Temperature Dependence of Elastic Constants of Alkaline Earth Oxides

Seema Gupta, S. P. Singh, Vipra Pandey, and S. C. Goyal

1 Department of Physics, Agra College, Agra 282002, India
2 Department of Applied Sciences, FET, R.B.S. College, Bichpuri, Agra 283105, India

Research Article

1. Introduction

The general theory for the thermoelastic behaviour of ionic solid was first of all given by Wallace [1]. Srivastava [2, 3] and Varshney [4] have applied it to the solids crystallizing in NaCl and CsCl structure. Kumar and coworkers [5–7] have analyzed the variation of elastic constant with temperature for MgO and CaO using different approaches modifying the Suzuki relation of equation of state [8]. However, their results [5–7] are better than Suzuki’s results but are much different from the experimental results. Any equation of state contains the bulk modulus and its derivatives as dependent parameter. The results obtained by Kumar and coworkers [5–7] show the worse agreement between the computed values of bulk modulus at different temperatures with their experimental results in case of MgO and CaO. This clearly indicates that modification improves some values of the elastic constants at different temperatures but shows poor agreement of bulk modulus at different temperature. It may be due to the reason that they have not considered the higher order terms that is, anharmonic terms, in the expansion of the logarithmic series of volume change. But the elastic properties are directly related to the lattice potential which consists of the various interaction systems.

In the present study, we have used many body Lundqvist potentials [13–15] incorporating thermal phonon pressure to study the second-order elastic constant of all alkaline earth oxides solid, that is, MgO, CaO, SrO, and BaO solid at different temperatures (up to 2000 K). This potential has been recently used [11, 16, 17] to explain the elastic properties of alkaline earth oxides (AEOs) and rare gas solids (RGSs) at different pressures. The potential has been suitably modify to take into consideration the changes in the lattice parameter due to the increase in temperature. Now we have derived the relation of second-order elastic constants by modifying the lattice parameter. The results predicted by the present theory are discussed and compared with available experimental and others theoretical results.

2. Theory

The total lattice energy of diatomic solid [14] is regarded as

\[
\Phi(r) = \frac{\epsilon_1^2}{2} \sum_{k} \sum_{k'} \sum_{l} \frac{\epsilon (k)}{r(l', kk')} + \frac{\epsilon_2^2}{2} \sum_{k} \sum_{l} \sum_{l'} \sum_{l''} \frac{V_{il}(l', kk')}{r(l', kk')}
\]

\[
+ \epsilon_2 \sum_{k} \sum_{k'} \sum_{l} \sum_{l'} \frac{f_{kl} \{r(l', kk')\}}{r(l', kk')},
\]

where \( \epsilon (k) \) is the valency of \( k \) type ion, \( \in \) the magnitude of \( r(l', kk') \) the interionic separation between ion \( k \) at origin to ion \( l' \). The first term represents Coulomb energy, the second the overlap repulsive energy coupling the neighbours and the third term the three body
Table 1: Values of input data at room temperature; \( a, r_+, r_-, \) and \( \rho \) are (all in \( \text{Å} \)), (in \( 10^{-12} \text{erg} \)), \( \beta (10^{-5} \text{K}^{-1}) \) and elastic constants and bulk modulus (in GPa).

| Solids | \( C_{11} \) | \( C_{12} \) | \( C_{44} \) | \( a \) | \( r_+ \) | \( r_- \) | \( \rho \) | \( b \) | \( \beta \) | \( K \) |
|--------|------------|------------|------------|------|------|------|------|------|------|------|
| MgO    | 298.96\(^{(a)}\) | 96.42\(^{(a)}\) | 157.13\(^{(a)}\) | 2.125\(^{(c)}\) | 0.78\(^{(d)}\) | 1.32\(^{(d)}\) | 0.347\(^{(d)}\) | 2.003\(^{(d)}\) | 3.12\(^{(d)}\) | 159.67\(^{(a)}\) |
| CaO    | 220.53\(^{(a)}\) | 57.67\(^{(a)}\) | 80.03\(^{(a)}\) | 2.42\(^{(c)}\) | 1.06\(^{(d)}\) | 1.32\(^{(d)}\) | 0.386\(^{(d)}\) | 2.010\(^{(d)}\) | 3.04\(^{(d)}\) | 111.96\(^{(a)}\) |
| SrO    | 173\(^{(b)}\) | 45\(^{(b)}\) | 56\(^{(b)}\) | 2.598\(^{(c)}\) | 1.27\(^{(d)}\) | 1.32\(^{(d)}\) | 0.390\(^{(d)}\) | 1.900\(^{(d)}\) | 4.2\(^{(d)}\) | 91\(^{(b)}\) |
| BaO    | 121\(^{(c)}\) | 50\(^{(c)}\) | 38\(^{(c)}\) | 2.776\(^{(c)}\) | 1.74\(^{(d)}\) | 1.32\(^{(d)}\) | 0.415\(^{(d)}\) | 1.747\(^{(d)}\) | 3.8\(^{(d)}\) | 69\(^{(c)}\) |

\(^{(a)}\)Ref[9], \(^{(b)}\)Ref[10], \(^{(c)}\)Ref[11], \(^{(d)}\)Ref[12].

Table 2

\( (a) \) Calculated values of \( C_{11} \) (GPa) for MgO at different temperatures \( T \) (K).

| T   | Pre | Su [7] | Ku [7] | Exp. [9] |
|-----|-----|--------|--------|----------|
| 300 | 299 | 298.96 | 298.96 | 298.96   |
| 400 | 293 | 293.08 | 293.1  | 292.94   |
| 500 | 287.1 | 287.17 | 287.24 |          |
| 600 | 281.2 | 281.22 | 281.38 | 280.62   |
| 700 | 275.4 | 275.22 | 275.55 |          |
| 800 | 269.7 | 269.18 | 269.76 | 268.22   |
| 900 | 264  | 263.09 | 264.02 |          |
| 1000| 258.4 | 256.97 | 258.34 | 255.74   |
| 1100| 252.8 | 250.8  | 252.72 |          |
| 1200| 247.3 | 244.59 | 247.18 | 243.22   |
| 1300| 241.8 | 238.34 | 241.72 |          |
| 1400| 236.3 | 232.05 | 236.36 | 230.96   |
| 1500| 231  | 225.71 | 231.08 |          |
| 1600| 225.6 | 219.34 | 225.91 | 219.04   |
| 1700| 220.3 | 212.91 | 220.84 |          |
| 1800| 215.1 | 206.45 | 215.88 | 208      |
| 1900| 209.9 | 199.94 | 210.97 |          |
| 2000| 204.7 | 193.39 | 206.22 |          |

\( (b) \) Calculated values of \( C_{12} \) (GPa) for MgO at different temperatures \( T \) (K).

| T   | Pre | Su [7] | Ku [7] | Exp. [9] |
|-----|-----|--------|--------|----------|
| 300 | 96.42 | 96.42  | 96.42  | 96.42    |
| 400 | 95.84 | 97.17  | 97.17  | 97.14    |
| 500 | 95.28 | 97.92  | 97.92  |          |
| 600 | 94.74 | 98.68  | 98.67  | 98       |
| 700 | 94.22 | 99.44  | 99.43  |          |
| 800 | 93.72 | 100.2  | 100.18 | 98.54    |
| 900 | 93.22 | 100.97 | 100.93 |          |
| 1000| 92.75 | 101.73 | 101.7  | 98.74    |
| 1100| 92.29 | 102.51 | 102.46 |          |
| 1200| 91.85 | 103.28 | 103.22 | 98.38    |
| 1300| 91.42 | 104.06 | 103.98 |          |
| 1400| 91.01 | 104.84 | 104.74 | 97.56    |
| 1500| 90.62 | 105.62 | 105.5  |          |
| 1600| 90.24 | 106.4  | 106.26 | 96.44    |
| 1700| 89.87 | 107.19 | 107.03 |          |
| 1800| 89.52 | 107.98 | 107.79 | 95.02    |
| 1900| 89.18 | 108.77 | 108.56 |          |
| 2000| 88.85 | 109.57 | 109.32 |          |
potential. The function $f$ is related to the overlap integrals of free-ion one electron wave functions and is assumed significant only for nearest neighbours and is related to overlap integrals reported by Hafmeister and Flygare \cite{18}. However, in the present study, we have chosen this function $f$ and its derivatives as disposable parameters at $r = a$, the nearest-neighbour distance. On simplification, the above lattice energy per unit cell $\phi(r)$ for alkaline earth oxide solids can be expressed as

$$\Phi(r) = \varepsilon \alpha_m \left( \frac{12 f(r)}{r} \right)e^2 + N\phi_1(r) + N'\phi_2(r),$$  \hspace{1cm} (2)$$

where $\alpha_m (= 1.7476)$ is the Madelung constant for NaCl structure. $N$ and $N'$ are the numbers of the nearest and next
Table 3

(a) Calculated values of $C_{11}$ (GPa) for CaO at different temperatures $T$ (K).

| $T$ | Pre | Su [7] | Ku [7] | Exp. [9] |
|-----|-----|--------|--------|---------|
| 300 | 221 | 220.53 | 220.53 | 220.5   |
| 400 | 216 | 220.03 | 215.62 | 215.7   |
| 500 | 212 | 219.54 | 210.72 | 210.7   |
| 600 | 208 | 219.03 | 205.82 | 205.9   |
| 700 | 204 | 218.51 | 200.96 | 201.2   |
| 800 | 200 | 217.99 | 196.14 | 196.6   |
| 900 | 196 | 217.46 | 191.37 | 192     |
| 1000| 192 | 216.93 | 186.67 | 187.2   |
| 1100| 188 | 216.38 | 182.03 | 182.7   |
| 1200| 184 | 215.83 | 177.47 | 178.1   |
| 1300| 180 | 215.27 | 172.99 |          |
| 1400| 176 | 214.71 | 168.61 |          |
| 1500| 173 | 214.14 | 164.32 |          |
| 1600| 169 | 213.56 | 160.13 |          |
| 1700| 165 | 212.97 | 156.03 |          |
| 1800| 161 | 212.36 | 152.04 |          |
| 1900| 158 | 211.79 | 148.15 |          |
| 2000| 154 | 211.18 | 144.37 |          |

(b) Calculated values of $C_{12}$ (GPa) for CaO at different temperatures $T$ (K).

| $T$ | Pre  | Su [7] | Ku [7] | Exp. [9] |
|-----|------|--------|--------|---------|
| 300 | 57.67| 57.6   | 57.6   | 57.67   |
| 400 | 57.39| 57.63  | 57.95  | 57.96   |
| 500 | 57.13| 57.66  | 58.3   | 58.23   |
| 600 | 56.87| 57.7   | 58.65  | 58.44   |
| 700 | 56.63| 57.73  | 59     | 58.66   |
| 800 | 56.39| 57.76  | 59.35  | 58.81   |
| 900 | 56.17| 57.79  | 59.71  | 58.98   |
| 1000| 55.95| 57.82  | 60.06  | 58.98   |
| 1100| 55.75| 57.85  | 60.41  | 58.96   |
| 1200| 55.55| 57.88  | 60.77  | 58.99   |
| 1300| 55.36| 57.9   | 61.12  |          |
| 1400| 55.18| 57.93  | 61.48  |          |
| 1500| 55.01| 57.96  | 61.83  |          |
| 1600| 54.84| 57.98  | 62.19  |          |
| 1700| 54.69| 58     | 62.55  |          |
| 1800| 54.54| 58.03  | 62.9   |          |
| 1900| 54.4 | 58.05  | 63.26  |          |
| 2000| 54.27| 58.07  | 63.62  |          |

(c) Calculated values of $C_{44}$ (GPa) for CaO at different temperatures $T$ (K).

| $T$ | Pre   | Su [7] | Ku [7] | Exp. [9] |
|-----|-------|--------|--------|---------|
| 300 | 80.03 | 80.03  | 80.03  | 80.03   |
| 400 | 79.83 | 79.96  | 79.33  | 79.35   |
| 500 | 79.66 | 79.88  | 78.62  | 78.7    |
to nearest neighbours. $\phi_1(r)$ and $\phi_2(r)$ are the short range potentials between nearest neighbours and next nearest neighbours related to Lundqvist potential as follows:

\[
\phi'_1(r) = \phi_1(r) + \frac{a_m}{a} \in f(r),
\]

\[
\phi'_2(r) = \phi_2(r)
\]

\[
= \frac{1}{2} b \left[ \beta_{++} \exp \left( \frac{2r_+}{\rho} \right) + \beta_{--} \exp \left( -\frac{\sqrt{2}r_-}{\rho} \right) \right] \exp \left( -\frac{\sqrt{2}r}{\rho} \right),
\]

(3)

where $b$ and $\rho$ are the Born repulsive parameters. $r_+$ and $r_-$ are the characteristic length for the positive and negative ions. $\beta_{ij}$ are Pauling coefficients [19] defined as follows:

\[
\beta_{ij} = 1 + \left( \frac{\epsilon_i}{p_i} \right) + \left( \frac{\epsilon_j}{p_j} \right),
\]

(4)

where $\epsilon_i$ and $\epsilon_j$ are the valencies of two ions. $p_i$ and $p_j$ are the number of outermost electrons in ions $i$ and $j$.

Considering that the vibrational energy of the solid is a purely temperature dependent function as

\[
\left( \frac{d\Phi}{dr} \right)_{r=a} = -P + T\beta K
\]

(5)
and using the above lattice potential functions (1) and (3), the expressions for second-order elastic constant at any temperature $T$ for alkaline earth oxides are derived as

$$C_{11} = -4.388T^2 \beta K_T + \frac{e^2}{4\eta^4} \left\{ A_1 + \frac{A_2}{2} + 4.388B_1 + 4.888B_2 + 9.3204 \right\},$$

$$C_{12} = 1.194T^2 \beta K_T + \frac{e^2}{4\eta^4} \left\{ \frac{A_2}{4} - 1.194B_1 - 1.444B_2 + 9.3204 \right\},$$

$$C_{44} = 2.194T^2 \beta K_T + \frac{e^2}{4\eta^4} \left\{ -1.194B_1 - 1.444B_2 + \frac{A_2}{4} \right\},$$

where $A_1, B_1, A_2,$ and $B_2$ are short range force constants defined as

$$\frac{\partial^2 \phi_1}{\partial r^2} \bigg|_{r=\eta} = \frac{A_1 e^2}{8\eta^3}, \quad \frac{1}{r} \frac{\partial \phi_1'}{\partial r} \bigg|_{r=\eta} = \frac{B_1 e^2}{8\eta^3},$$

$$\frac{\partial^2 \phi_2'}{\partial r^2} \bigg|_{r=\eta/\sqrt{2}} = \frac{A_2 \sqrt{2} e^2}{8(\eta/\sqrt{2})^3}, \quad \frac{1}{r} \frac{\partial \phi_2}{\partial r} \bigg|_{r=\eta/\sqrt{2}} = \frac{B_2 \sqrt{2} e^2}{8(\eta/\sqrt{2})^3}.$$  

The equilibrium condition $(d\phi(r))/dr = 0$ is written as

$$T^2 \beta K_T = \frac{e^2}{4\eta^4} \left[ 1.165 \in (\in + 12f(r)) + B_1 + B_2 \right],$$

where $\beta$ is the coefficient of volume thermal expansion, $a$ is the nearest neighbour distance, $K_T$ is the bulk modulus, and $\eta = a[1 + \beta(T - T_0)].$

### 3. Results and Discussion

In order to compute the values of elastic constants and bulk modulus with the help of the above described theory, one requires $f(r), adf/dr, A_1, B_1, A_2,$ and $B_2.$ Out of these the first four parameters are evaluated with the help of (6, 11) at $T = 300$ K using the input data from Table 1. The remaining two parameters $A_2$ and $B_2$ are evaluated by using (7). The computed parameters are used to evaluate the values SOE constants and bulk modulus for MgO, CaO, SrO, and BaO at different temperatures with the help of (6). The results are shown in the Tables 2, 3, 4, and 5.

It is interesting to note from Tables 2–5 that the values of $C_{11}$ are decreasing with increase of temperature in all cases (MgO, CaO, SrO and BaO). The values of $C_{11}$ for MgO and CaO are much better than previous theoretical results [5, 7] and very close to the experimental results [9]. Similarly the computed values of $C_{12}$ of MgO, CaO, SrO, and BaO are decreasing slowly with the increase of temperature and are much better than the earlier computed values [5, 7] in case of MgO and CaO. The computed values of $C_{44}$ are close to the experimental values [9] up to 1200 K and are better than the earlier reported values [5–7] in case of CaO. Our calculated values of $C_{44}$ are not so good in case of MgO. This may be due to the reason that many body interactions do not show

### Table 4: Calculated values of $C_{11}, C_{12}, C_{44},$ and $K$ (GPa) for SrO at different temperatures $T$ (K).

| $T$ (K) | $C_{11}$ | $C_{12}$ | $C_{44}$ | $K$  |
|---------|----------|----------|----------|------|
| 300     | 173      | 45       | 56       | 87.67 |
| 400     | 168.36   | 44.73    | 55.94    | 85.94 |
| 500     | 163.78   | 44.47    | 55.92    | 84.25 |
| 600     | 159.27   | 44.24    | 55.91    | 82.58 |
| 700     | 154.81   | 44.01    | 55.91    | 80.95 |
| 800     | 150.41   | 43.8     | 55.92    | 79.34 |
| 900     | 146.06   | 43.6     | 55.96    | 77.76 |
| 1000    | 141.77   | 43.42    | 56.01    | 76.2  |
| 1100    | 137.54   | 43.28    | 56.08    | 74.68 |
| 1200    | 133.35   | 43.13    | 56.17    | 73.17 |
| 1300    | 129.21   | 42.98    | 56.27    | 71.7  |
| 1400    | 125.13   | 42.8     | 56.38    | 70.25 |
| 1500    | 121.08   | 42.68    | 56.51    | 68.81 |
| 1600    | 117.09   | 42.57    | 56.65    | 67.41 |
| 1700    | 113.15   | 42.47    | 56.81    | 66.03 |
| 1800    | 109.24   | 42.38    | 56.98    | 64.67 |
| 1900    | 105.38   | 42.31    | 57.16    | 63.33 |
| 2000    | 101.56   | 42.24    | 57.36    | 62.01 |

In the above table, $C_{11}, C_{12}, C_{44},$ and $K$ are given in GPa.
their contribution to the shear moduli $C_{44}$. Similar trend of variation of second-order elastic constants of AEO solids with pressure is obtained by Baltache et al. [9] and by Singh et al. [20]. Thus these AEOs show systematic variation in the values of SOE constant either with increase of pressure [9, 20] or with increase of temperature as compared to the values of these constants at ambient condition [10, 11].

On the other hand the values of bulk modulus are in excellent agreement with the experimental values [9] at different temperatures and are better than the earlier study which are based on the equation of state. The values of bulk modulus are decreasing at different temperatures as we move from lighter to heavier alkaline earth oxides. On the other hand, the value of bulk modulus is decreasing with the increase of temperature in all cases. The reason for this may be that the constant $C_{11}$ is a longitudinal elastic constant (like Young’s modulus) relating longitudinal stress and longitudinal strain. A longitudinal force causes the lattice to stretch. This causes a change in volume of the crystal lattice. It is well known that the internal energy is the function of volume ($V$) and temperature ($T$). The temperature dependence is both explicit via the Boltzmann factor and implicit via the static lattice energy and normal mode frequency. Both static lattice energy and normal mode frequency are the function of the volume ($V$), which heavily depend on temperature. Thus the constant $C_{11}$ depends on the temperature. On the other hand, the constants $C_{44}$ and $C_{12}$ are shearing constant relating shearing stress to shearing strain. Shearing is caused by tangential force, and the lattice constant is unaffected by the shearing, and consequently the $C_{44}$ and $C_{12}$ depend less on temperature. This agreement demonstrates the validity of the contribution of many body interactions considered in developing the present theory.

The various results predicted in the present paper regarding the variation of the elastic constants with temperature for SrO and BaO up to 1800 K will be useful in analyzing the experimental data perhaps which are not yet available. Therefore the present study may be useful to study the elastic and thermal properties of alkaline earth chalcogenides and in geophysics.

Acknowledgments

S. C. Goyal is grateful to the Principal, R.B.S. College, Agra for providing the facilities and UGC(Delhi) for providing the financial assistance. He is also thankful to the Principal, Agra College, Agra, while Seema Gupta is grateful to DST (Delhi) for providing financial assistance through research project.

References

[1] D. C. Wallace, in Solid State Physics, H. Ehrenreich, F. Seitz, and D. Turnbull, Eds., vol. 25, pp. 302–404, Academic Press, New York, NY, USA, 1970.
[2] U. C. Shrivastava, “Temperature dependence of the elastic constants of alkali halides,” Physical Review B, vol. 21, no. 6, pp. 2602–2606, 1980.
[3] U. C. Shrivastava, “Theory of the anomalous temperature dependence of $C_{12}$ in NaCl-like structure solids direct observation of phonon—lattice interactions,” Physica Status Solidi B, vol. 100, no. 2, pp. 641–649, 1980.
[4] R. K. Varshney and J. Shanker, “Temperature dependences of third-order elastic constants of CsCl, CsBr, and CsI crystals,” Physica Status Solidi B, vol. 126, no. 1, pp. 77–82, 1984.
[5] M. Singh, P. P. Singh, M. Kumar, and B. R. K. Gupta, Indian Journal of Physics, vol. 74A, no. 6, pp. 613–616, 2000.
[6] M. Kumar, “Application of high pressure–high temperature equation of state for elastic properties of solids,” *Physica B*, vol. 311, no. 3–4, pp. 340–347, 2002.

[7] P. P. Singh and M. Kumar, “Temperature dependence of bulk modulus and second-order elastic constants,” *Physica B*, vol. 344, no. 1–4, pp. 41–51, 2004.

[8] I. Suszki, S. Okajima, and K. Seya, “Thermal expansion of single-crystal manganosite,” *Journal of Physics of the Earth*, vol. 27, no. 1, pp. 63–69, 1979.

[9] O. L. Anderson and D. G. Isaak, *Mineral Physics and Crystallography: A Hand Book of Physical Constants*, vol. 2, American Geophysical Union, UCLA Press, Los Angeles, Calif, USA, 1995.

[10] P. R. Son and R. A. Bartels, “CaO and SrO single crystal elastic constants and their pressure derivatives,” *Journal of Physics and Chemistry of Solids*, vol. 33, no. 4, pp. 819–828, 1972.

[11] H. Baltache, R. Khennata, M. Sahnoun, M. Driz, B. Abbar, and B. Bouhafs, “Full potential calculation of structural, electronic and elastic properties of alkaline earth oxides MgO, CaO and SrO,” *Physica B*, vol. 344, no. 1–4, pp. 334–342, 2004.

[12] M. P. Tosi, “Cohesion of ionic solids in the born model,” *Solid State Physics*, vol. 16, pp. 1–120, 1964.

[13] S. O. Lundqvist, *Arkiv för Fysik*, vol. 6, pp. 25–44, 1952.

[14] S. O. Lundqvist, “On the limiting vibrational frequencies of a cubic ionic lattice,” *Arkiv för Fysik*, vol. 9, no. 5, pp. 435–456, 1955.

[15] S. O. Lundqvist, “On the lattice vibrations in cubic ionic crystals,” *Arkiv för Fysik*, vol. 12, no. 3, pp. 263–275, 1957.

[16] S. Gupta and S. C. Goyal, “Pressure derivatives of isothermal bulk modulus of rare gas solids,” *Solid State Communications*, vol. 126, no. 5, pp. 297–300, 2003.

[17] S. Gupta and S. C. Goyal, “Effect of temperature on elastic properties of rare gas solids,” *Physica B*, vol. 352, no. 1–4, pp. 24–35, 2004.

[18] W. H. Flygare and D. W. Hafemeister, “Calculation and interpretation of the129I isomer shifts in the alkali iodide lattices,” *The Journal of Chemical Physics*, vol. 43, no. 3, pp. 789–794, 1965.

[19] L. Pauling and Z. Krist, “The sizes of ions and their influence on the properties of salt-like compounds,” *Zeitschrift für Kristallographie*, vol. 67, pp. 377–404, 1928.

[20] S. P. Singh, S. Gupta, and S. C. Goyal, “Elastic properties of alkaline earth oxides under high pressure,” *Physica B*, vol. 391, no. 2, pp. 307–311, 2007.