq. (9) may be rewritten as follows:

$$\frac{V}{V_0} - 1 = \frac{1 - [1 - 2\left(\frac{B_0^1 + 1}{B_0}\right)P_{Th}]^{1/2}}{(B_0^1 + 1)} , \quad (11)$$

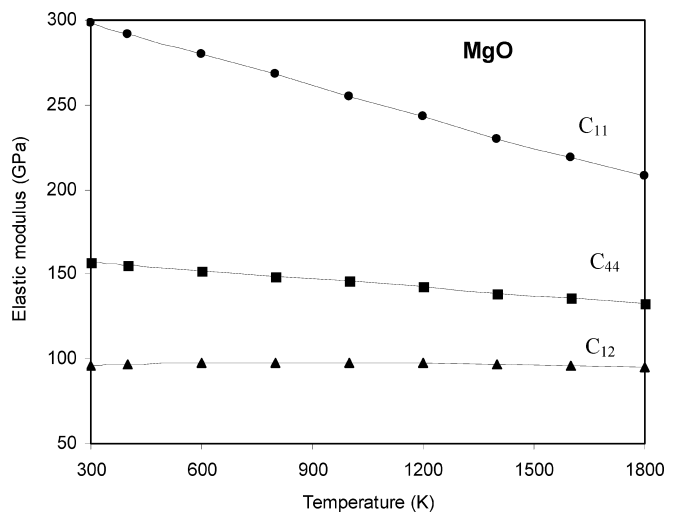
## Results and discussion

Compare Eqs. (7), (8) and (11), it is very clear that Eqs. (8) and (11) are same. Thus, the statement of Shanker et al. (1997), that they investigated a new relation, is flawed. A comparison of Eqs. (7) and (11) shows that the term  $(B_0^1 - 1)$  in the Suzuki formulation (Eq. 7) has been replaced by  $(B_0^1 + 1)$  in the Kumar formulation (Eq. 11). To judge on the suitability of Suzuki and

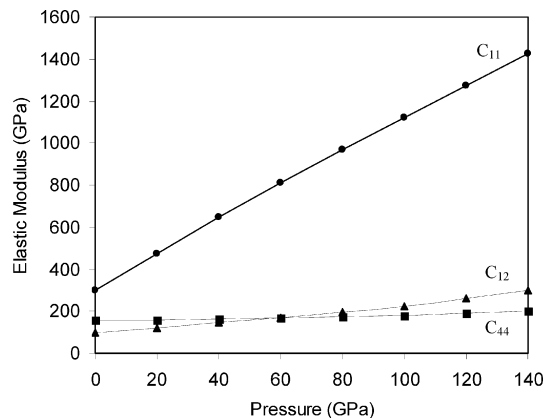
**Table 1** Calculated values of  $V/V_0$  at highest temperatures. *a* Using Suzuki formulation (Eq. 7). *b* Kumar formulation (Eq. 9). *c* Experimental (Anderson 1995)

	T(K)	a	b	c
MgO	1800	1.063	1.067	1.069
CaO	1200	1.033	1.035	1.036
MgAl <sub>2</sub> O <sub>4</sub>	1000	1.017	1.018	1.018
Pyrope-rich garnet	1000	1.019	1.020	1.020
Grossular garnet	1300	1.034	1.034	1.027
Al <sub>2</sub> O <sub>3</sub>	1800	1.039	1.041	1.042
Mg <sub>2</sub> SiO <sub>4</sub>	1700	1.049	1.052	1.055
Olivine Fo <sub>90</sub> Fa <sub>10</sub>	1500	1.041	1.043	1.044
Fe <sub>2</sub> SiO <sub>4</sub>	1700	1.011	1.012	1.012
Mn <sub>2</sub> SiO <sub>4</sub>	1700	1.100	1.011	1.011
Co <sub>2</sub> SiO <sub>4</sub>	700	1.011	1.011	1.012
MnO	500	1.007	1.007	1.007
NaCl	750	1.058	1.061	1.066
KCl	850	1.067	1.071	1.077

Kumar formulations, I used Eqs. (7) and (9) to predict  $V/V_0$  as a function of temperature for 14 mantle minerals for which the required data were compiled by Anderson (1995). It was found that the deviations are maximum at highest temperatures. I have therefore selected the highest temperature for comparison purposes. The values of  $B_0^1 = 4.13$  for MgO and  $B_0^1 = 4$  have been used for other minerals (Shanker et al. 1997; Shim and Duffy 2000). The results thus obtained are given in Table 1 along with the experimental data (Anderson 1995). It is found that Eq. (9) improves the results obtained by Eq. (7) and there is an insignificant difference in Eq. (9) and (11). One more important point is that Eq. (7) gives the results under isobaric condition (constant pressure), whilst Eq. (1) may be used at the required value of  $P$  and  $T$ . Thus, the application of Eq. (1) is far better than the Suzuki equation based on the Mie–Gruneisen–Debye theory. It



**Fig. 1** Variation of elastic moduli with temperature. The *symbols* represent the values calculated in the present study (Eq. 4) and the results of Anderson and Isaak (1995) are represented by *continuous* line



**Fig. 2** Variation of elastic moduli with pressure. The *symbols* represent the values calculated in the present study (Eq. 4) and the results of Karki et al. (1997) are represented by *continuous* line

is also pertinent to mention here that to include a higher-order term (Shanker et al. 1997) in the Gruneisen theory of thermal expansion, as formulated by Born and Huang (1954) regarding the change in the volume, gives nothing new (Eq.8), but reproduces the theory reported by Kumar, as discussed above.

Equation (4) was used to calculate  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  at different temperatures for MgO using corresponding values of  $V/V_0$  obtained from Eq. (1) at  $P = 0$ . The results thus obtained are reported in Fig. 1. For the temperature dependence of elastic constants, the techniques of resonant ultrasound spectroscopy (RUS) are well known. It has been found that in several RUS techniques the predominant technique used to obtain the data is the rectangular parallelepiped technique as used by Ohno (1976) and Sumino (1979). The results based on this technique have been compiled by Anderson and Isaak (1995). These data are included in Fig. 1 for the sake of comparison. There is good agreement between theory and experiment for all three SOEC. Equation (4) encompasses a complete  $C_{ij}-V-T$  equation of state. I have therefore used Eq. (4) also to compute the pressure dependence of SOEC. The results thus obtained for MgO are reported in Fig. 2. The elastic properties of MgO under pressure were studied by Karki et al. (1997) up to 150 GPa using the first-principles pseudopotential method within the local density approximation. These results are included in Fig. 2 for the sake of comparison. The results are in good agreement with each other. It is observed that  $C_{11}$  varies largely under the effect of temperature and pressure as compared with the variation of  $C_{12}$  and  $C_{44}$ . The constant  $C_{11}$  represents elasticity in length. A longitudinal strain produces a change in volume without a change in shape. The volume change is highly related to the temperature/pressure, thus producing a large change in  $C_{11}$ . The constants  $C_{12}$  and  $C_{44}$  are related to the elasticity in shape which is a

shear constant. A transverse strain or shearing causes a change in shape without a change in volume. Thus,  $C_{12}$  and  $C_{44}$  are less sensitive to temperature and pressure than  $C_{11}$ .

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