

A Simple, Potential-Free Model to Calculate Elastic Constants of Solids at High Temperature

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Abstract A simple method for the determination of temperature dependent second order elastic constants (SOEC) of MgO, CaO, Mg₂SiO₄ and Grossular garnet[Ca₃Al₂(SiO₄)₃] using a potential free model based on thermodynamical relationships, has been proposed. The equations developed here are based on the linear relationship between elastic constants at temperatures higher than the Debye temperature. The extrapolated data for elastic constants at very high temperatures obtained in the present study are useful to understand the thermoelastic properties of given solids. It is found that the calculated values of elastic constants, in general, decrease with temperature. The theoretical predictions incorporating the concept of Debye temperature, reported in this paper, are well supported by the available experimental data. The proposed empirical relationship provides a method to estimate the thermoelastic properties of geophysical minerals and solids at high temperature range.

Keywords Elastic Constants, High Temperature, Thermodynamical Relationships

1. Introduction

A thorough understanding of the elastic properties of various solids and their variations with temperature is essential in the study of geophysical and geochemical theories of earth interior[1],[2]. Behaviour of minerals under extreme conditions of temperature plays an important role in understanding the dynamics and evolution of lower mantle of earth. Knowledge of elastic constants is essential to interpret the thermodynamic and thermoelastic properties of minerals and solids at high temperatures. The study of temperature dependence of elastic constants for solids has been a subject of wide interest[3],[4]. Therefore, a number of theoretical as well as experimental physicists are currently engaged in the investigations related to elastic constants of diverse materials, employing a wide variety of approaches[5-10]. The elastic constants of some minerals have been calculated starting from the room temperature to higher temperatures, but there are deviations from experimental results after Debye temperature[10-12]. As far as the theoretical studies are concerned, methods like the Monte-Carlo and lattice dynamical simulation using a rigid body model[13] and three-body potential model[14] have been adopted with reasonable amount of success. Nevertheless, there have been some serious weaknesses in these models. For example, in the three-body potential model[14], the short-range overlap potential parameters

calculated at 300 K, have been used in the high temperature range as such, presuming to be independent of temperature. Moreover, the Van der Waal's coefficient calculated from the lattice sums was also taken as temperature independent. The interior separations (r) in various minerals and crystals varies with temperature (Vandana et al[15]) and therefore, it is imperative to consider the short range overlap, as well as the Van der Waal's interaction parameters, as temperature dependent quantities.

In order to overcome the above mentioned discrepancies in existing theories, and to make the theory simpler we have employed a potential free model based on thermodynamical relationships. In this article, we report temperature dependent second order elastic constants (SOEC) of some solids calculated in the higher temperature ($T > T_D$; T_D is the Debye temperature)[16] region, using a simple and straightforward theoretical model based on some approximations. This model may be used to calculate the thermoelastic properties of any type of minerals. We have chosen four different crystals, viz., MgO, CaO, Mg₂SiO₄ and Grossular garnet[Ca₃Al₂(SiO₄)₃], to test the outcome of our theory. Among these, MgO and CaO are common oxides, Mg₂SiO₄ is a material of geophysical importance, and Grossular garnet is a well-known mineral. Basically all these four solids possess cubic crystal structure. However, MgO and CaO have octahedral; Mg₂SiO₄ has hexoctahedral, and Grossular garnet, dodecahedral coordination geometry. Experimentally determined values of elastic constants for MgO, CaO, Mg₂SiO₄ and Grossular garnet solids are available in the temperature range starting from 300 K up to 1800 K, 1200 K, 1700 K and 1350 K, respectively[3].

The method of analysis is given in section 2 and results

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are discussed and compared with experimental data in section 3.

2. Method of Analysis

Starting with the expressions for SOEC[17], as employed on the cubic crystals under isotropic pressure[18]:

$$C_{11} = C_{11}^0 - p_{phonon}, \quad (1)$$

$$C_{12} = C_{12}^0 + p_{phonon}, \quad (2)$$

and,

$$C_{44} = C_{44}^0 - p_{phonon}. \quad (3)$$

Here, C_{ij} is the SOEC at temperature T , and C_{ij}^0 represents their values at 300 K (T_0). The quantity p_{phonon} is phonon pressure, equivalent to the thermal pressure (p_{Th}), which may be evaluated using the following relationship[3],[19],[20]:

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial p_{Th}}{\partial T}\right)_V = \alpha_0 K_T^0, \quad (4)$$

Where, V is the volume. Also, α_0 and K_T^0 are the coefficient of volume thermal expansion, and bulk modulus, respectively, at $T = T_0$ (i.e., at 300 K).

One can get the expression for p_{Th} from Eq. 4 as,

$$p_{Th} = \int_{T_0}^T \alpha_0 K_T^0 dT, \quad (5)$$

Or,

$$p_{Th} = \alpha_0 K_T^0 (T - T_0). \quad (6)$$

The Anderson-Gruneisen parameter at a given temperature T is defined as[19],

$$\delta_T = -\frac{1}{\alpha K_T} \left(\frac{dK_T}{dT}\right)_P, \quad (7)$$

Which may be used to determine the rate of change of bulk modulus K_T with respect to temperature as,

$$\left(\frac{dK_T}{dT}\right) = -\alpha K_T \delta_T, \quad (8)$$

at constant pressure. Integration of Eq. 8 leads to the expression for bulk modulus as a function of temperature as follows,

$$K_T = K_T^0 [1 - \alpha_0 \delta_0 (T - T_0)]. \quad (9)$$

We assume δ_T and αK_T as temperature independent quantities, which has already been assumed empirically in the case of solids studied in[1]. The quantity $\alpha_0 K_T^0 (T - T_0)$ involved in this equation is thermal pressure p_{Th} as obtained in Eq. 6 above. Obviously, p_{Th} would change with temperature resulting in change in volume. Accordingly, the bulk modulus, as well as other elastic constants, would be temperature dependent. The same inference may also be drawn directly from Eqs. 1-3.

Presuming that similar trend of variation with respect to temperature is followed by other elastic constants also; one can generalize Eq. 9[21] to obtain the expressions for the latter, which may be collectively written as:

$$\frac{m}{m_0} = [1 - \alpha_0 \delta_m^0 (T - T_0)] \quad (10)$$

Where, m represents any of the elastic moduli such as C_{11} , C_{12} , C_{44} , etc. This expression nicely holds in the $T > T_0$ region for the solids whose Debye temperature is near T_0 (room-temperature, 300 K), such as the ionic crystals NaCl, KCl, etc.[22]. However, when $T_D > T_0$, it holds only up to T_D for the calculated values of some SOEC, such as, C_{12} , and then some deviations may occur.

Equation 10 therefore, may be modified to accommodate the $T > T_D$ temperature regime by replacing the values of input parameters with those corresponding to T_D . In the modified picture, the relevant expressions for SOEC at $T > T_D$ can be collectively written as follows:

$$\frac{C_{ij}}{C_{ij}^D} = [1 - \alpha_D \delta_{ij}^D (T - T_D)], \quad (11)$$

In Eq. 11, δ_{ij}^D are constants corresponding to C_{ij} , defined as[23],

$$\delta_{ij}^D = -\frac{1}{\alpha_D C_{ij}^D} \left(\frac{dC_{ij}}{dT}\right)_D, \quad (12)$$

and, the letter D refers to values of the corresponding quantities at Debye temperature, T_D [16].

Table 1. Values of Debye temperature T_D and the input parameters (near T_D) used in calculations[3]

Parameters (units)	MgO	CaO	Mg ₂ SiO ₄	Grossular Garnet	
T_D	(K)	945	671	763	824
α_D	(10 ⁻⁵ K ⁻¹)	4.38	3.92	3.59	2.78
δ_D		4.78	5.07	5.47	4.64
C_{11}^D	(10 ¹⁰ N/m ²)	26.19	20.12	30.03	30.02
C_{12}^D	(10 ¹⁰ N/m ²)	9.86	5.866	6.07	9.04
C_{44}^D	(10 ¹⁰ N/m ²)	14.81	7.718	6.01	9.76
$(dC_{11}/dT)_D$	(10 ⁷ N/m ² /K)	-6.20	-4.60	-4.0	-3.7
$(dC_{12}/dT)_D$	(10 ⁷ N/m ² /K)	-0.20	0.15	-1.3	-0.2
$(dC_{44}/dT)_D$	(10 ⁷ N/m ² /K)	-1.60	-0.72	-1.35	-1.1

Table 2. Values of slopes of the theoretical lines. Corresponding values of slopes of the best-fit straight lines to experimental data are shown within brackets

Parameters (10^7 N/m ² /K)	MgO	CaO	Mg ₂ SiO ₄	Grossular Garnet
dC_{11}/dT	-5.855 (-6.020)	-4.850 (-4.630)	-4.150 (-4.510)	-3.700 (-3.920)
dC_{12}/dT	-0.463 (-0.417)	0.348 (0.060)	-0.001 (-0.001)	-0.400 (-0.354)
dC_{44}/dT	-1.250 (-1.680)	-0.700 (-0.799)	-1.300 (-1.350)	-1.100 (-1.160)
dC_s/dT	-3.300 (-2.780)	-2.600 (-2.340)	-1.550 (-1.730)	-1.680 (-1.810)

From this simple theory, taking T_D as the reference temperature, one can calculate the values of SOEC that are in excellent agreement with the experimental data. The constants δ_{ij}^D are calculated using Eq. 12 and the input parameter[3] given in Table 1, and then substituted with other quantities in Eq. 11 to obtain the theoretical values of SOEC at different temperatures. The values of dC_{ij}/dT were not available, and therefore, we have used the interpolated values of these quantities at Debye temperature, obtained from the data given in Ref.[3]. These values are listed in Table 1.

3. Results and Discussion

Many authors have reported theoretically calculated values of SOEC taking T_0 (300 K) as the reference temperature[7],[8]. Therefore, we first calculated all the SOEC values, viz., C_{11} , C_{12} , C_{44} and C_s for four different solids MgO, CaO, Mg₂SiO₄ and Grossular garnet[Ca₃Al₂(SiO₄)₃], taking the reference temperature at 300 K instead of T_D , to understand the inconsistency. To accomplish this, we used room temperature values of the input parameters in Eq. 11. The values of SOEC thus calculated were found to agree to great extent with the available experimental data for all the four solids considered in this work. It was observed that the values of SOEC decrease with increasing T in all four solids, in concurrence with the experimentally reported values, except for the case of C_{12} in MgO and CaO. Experimentally, it was observed that for MgO, C_{12} slowly increases with temperature up to 900 K, and then decreases[3]. Mathematically, the slow initial increase of C_{12} is associated with a positive $(dC_{12}/dT)_0$, which is because of a negative value of δ_{12}^0 , or *vice-versa*. At higher temperature ($T > 900$ K), C_{12} decreased with temperature, which was a reflection of positive δ_{12}^0 . In the case of CaO, the dependence of C_{12} (experimental) on temperature becomes very small, after about 650 K. It may be noted that the change in trend occurs near the respective values of T_D , i.e., 945 K (for MgO) and 671 K (for CaO)[3]. Therefore, the observed change in trend must essentially be associated with T_D . Like all physical quantities associated with the lattice phonons in solids, p_{Th} must also change its temperature dependence at T_D . Effectively, the SOEC that are dependent on p_{Th} (Eqns. 1-3) should also be expected to change their dependence on temperature beyond T_D .

In order to overcome this discrepancy, we changed the reference temperature from 300 K to the respective Debye temperature T_D of the solids in Eq. 11, and calculated the SOEC again. Accordingly, the input parameters corresponding to T_D (Table 1) were used in the calculations. Due to the unavailability of experimental SOEC data beyond 1800 K, 1200 K, 1700 K and 1350 K, for MgO, CaO, Mg₂SiO₄ and Grossular garnet, we calculated the values of elastic constants only up to 1800, 1600, 1700 and 1700 K, respectively, for proper comparison of results.

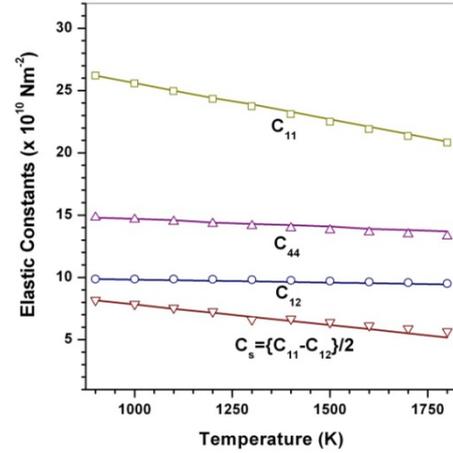


Figure 1. Variation of C_{11} , C_{12} , C_{44} and C_s (10^{10} N/m²) for MgO with temperature. Values calculated in the present study using equation (11) are shown with continuous lines and the experimental data[3], with points

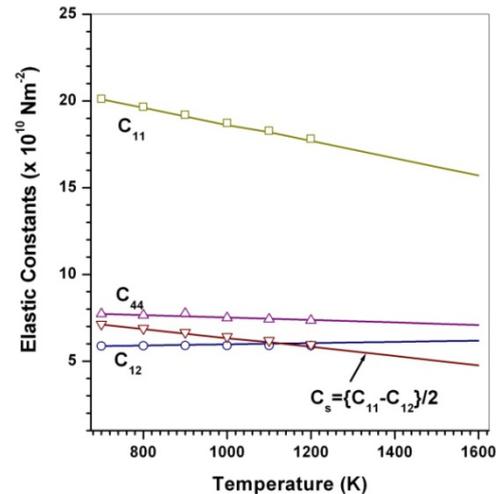


Figure 2. Variation of C_{11} , C_{12} , C_{44} and C_s (10^{10} N/m²) for CaO with temperature. Values calculated in the present study using equation (11) are shown with continuous lines and the experimental data[3], with points

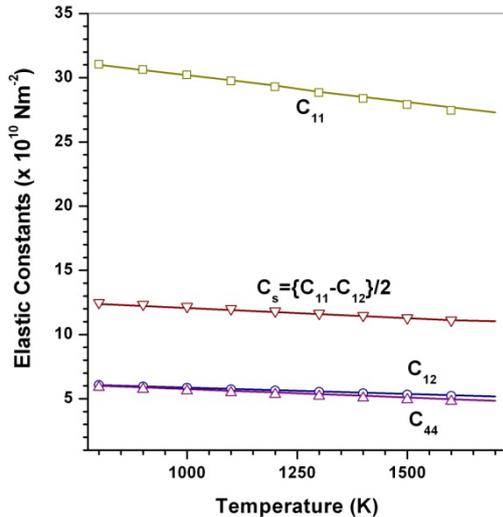


Figure 3. Variation of C_{11} , C_{12} , C_{44} and C_s (10^{10} N/m²) for Mg₂SiO₄ with temperature. Values calculated in the present study using equation (11) are shown with continuous lines and the experimental data[3], with points

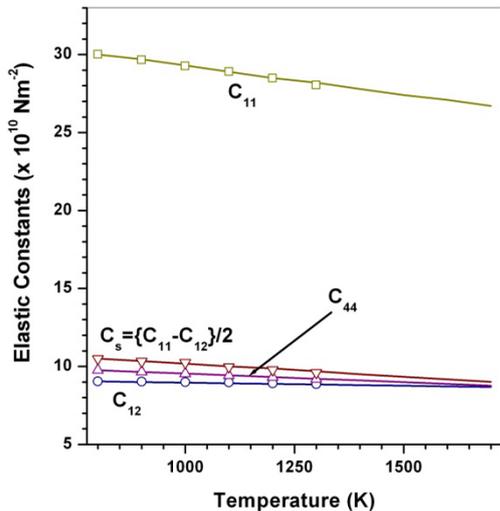


Figure 4. Variation of C_{11} , C_{12} , C_{44} and C_s (10^{10} N/m²) for Grossular garnet with temperature. Values calculated in the present study using equation (11) are shown with continuous lines and the experimental data[3], with points

The variation of C_{11} with temperature is found to be large but for C_{12} , it is small, and for C_{44} even smaller. This is because the constant C_{11} represents elasticity in length, and a longitudinal strain produces a change in volume without any change in shape. The volume change is closely related to temperature and therefore, produces a large change in C_{11} . On the other hand, C_{12} and C_{44} are related to elasticity in shape without the change in volume, which makes C_{12} and C_{44} less temperature sensitive.

Variations of the elastic constants C_{11} , C_{12} , C_{44} and C_s with temperature, for $T > T_D$, calculated using T_D as the reference temperature, are shown in Figs. 1-4 for the MgO, CaO, Mg₂SiO₄ and Grossular garnet, respectively. For comparison, the experimentally determined values of the corresponding elastic constants are also shown. It may easily be noted that the calculated values, in general, are in very good agreement with the available experimental

data[3]. This observation has been consolidated with the estimation of slopes of each of the theoretical lines, as well as that of the best fitting straight lines to experimental data. Values of these slopes, which essentially represent the rate with which a given SOEC varies with respect to temperature, are listed in Table 2. A comparison between theoretical, and the corresponding experimental, values of the slopes immediately reveals the significant agreement between the two. Moreover, since C_{12} is a monotonically decreasing function of temperature (Eq. 11), when the reference temperature is set at T_D , as we have done in our calculations, the theory is expected to agree with the experimental data even up to the melting temperature of the solid under consideration.

Finally, so far as the validity of theory in the temperature regime $T_0 < T < T_D$ is concerned, values obtained with T_D as the reference temperature are better than those obtained with T_0 as the reference. This is evidenced from the fact that the maximum observed difference in theoretical and experimental values of C_{12} for MgO and CaO, are larger with the latter reference temperature. Therefore, it can be concluded that the theory reported here is valid at higher temperatures, especially beyond the Debye temperature.

4. Conclusions

The Variation of SOEC of solids has been investigated on the basis of Anderson equation[19] with first order approximations. Good conformity between calculated and experimental values of SOEC from Debye temperature to higher temperature for solids under study reveals the validity of relationships used in the present analysis. The simple method developed in the present work is free from the theory of potential, and the results obtained are in good agreement with complete simulation studies as well. On the basis of overall descriptions, the method was found to be better than those reported earlier[10],[12], as far as the simplicity and applicability are concerned. The approach is independent of crystal structure and may be extended to the more complex solids like minerals of geophysical importance up-to their respective melting temperature. Due to the simplicity of calculations and potentially wider applicability, this model might be used in calculating the thermoelastic properties of various nanomaterials[24],[25]. More work in this direction is in progress.

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