Anharmonic properties of potassium halide crystals

Krishna Murti RAJU

Department of Physics, Brahmanand Post-Graduate College
Rath, Hamirpur, U.P., 210 431, INDIA
e-mail: rajukm@yahoo.com

Abstract

An effort has been made to obtain the anharmonic properties of potassium halides starting from primary physical parameters viz. nearest neighbor distance and hardness parameters assuming long- and short- range potentials at elevated temperatures. The elastic energy density for a deformed crystal can be expanded as power series of strains for obtaining coefficients of quadratic, cubic and quartic terms which are known as the second, third and fourth order elastic constants respectively. When the values of the higher order elastic constants are known for a crystal, many of the anharmonic properties of the crystal can be treated within the limit of the continuum approximation in a quantitative manner. In this study, higher order elastic constants are computed up to their melting temperature for potassium halides. The first order pressure derivatives of second and third order elastic constants, the second order pressure derivatives of second order elastic constants and partial contractions are also evaluated at different temperatures for these substances. The results thus obtained are compared with experimental data and found in well agreement with present values.

1. Introduction

In the present decade, considerable interest has been taken in investigation of anharmonic properties of materials of various kinds [1–4]. Many workers have contributed to this field through their experimental and theoretical work. Several efforts have been made in the study of physical and anharmonic properties of solids of different types [5–10] utilizing different physical conditions and using several techniques. Some interesting results have been presented by several investigators while studying the anharmonic properties of the substances possessing various crystal structures. Some have studied temperature variation of anharmonic properties of mixed alkali halides and cyanides [11], of a few alkali cyanides, of rare gas materials [12], of alkali halides [10, 11, 13] using ultrasonic [14–15], theoretical [6] and Brillouin scattering [16] methods. No complete experimental or theoretical effort has been made so for in obtaining the temperature variation of anharmonic properties such as higher order elastic constants and their pressure derivatives of materials possessing different crystal structures.

In this work, a theory for obtaining anharmonic properties such as higher order elastic constants of materials which possess face centered cubic crystal structure has been developed starting from primary physical parameters viz. nearest neighbor distance and hardness parameter using long- and short- range potentials. The elastic energy density for a deformed crystal can be expanded as a power series of strains using Taylor's series expansion. The coefficients of quadratic, cubic and quartic terms are known as the second, third and fourth order elastic constants (SOECs, TOECs and FOECs) respectively. When the values of these elastic constants of crystals are known, many of the anharmonic properties of the substances can be treated within the limit of the continuum approximation in a quantitative manner. Several physical properties and crystal anharmonicities such as thermal expansion, specific heat at higher temperature, temperature variation of acoustic velocity and attenuation, the first order pressure derivatives (FOPDs) of SOECs, Grüneisen numbers and temperature derivatives of SOECs are directly related to SOECs and TOECs. While discussing higher order anharmonicities such as the FOPDs of TOECs, the second order pressure derivatives (SOPDs) of SOECs, partial contraction and deformation of crystals under large forces, the FOECs are to be considered extensively.

The present work is concerned with the formulation to evaluate the second, third and fourth order elastic constants, the FOPDs of the SOECs and TOECs and the SOPDs of SOECs and the partial contractions; using long-and short- range potentials starting from the nearest neighbor distance and hardness parameter. Section 2 deals with the derivation of the theory. In Section 3, the theory is tested for potassium halides. The results thus obtained are widely discussed in Section 4.

2. Formulation

The elastic energy density for a crystal [17, 18] of a cubic symmetry can be expanded up to quartic terms as shown below:

$$
\begin{aligned}
U_0 &= U_2 + U_3 + U_4[1/2!]C_{ijkl}x_{ij}x_{kl} + [1/3!]C_{ijklmn}x_{ij}x_{kl}x_{mn} + [1/4!]C_{ijklmnpq}x_{ij}x_{kl}x_{mn}x_{pq} \\
&= \frac{1}{2}C_{11}(x_{11}^2 + x_{22}^2 + x_{33}^2) + C_{12}(x_{11}x_{22} + x_{22}x_{33} + x_{33}x_{11}) + 2C_{44}(x_{12}^2 + x_{23}^2 + x_{31}^2) \\
&\quad + \frac{1}{6}C_{111}(x_{11}^3 + x_{22}^3 + x_{33}^3) + \frac{1}{2}C_{112}^2 \left[x_{11}^2(x_{22} + x_{33}) + x_{22}^2(x_{33} + x_{11}) + x_{33}^2(x_{11} + x_{22}) \right] \\
&\quad + C_{123}x_{11}x_{22}x_{33} + 2C_{144}(x_{11}x_{23}^2 + x_{22}x_{31}^2 + x_{33}x_{12}^2) \\
&\quad + 2C_{166} \left[x_{12}^2(x_{11} + x_{22}) + x_{23}^2(x_{22} + x_{33}) + x_{31}^2(x_{33} + x_{11}) \right] + 8C_{456}x_{12}x_{23}x_{31} \\
&\quad + \frac{1}{24}C_{1111}(x_{11}^4 + x_{22}^4 + x_{33}^4) + \frac{1}{6}C_{1112} \left[x_{11}^3(x_{22} + x_{33}) + (x_{22}^3(x_{33} + x_{11}) + x_{33}^3(x_{11} + x_{22}) \right] \\
&\quad + \frac{1}{4}C_{1122}(x_{11}^2x_{22}^2 + x_{22}^2x_{33}^2 + x_{33}^2x_{11}^2) + \frac{1}{2}C_{1123}x_{11}x_{22}x_{33}(x_{11} + x_{22} + x_{33}) \\
&\quad + C_{1144}(x_{11}^2x_{23}^2 + x_{22}^2x_{31}^2 + x_{33}^2x_{12}^2) + C_{1155} \left[x_{11}^2(x_{31}^2 + x_{12}^2) + x_{22}^2(x_{12}^2 + x_{23}^2) + x_{33}^2(x_{23}^2 + x_{31}^2) \right] \\
&\quad + 2C_{1255} \left[x_{11}x_{22}(x_{23}^2 + x_{31}^2) + x_{22}x_{33}(x_{31}^2 + x_{12}^2) + x_{33}x_{11}(x_{12}^2 + x_{23}^2) \right] \\
&\quad + 2C_{1266}(x_{11}x_{22}x_{12}^2 + x_{22}x_{33}x_{23}^2 + x_{33}x_{11}x_{31}^2) + 8C_{1456}x_{12}x_{23}x_{31}(x_{11} + x_{22} + x_{33}) \\
&\quad + \frac{2}{3}C_{4444}(x_{12}^4 + x_{23}^4 + x_{31}^4) + 4C_{4455}(x_{12}^2x_{23}^2 + x_{23}^2x_{31}^2 + x_{31}^2x_{12}^2).
\end{aligned} \tag{1}
$$

Here, C_{ijkl}, C_{ijklmn} and $C_{ijklmnpq}$ are the SOECs, TOECs and FOECs in tensorial form; x_{ij} are the Lagrangian strain components; C_{IJ}, C_{IJK} and C_{IJKL} are the SOECs, TOECs and FOECs in Brügger's definition and Voigt notations.

The SOECs, TOECs and FOECs are

$$C_{ijkl} = C_{IJ} = (\partial^2 U/\partial x_{ij}\partial x_{kl})_{x=0} \quad C_{ijklmn} = C_{IJK} = (\partial^3 U/\partial x_{ij}\partial x_{kl}\partial x_{mn})_{x=0},$$

and

$$C_{ijklmnpq} = C_{IJKL} = (\partial^4 U/\partial x_{ij}\partial x_{kl}\partial x_{mn}\partial x_{pq})_{x=0}. \tag{2}$$

The free energy density [19, 20] of a crystal at a finite temperature T is

$$U_{Total} = U_\circ + U^{vib}$$

$$U^{vib} = \frac{KT}{NV_C} \sum_{i=1}^{3sN} \ln 2 \, \sinh(\hbar\omega_i/K_B T), \tag{3}$$

where $U_\circ$ is the internal energy per unit volume of the crystal when all ions are at rest on their lattice points, U^{vib} is the vibrational free energy, V_C is the volume of the primitive cell, N is the number of the primitive cells in the crystal and s is the number of ions in the elementary cell. Other notations used in this equation have their usual meanings.

The elastic constants each have two terms as follows:

$$C_{IJ} = C_{IJ}^0 + C_{IJ}^{vib}, C_{IJK} = C_{IJK}^0 + C_{IJK}^{vib}, \text{ and } C_{IJKL} = C_{IJKL}^0 + C_{IJKL}^{vib}. \tag{4}$$

The first part is the strain derivative of the internal energy U_o and is known as the "static" elastic constant. The second part is the strain derivative of the vibrational free energy U^{vib} and is called the "vibrational" elastic constant. The superscript "0" has been introduced to emphasize that the static elastic constants correspond to temperature $T = 0$ K.

The energy density of the non- deformed crystal is expressed as:

$$U_0 = \left[\frac{1}{2}V_C\right] \sum_{v=1}^{s} \sum_{\left|\begin{smallmatrix} m \neq o \\ u \neq v \end{smallmatrix}\right|} Q_{uv}\left(R_{uv}^{mo}\right) = \sum{}' \frac{Q_{uv}(R)}{2V_C}. \tag{5}$$

Here, R_{uv}^{mo} is the distance between the vth ion in the oth cell and the uth ion in the mth cell and Q_{uv} is the interaction potential between the ions. The indices (v, o) and (u, m) are sometimes dropped when no confusion occurs. One assumes that Q_{uv} is the sum of the long-range Coulomb and the short-range Börn-Mayer [21] potentials:

$$Q_{uv}(r_0) = \pm\left(\frac{e^2}{r_0}\right) + A\exp\left(\frac{-r_0}{q}\right). \tag{6}$$

Here, e is the electric charge, the sign $\pm$ applies to like and unlike ions, respectively, r_0 is the nearest-neighbor distance, q is hardness parameter and A is

$$A = \frac{-0.29126q\frac{e^2}{r_0^2}}{\exp\left(\frac{-r_0}{q}\right) + 2\sqrt{2}\exp\left(\frac{-r_0\sqrt{2}}{q}\right)} \tag{7}$$

It is assumed that the crystal is deformed homogeneously. When the crystal is deformed homogeneously, the distance between ions (v, o) and (u, m) in the deformed and non-deformed states, R_{uv}^{mo} and r_{uv}^{mo}, are related to the Lagrangian strains x_{ij} via

$$(R_{uv}^{mo})^2 - (r_{uv}^{mo})^2 = 2Y_{uvi}^{mo}Y_{uvj}^{mo}x_{ij} = 2Z_{uv}^{mo}, \tag{8}$$

where Y_{uvi}^{mo} is the ith Cartesian component of the vector r_{uv}^{mo} The definition of the quantity Z_{uv}^{mo} is as expressed in equation (8). The internal energy U_o given by equation (5) can be expanded in terms of Z_{uv}^{mo}, which will yield quadratic, cubic and quartic terms as given below:

$$U_2 = \frac{1}{2}V_c\sum{}' \left[\frac{1}{2!}Z^2 D^2 Q(R) \right]_{R=r} = \frac{1}{4}V_c \left[x_{ij}x_{kl}\sum{}' Y_i Y_j Y_k Y_l D^2 Q(R) \right]_{R=r}$$

$$U_3 = \frac{1}{2}V_c\sum{}' \left[\frac{1}{3!}Z^3 D^3 Q(R) \right]_{R=r} = \frac{1}{12}V_c \left[x_{ij}x_{kl}x_{mn}\sum{}' Y_i Y_j Y_k Y_l Y_m Y_n D^3 Q(R) \right]_{R=r}$$

$$U_4 = \frac{1}{2}V_c\sum{}' \left[\frac{1}{4!}Z^4 D^4 Q(R) \right]_{R=r} = \frac{1}{48}V_c \left[x_{ij}x_{kl}x_{mn}x_{pq}\sum{}' Y_i Y_j Y_k Y_l Y_m Y_n Y_p Y_q D^4 Q(R) \right]_{R=r}. \tag{9}$$

Here, is defined the operator $D \equiv \frac{d}{RdR}$.

With reference to equations (3) and (4), and comparison of equations (1) and (9), one may obtain the static elastic constants presented in Table 1. For a central force model, there are only two independent SOECs, three independent TOECs and four independent FOECs at absolute zero temperature. As in the case of the internal energy U_0, the vibrational free energy is also expanded in terms of strains, the quadratic, cubic and quartic terms are as below:

$$U_2 = [1/V_c 2!]\sum{}'\sum{}''[Z'Z(D'D)U^{vib}]_{Z=0} = [1/2V_c]x_{ij}x_{kl}f_{ijkl}$$

$$U_3 = [1/V_c 3!]\sum{}'\sum{}''\sum{}'''[Z'Z''Z(D'D''D)U^{vib}]_{Z=0} = [1/6V_c]x_{ij}x_{kl}x_{mn}f_{ijklmn}$$

$$U_4 = [1/V_c 4!]\sum{}'\sum{}''\sum{}'''\sum{}'''[Z'Z''Z'''Z(D'D''D'''D)U^{vib}]_{Z=0} = [1/24V_c]x_{ij}x_{kl}x_{mn}x_{pq}f_{ijklmnpq} \tag{10}$$

where,

$$f_{ijkl} = \sum{}'\sum{}''[Y_iY_jY_k'Y_l'(D'D)U^{vib}]_{R=r}$$

$$f_{ijklmn} = \sum{}'\sum{}''\sum{}'''[Y_iY_jY_k'Y_l'Y_m''Y_n''(D''D'D)U^{vib}]_{R=r}$$

and

$$f_{ijklmnpq} = \sum{}'\sum{}''\sum{}'''\sum{}''"[Y_iY_jY_k'Y_l'Y_m''Y_n''Y_p'''Y_q'''(D'''D''D'D)U^{vib}]_{R=r}.$$

Here, the abbreviations $Z_{u'v'}^{m'o} \rightarrow Z' \left[\frac{d}{R_{u'v'}^{m'o}dR_{u'v'}^{m'o}} \right] \rightarrow D'$, etc., are used. On comparison of equations (1) and (10), one determines the vibrational elastic constants. The prime marks in the summations $\sum'$, $\sum''$ etc., denote summation over all lattice points except $m = 0$, $u = v$.

Table 1. Expression for the SOECs, TOECs and FOECs at 0 K for potassium halides.

$$C_{11}^0 = \text{-}1.56933G + G_1 + 2G_2$$
$$C_{12}^0 = C_{44}^0 = 0.347775G + G_2$$
$$C_{111}^0 = 10.2639G - G_3 - 2G_4$$
$$C_{112}^0 = C_{166}^0 = 1.208625G - G_4$$
$$C_{123}^0 = C_{144}^0 = C_{456}^0 = 0.678375G$$
$$C_{1111}^0 = \text{-}80.71455G + G_5 + 2G_6$$
$$C_{1112}^0 = C_{1155}^0 = 4.43205G + G_6$$
$$C_{1122}^0 = C_{1266}^0 = C_{4444}^0 = 5.615925G + G_6$$
$$C_{1123}^0 = C_{1144}^0 = C_{1255}^0 = C_{1456}^0 = C_{4455}^0 = \text{-}1.584975G$$
where, $G = e^2/r_0^4$, $G_1 = (1/r_0 + 1/q)Q\ (r_0)/\ qr_0$
$$G_2 = (\sqrt{g}/2r_0 + 1/q)Q\ (r_0\sqrt{g})/qr_0$$
$$G_3 = (3/r_0^2 + 3/qr_0 + 1/q^2)Q\ (r_0)/q$$
$$G_4 = (3\sqrt{g}/r_0^2 + 6/qr_0 + 2\ \sqrt{g}/q^2)Q\ (r_0\sqrt{g})/4q$$
$$G_5 = (15/r_0^3 + 15/qr_0^2 + 6/q^2r_0 + 1/q^3)r_0Q(r_0)/q$$
$$G_6 = (15\sqrt{g}/4r_0^3 + 15/2qr_0^2 + 3\sqrt{g}2/q^2r_0 + 1/q^3)r_0Q(r_0\sqrt{2})/2q$$

Vibrational contributions to SOECs, TOECs and FOECs are shown in Table 2. These are shown as a combination of g_n'S and F_n'S which are evaluated conveniently by taking crystals symmetry [22] into account and the expressions for g_n and F_n are tabulated in Tables 3 and 4. By adding the vibrational elastic constants to the static elastic constants, one may get SOECs, TOECs and FOECs at any temperature for monovalent fcc crystals.

Table 2. Expressions for Vibrational Contribution to the SOECs, TOECs and FOECs for potassium halides.

$$C_{11}^{vib} = g_1F_1^2 + g_1F_2$$
$$C_{12}^{vib} = g_2F_1^2 + g_1F_5$$
$$C_{44}^{vib} = g_1F_5$$
$$C_{111}^{vib} = g_3F_1^3 + g_2F_2F_1 + g_1F_3$$
$$C_{112}^{vib} = g_1F_1^3 + g_2F_1(2F_5 + F_2) + g_1F_6$$
$$C_{123}^{vib} = g_3F_1^3 + 3\ g_2F_1F_5$$
$$C_{144}^{vib} = g_2F_1F_5$$
$$C_{166}^{vib} = g_2F_1F_5 + g_1F_6$$
$$C_{456}^{vib} = 0$$
$$C_{1111}^{vib} = g_4F_1^4 + 6g_3F_1^2F_2 + 3g_2F_2^2 + 4g_2F_1F_3 + g_1F_4$$
$$C_{1456}^{vib} = 0$$
$$C_{1112}^{vib} = g_4F_1^4 + 3g_3F_1^2(F_5 + F_2) + 3g_2F_5F_2 + g_2F_1(3F_6 + F_3) + g_1F_7$$
$$C_{1122}^{vib} = g_4F_1^4 + 2g_3F_1^2(2F_5 + F_2) + g_2\ (2F_5^2 + F_2^2) + 4g_2F_1F_2 + g_1F_7$$
$$C_{1123}^{vib} = g_4F_1^4 + g_3F_1^2(5F_5 + F_2) + g_2F_1\ (2F_5 + F_2\ ) + 2g_2F_1F_6$$
$$C_{1144}^{vib} = g_3F_1^2F_5 + g_2F_5F_2$$
$$C_{4444}^{vib} = 3\ g_2F_5^2 + g_2F_7$$
$$C_{1155}^{vib} = g_3F_1^2F_5 + g_2F_5F_2 + 2g_2F_1F_6 + g_1F_7$$
$$C_{4455}^{vib} = g_3F_5^2$$
$$C_{1255}^{vib} = g_3F_1^2F_5 + g_2F_5^2 + g_2F_1F_6$$
$$C_{1266}^{vib} = g_3F_1^2F_5 + g_2F_5^2 + 2g_2F_1F_6 + g_1F_7$$

Table 3. Expression for g_n's for potassium halides.

$g_1 = g_0 S;$
$g_2 = g_0[(X/S_1) + S]/2;$
$g_0 = \omega_0/8r_0^3;$
$g_3 = g_0[(2X^2 S/3S_1) + (X/S_1) + S]/48;$
$X = g\omega_0 / 2KT;$
$g_4 = -g_0 [(X^3 S^2/3S_1) + (X^3/6S_1^2) + (X^2 S/S_1) + (5X/4S_1) + (5S/4)]/144;$
$\omega_0 = (1/M^+ + 1/M^-)/qr_0 F_0;$
$S = \text{Coth } X; \ S_1 = \text{Sinh}^2 X.$

Table 4. Expression for F_n's for potassium halides.

$F_0 = 1/[(q_0 - 2)(Q(r_0) + 2(q_0 - \sqrt{g})Q(r_0\sqrt{g})$
$q_0 = r_0/q;$
$F_1 = 2[(2 + 2q_0 - q_0^2)Q(r_0) + 2 (\sqrt{g} + 2q_0 - \sqrt{g}q_0^2)Q(r_0\sqrt{g})]F_0;$
$F_2 = 2(- 6 - 6q_0 - q_0^2 + q_0^3)Q (r_0)F_0 + 2F_5;$
$F_3 = 2(- 30 - 30q_0 - 9q_0^2 + q_0^3 - q_0^4)Q (r_0)F_0 + 2F_6;$
$F_4 = 2(- 210 - 210q_0 - 75q_0^2 - 5q_0^3 + 4q_0^4 + q_0^5)Q (r_0)F_0 + 2F_7;$
$F_5 = (- 3\sqrt{g} - 6q_0 - \sqrt{g}q_0^2 + 2q_0^3)Q(r_0\sqrt{g})F_0;$
$F_6 = [(15/ \sqrt{g}) + 15q_0 - (9/ \sqrt{g})q_0^2 - q_0^3 - \sqrt{g}q_0^4] Q (r_0\sqrt{g})F_0;$
$F_7 = [-(105/ 2 \sqrt{g}) - (105/2)q_0 - (75/ 2\sqrt{2})q_0^2 - (5/2)q_0^3 + 2\sqrt{2} q_0^4 + q_0^5]Q (r_0\sqrt{g})F_0;$

The FOPDs of SOECs are concerned with SOECs and TOECs. The FOPDs of TOECs and SOPDs of SOECs are directly related to the SOECs, TOECs and FOECs. The Partial contractions are mere combination of FOECs. The expressions for the FOPDs and SOPDs of SOECs and the FOPDs of TOECs [23, 24], partial contractions for monovalent fcc solids [25, 26] are given in Tables 5 and 6.

Table 5. Expression for the FOPDs of the SOECs and TOECs for potassium halides.

$dC_{11}/dP = (C_{11} + Q_Q + C_{111} + C_{112})C^0; C_Q = C_{11} + 2C_{12}$
$dC_{12}/dP = -(- C_{11} + C_{12} + C_{123} + 2C_{112})C^0; \ C^0 = 1/C_Q;$
$dC_{44}/dP = -(C_Q + C_{44} + C_{144} + 2C_{166})C^0;$
$dC_{111}/dP = -(-3C_Q + 3C_{111} + C_{1111} + 2C_{1112})C^0;$
$dC_{112}/dP = -(C_Q + 3C_{112} + C_{1112} + C_{1122} + C_{1123})C^0;$
$dC_{113}/dP = -(-C_Q + 3C_{113} + 3C_{1123})C^0;$
$dC_{144}/dP = -(C_Q + 3C_{144} + C_{1144} + 2C_{1244})C^0;$
$dC_{166}/dP = -(-C_Q + 3C_{166} + C_{1166} + 2C_{1244})C^0;$
$dC_{456}/dP = -(-C_Q + 3C_{456} + 3C_{1456})C^0;$

Table 6. Expression for the SOPDs of the SOECs and for Partial Contraction of the FOECs.

$d^2C_{11}/dP^2 = [(1 + 3C_P)C_{11} + (4 + 3C_P)(C_{111} + 2C_{112}) + C_{1111} + 4C_{1112} + 2C_{1122} + 2C_{1123}] \ C^{02};$
$d^2C_{12}/dP^2 = [(1 + 3C_P)C_{12} + (4 + 3C_P)(2C_{112} + C_{123}) + 2C_{1122} + 5C_{1123}]C^{02};$
$d^2C_{44}/dP^2 = [(1 + 3C_P)C_{44} + (4 + 3C_P)(C_{144} + 2C_{166}) + C_{1144} + 2C_{1166} + 4C_{1244} + 2C_{1266}] \ C^{02};$
$C_P = (4C_{11} + C_{111} + 6C_{112} + 2C_{123})C^0;$
$Y_{11} = C_{1111} + 4C_{1112} + 2C_{1122} + 2C_{1123};$
$Y_{12} = 2C_{1112} + 2C_{1122} + 5C_{1123};$
$Y_{44} = C_{1144} + 2C_{1166} + 4C_{1244} + 2C_{1266}.$

3.   Evaluation

Extensive efforts have been committed by the theoretical workers to study the attention-grabbing features of materials [27–31]. The detailed study of formulation is given in the preceding Section 2. The expressions for different elastic constants and pressure derivatives of the potassium halides are shown in Tables 1–6. Using the concept of nearest-neighbour distance and hardness parameter [6], the elastic constants and pressure derivatives for potassium halides are evaluated at different temperatures (from 100 K to up to their melting points [32]; given in Tables 7) using the expression of Tables 1–6 and shown in Figures 1–15. The values of SOECs, TOECs, FOECs, FOPDs and SOPDs of SOECs and FOPDs of TOECs at 0 K and at room temperature for these crystals are given in Table 7–11. The experimental and theoretical data are also given, wherever possible, for comparison. The whole evaluation is based on the assumption that the fcc crystal structure of the material does not change when temperature varies up to their melting point. The values of the nearest neighbor distance (r_0) and hardness parameter (q) [6, 32, 33] are given in Table 7. Thermal expansion coefficients (α) [15, 31–33] for different solids are taken into account as $r = r_0 (1 + \alpha \mathrm{T})$, where $\alpha = A_1 + A_2 \mathrm{T} + A_3 T^2 + A_4 T^3 + A_5 T^4$ (for KI, KCl, KBr). Equations for α, are computed using curve fitting and A_1, A_2, A_3, A_4, A_5 are shown in Table 12.

Table 7. The nearest neighbors distance (r_0), hardness parameter (q) (10^{-10} m), melting points and the SOECs and TOECs in 10^{10} Newton/m^2 at 0 K. Comparison data taken from A. Cox et al, J. Phys C, 15 (1982) 4473. (Experimental values are given in bold.)

Crystal	Melting Point, K	r_0	q	C_{11}^0	C_{44}^0	C_{111}^0	C_{112}^0	C_{123}^0
KF	1153	2.6568	0.278	6.74	1.86 1.28 **1.34**	−113.77	−7.55	3.14
KCl	1063	3.1150	0.296	4.28	0.95 0.81 **0.66**	−76.61	−3.79	1.66
KBr	1003	3.2580	0.305	3.68	0.79 0.69 **0.52**	−66.37	−3.15	1.38
KI	996	3.4840	0.319	2.92	0.60 0.58 **0.37**	−53.51	−2.38	1.06

4.   Results and discussions

A literature survey shows that, at present time, several efforts have been made by the experimental and theoretical workers to study the motivating features of these solids, such as anharmonic effects, higher order elastic constants, pressure derivatives and phonon-induced phase transition etc. in elevated temperature region. The SOECs and TOECs in 10^{10} N/m^2 at 0 K for halides of potassium are shown in Table 7 along with the experimental values reported by other workers. For a cubic crystal there are three independent second order elastic constants at absolute zero namely C_{11}^0, C_{12}^0 and C_{44}^0. In this investigation Brugger's definition [21] of

Table 8. The SOECs and TOECs in 10^{10} N/m^2 at room temperature. (Experimental values are given in bold numerals.)

Crys.	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}	Ref.
KF	7.615	1.555	1.885	-119.28	-6.327	1.266	3.207	3.207	-7.630	
	6.185	1.440	1.250							13
	7.71	**1.59**	**1.29**							34
KCl	3.869	1.161	0.922	-81.19	-2.669	0.035	1.622	-3.701	1.586	
	3.838[a]	0.683[a]	0.633[a]	**-72.6[b]**	**-2.4[b]**	**1.1[b]**	**2.3[b]**	**2.6[b]**	**1.6[b]**	13[a],54[b]
				-70.1	**-2.24**	**1.33**	**1.27**	**-2.45**	**1.18**	25
	4.940[c]	**0.664**	**0.662**							56[c],34
KBr	3.304	0.550	0.765	-70.37	-2.124	-0.098	1.354	-3.065	1.324	
	3.263	0.564	0.504							13
	4.250[d]	**0.510[d]**	**0.583**							35[d],34
KI	2.601	0.763	0.579	-56.88	-1.492	-0.238	1.034	-2.312	1.010	
	2.577	0.456	0.370							13
	3.499	**0.299**	**0.389**							34

Table 9. FOECs in 10^{10} N/m^2 at room temperature.

Crys.	C_{1111}	C_{1112}	C_{1122}	C_{1123}	C_{1144}	C_{1155}	C_{1255}	C_{1266}	C_{1456}	C_{4444}	C_{4455}	Ref
KF	184	2.79	3.22	-1.09	-0.929	-0.564	-0.738	0.230	-0.623	-0.214	-1.30	
	1716	26	31.4	-7.49	-7.45			31.0	-4.64	31.0		47
	1865	31.117	41.19	-6.29	-5.53			30.99		32.18		48
KCl	124	0.978	0.789	-0.530	-0.460	-0.486	-0.372	-0.404	-0.338	-0.568	-0.607	
	1141	17	20.1	-2.95	-3.56			26.8	2.59	27.7		47
	1220	13.85	-0.08	-1.18	-0.97			14.22		17.31		48
KBr	108	0.490	0.528	-0.453	-0.385	-0.871	$-.309$	-0.551	-0.276	-0.695	-0.522	
	991	20	22.7	-2.22	-2.88			30.0	-1.99	30.9		47
	1085	13.13	-5.90	-0.14	-0.11			12.89		16.68		48
KI	88.3	0.478	0.425	-0.377	-0.305	-0.869	-0.238	-0.603	-0.202	-0.738	-0.441	
	792	25	27.5	-1.48	-2.11			34.6	-1.31	35.5		47
	957	13.2	-1.44	$-0.10b$	-0.25			12.19		15.25		48

second order elastic constants have been used. In the central force model for the elastic constants; the Cauchy's relations are as $C_{12}^0 = C_{44}^0$. Hence only two independent second order elastic constants at absolute zero have been used here. The Cauchy's relation $C_{12}^0 = C_{44}^0$, which is a consequence of any central force law, is of course satisfied in our study. The abnormal behaviour of the temperature dependence of the elastic constant C_{12} is related to the existence of many body potential and non-central potentials in solids, which are responsible for the breakdown of the Cauchy relation $C_{12} = C_{44}$ [27]. The Cauchy relation $C_{12}^0 = C_{44}^0$ is valid only when all interatomic forces are central under static lattice conditions. The following Cauchy relations are satisfied by these solids: $C_{166}^0 = C_{112}^0$ and $C_{144}^0 = C_{456}^0 = C_{123}^0$. Since these studies were based on two-body potentials and could explain Cauchy relation, which are significant in all the monovalent crystals. The semi-empirical studies [28, 29] on lattice dynamics and statics have shown that non additive three-body interactions are important in these types of materials as there occurs appreciable decrease in their nearest neighbor separations at high pressures. The need for inclusion of three-body interaction forces was also emphasized by Sims et al. [30] for better matching of results. However, the recent experimental data on elastic constants measured at low temperatures, show that the Cauchy relations are strongly violated by many ionic crystals and these violations

cannot be ignored. It is possible that the discrepancy in respect of the elastic behaviour of solids inherent in the current theories is responsible for physically unrealistic values of the parameters obtained in the models when they are fitted with the neutron data. Obviously, the search for a model that gives the correct description of the dielectric behaviour as well as the elastic behaviour of these solids is quite pertinent. A possible explanation of this behaviour can be sought from the fact that the many-body and/or, thermal effects might be more pronounced in SOECs than TOECs.

Table 10. The FOPDs and SOPDs (in 10^{-11} N/ m^2) of the SOECs and partial contractions (in 10^{12} N/m^2). (Experimental values are given in bold numerals.)

Crystal	$\frac{dC_{11}}{dP}$	$\frac{dC_{12}}{dP}$	$\frac{dC_{44}}{dP}$	$\frac{ds}{dP}$	$\frac{dk}{dP}$	$\frac{d^2C_{11}}{dP}$	$\frac{d^2C_{12}}{dP}$	$\frac{d^2C_{44}}{dP}$	Y_{11}	Y_{12}	Y_{44}	Ref
KF	10.59	1.63	−0.05	4.34	4.81	−5.78	−1.07	−0.84	1868	77.4	76	
			-0.43[a]		**5.26**[a]	−5.26	−0.47	−0.76				5[a],47
						−5.78	−1.07	−0.838				37
KCl	11.81	1.52	−0.21	5.03	5.10	−14.6	−1.50	−1.18	−12.84	−24.13	−5.15	
	12.93[a]	**1.58**[a]	**-0.39**[a]	**5.61**[a]	**5.34**[a]	−8.87	−0.59	−1.53				55[a],47
						−14.6	−1.50	−1.18				37
KBr	12.01	1.51	−0.23	5.14	5.16	−12.5	−1.99	−1.64	−3.063	−12.845	−2.699	
			-0.33[a]		**5.38**[a]	−10.0	−0.61	−2.10				55[a],47
						−12.5	−1.99	−1.46				37
KI	12.31	1.49	−0.26	5.31	5.23	−15.8	−2.61	−2.00	−.03	−7.92	−1.66	
			-0.24[a]		**5.47**[a]	−16.9	−1.40	−4.42				55[a],47
						-12.7	**-1.6**	**-1.08**				26
						−15.8	−2.61	2.0 0				37

Table 11. The FOPDs of the TOECs at room temperature.

Crystal	$\frac{dC_{111}}{dP}$	$\frac{dC_{112}}{dP}$	$\frac{dC_{123}}{dP}$	$\frac{dC_{144}}{dP}$	$\frac{dC_{166}}{dP}$	$\frac{dC_{456}}{dP}$	Ref.
KF	10.1	211	218	−1.19	72.3	2.17	
	−132	−4.21	2.25	0.24	1.59	2.24	47
KCl	0.42	130	137	−1.16	46.7	2.05	
	−155	−5.23	1.76	0.08	0.18	2.25	47
KBr	−52.1	81.6	87.7	−1.16	29.8	2.03	
	−153	−6.86	1.60	0.01	−0.75	2.20	47
KI	−73.9	63.9	69.8	−1.16	24.2	2.01	
	−174	−11.7	1.50	0.04	−2.97	2.31	47

Table 12. Numerical Coefficients for different compounds.

Coefficients	A_1	A_2	A_3	A_4	A_5
KI	4.3749	0.3395	$−1.1212 \times 10^{-3}$	1.5876×10^{-6}	$−7.4395 \times 10^{-10}$
KCl	−1.7935	0.3031	$−8.0212 \times 10^{-4}$	9.2505×10^{-7}	$−3.6340 \times 10^{-10}$
KBr	−0.7222	0.3828	$−1.2936 \times 10^{-3}$	1.8220×10^{-6}	$−8.5402 \times 10^{-10}$

Cauchy (1822) has derived the general mathematical theory of elasticity. That hypothesis suggests the strains in terms of differential displacements of neighboring points in the material and the stresses in

terms of attractive forces on infinitesimal areas in the similar position. The theory does not utilize these representations completely, but following Cauchy, implements them in modified forms on the foundation of arguments proposed by him and considered as reliable ever since. However, a crucial check of those arguments makes them indefensible [31]. Cauchy's assumptions are limited to the homogeneous strains only; and the more general case of heterogeneous strains, including especially all cases of wave-propagation and static deformations in the nature of torsion and flexure, lie outside its range. On the other hand, the mathematics of elasticity has been applied to these cases and the constants appearing in the formulae have been evaluated experimentally. For instance, the results of experimental work on cubic crystals have been expressed in terms of three constants generally selected as C_{11}, C_{12} and C_{44}, respectively. Hence, by an examination of the experimental data for those cubic crystals which have been investigated with adequate precision by different methods, it should be possible to decide whether those data are expressible in terms of three constants only, or whether four constants are actually needed [31].

The SOECs and TOECs in units of $\times 10^{10}$ N/m^2 at room temperature for halides of potassium are shown in Table 8. The experimental values reported by other workers are also given in this Table. The experimental values of potassium halides [13, 25, 34, 35] are of the same order and are in well agreement with present results, which shows the validity of the present theory. The Temperature variation of SOECs for potassium halides are shown in Figures 1(a–c) along with available experimental data [34, 35]. The agreement is satisfactory in view of the large experimental uncertainties. The elastic constants of solids in general decrease with temperature and such a decrease has been explained by many available theories. But in the NaCl- like structure the elastic constant C_{12} of some alkali halides (for example KCl, KBr etc.) is increasing with temperature. This phenomenon is known as the anomalous temperature dependence of C_{12} in these solids. In the present work, the temperature dependence of C_{12} is found to explain the observed anomalous temperature dependence of C_{12} in alkali halides with NaCl-Structure. Results are presented for potassium halides. We see that an anomalous temperature dependence of C_{12} does not occur in sodium halides, but does in potassium halides. These results are firmly supported by the available experimental data. The variation of C_{11} with temperature is found to be large as compared with C_{12} and C_{44}. The constant C_{11} represents elasticity in length. A longitudinal strain produces a change in volume without change in shape. The volume change is closely related to the temperature and thus produces a large change in C_{11}. On the other hand, the constant 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. Therefore, C_{12} and C_{44} are less sensitive to the temperature. Thus, study of the temperature dependence of C_{11} may provide a more critical test of the theory.

The higher order elastic constants are strongly related to other anharmonic properties; such as thermal expansion, thermo elastic constants and thermal conductivity. The knowledge of TOECs may provide further critical data for testing the machines for non-destructive-testing. Furthermore, we expected to obtain additional data for the discussion of the influence of asymmetric ions on non-linear elastic properties, in particular for crystals of rock salt type. Third order elastic constants play an important role in solid-state physics. They allow an evaluation of first order anharmonic terms of the inter-atomic potential or of generalized Grüneisen parameters, which enter the theories of all anharmonic phenomena, such as the interaction of acoustic and thermal phonons and the equation of state. The present study of the temperature variation of TOECs could prove useful in studies of various anharmonic properties of ionic solids in general. The TOECs play an important role when it comes to explain anharmonic phenomena in solids (interactions of ultrasonic vibration with thermal phonons, harmonic generators, equation of state etc.). As a result of the anharmonicity of the crystal lattice

vibrations, the elastic constants vary with temperature. The present results of TOECs in 10^{10} N/m^2 at room temperature for halides of potassium are shown in Table 8. The experimental values obtained by other workers are also given in this Table. The experimental values of potassium halides [25, 34] are of the same order and are in well agreement with present results, which shows the validity of the present theory. The Temperature variation of TOECs potassium halides are shown in Figures 2 and 3. Expressions obtained in the present work are more general than those derived previously [36, 37]. This is in view of the fact that we have taken the thermal expansion coefficient [15, 31–33] into account. Among the calculated third order elastic constants of these materials, C_{111}'s are the largest in their absolute values and an order of magnitude larger than the SOEC. Magnitude of other C_{ijk}'s are markedly smaller than those of C_{111}.
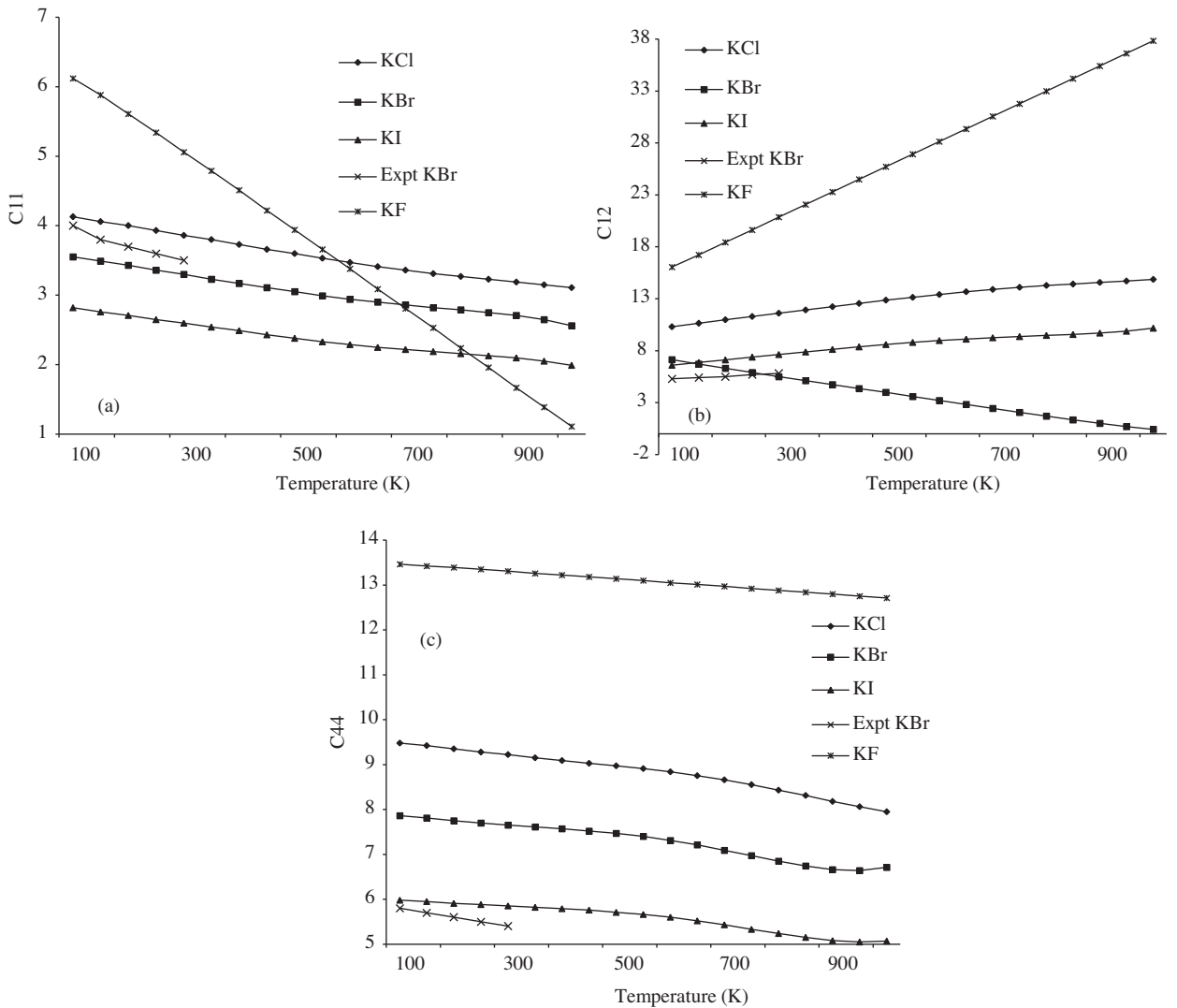
Figure 1. Temperature variation of SOECs for potassium halides. **(a)** Temperature variation of elastic constant $C_{11}(\times 10^{10}$ Newton/m$^2)$. Experimental data is from [34]. **(b)** Temperature variation of $C_{12}(\times 10^9$ Newton/m$^2)$. Experimental data is from [35]. **(c)** Temperature variation of $C_{44}(\times 10^9$ Newton/m$^2)$. Experimental data is from [34].
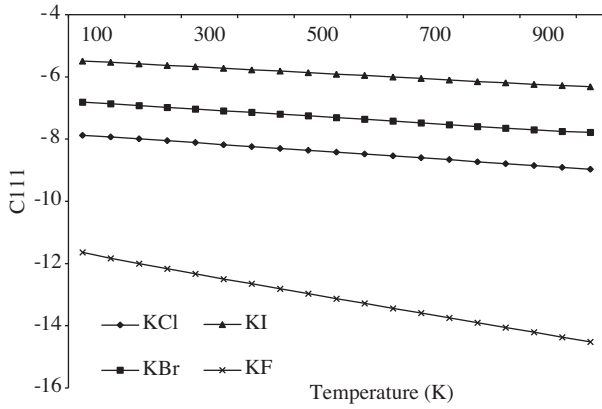
Figure 2. Temperature variation of C_{111} (in $\times 10^{11}$ Newton/m^2).
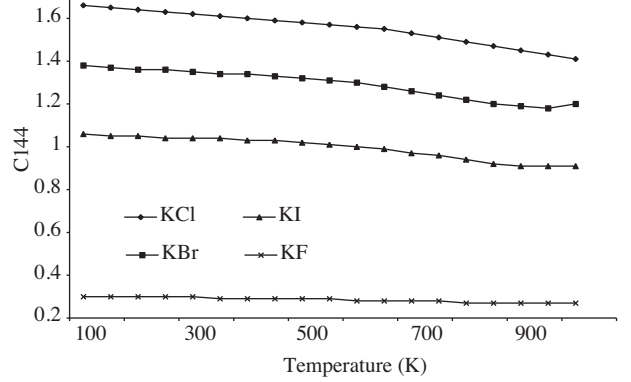
Figure 3. Temperature variation of C_{144}.

Third and fourth order elastic constants are required to study many anharmonic properties of crystals and therefore their accurate evaluation is essential. Recent attempts have been made to calculate anharmonic properties of ionic crystals [38–44]. Only a few of them [45, 46] have taken account the temperature dependence of these properties. The thermal contribution to elastic constants is very significant. The experimental data reveal that in going from 100 K to higher temperatures, the values of second order elastic constants (SOECs) are changed considerably even for highly ionic solids like alkali halides. We have already discussed the temperature variation of second and third order elastic constants of potassium halides. Since the contribution from third and fourth order coupling parameters to many anharmonic properties are of the same order of magnitude, the knowledge of FOECs is equally important as that of TOECs. The FOECs for halides of potassium are given in Table 9. Some theoretical results [47, 48] are also presented. Due to non-availability of experimental data, the comparison is not made. The Partial Contractions in 10^{12} N/m^2 for potassium halides are given in Table 10. Calculated results of fourth order elastic constants at different temperatures are reported in Figures 4–10. The Partial Contractions are shown in Figure 11.
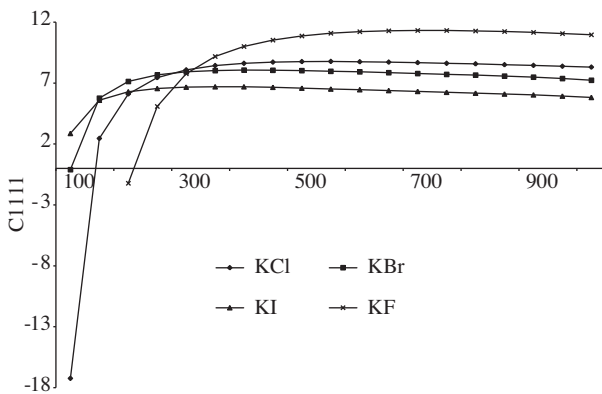
Figure 4. Temperature variation of $C_{1111}(\times 10^{12}$ Newton/m^2).
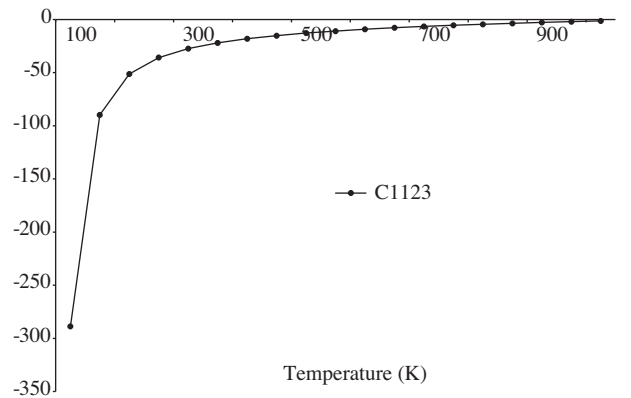
Figure 5. Temperature variation of FOEC for KCl ($\times 10^{11}$ Newton/m^2).
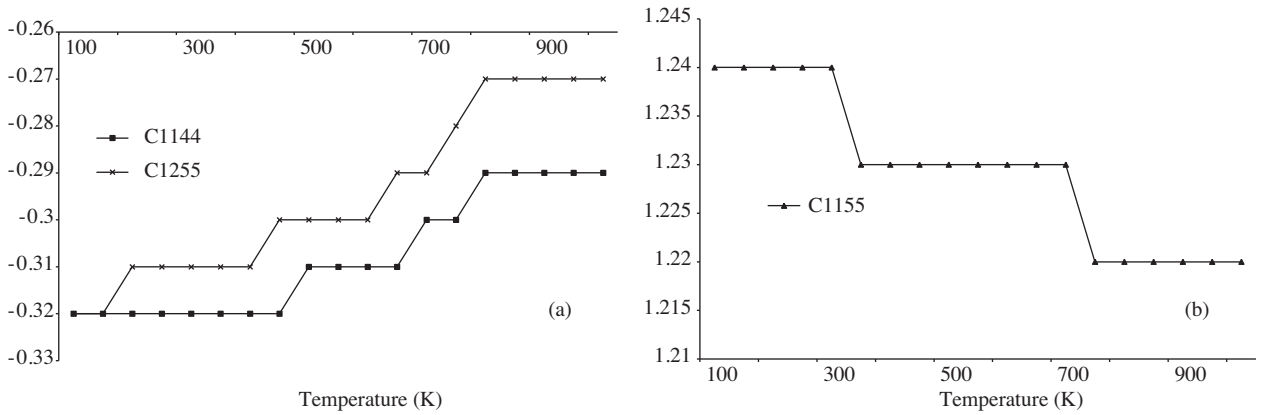
Figure 6. (a) Variation of C_{1144} and C_{1255} with temperature for KBr ($\times 10^{12}$ N/m^2). (b) Variation with temperature of C_{1155} for KBr ($\times 10^{12}$ N/m^2).
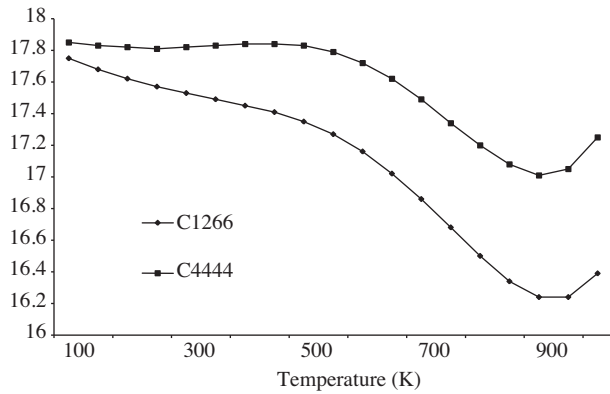

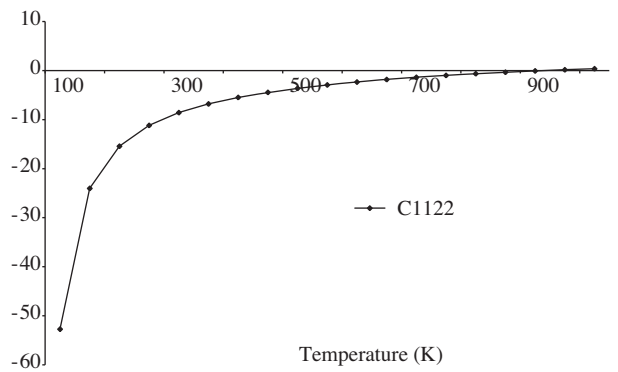**Figure 7.** Variation of FOECs with temperature for KBr ($\times 10^{11}$ N/m^2).

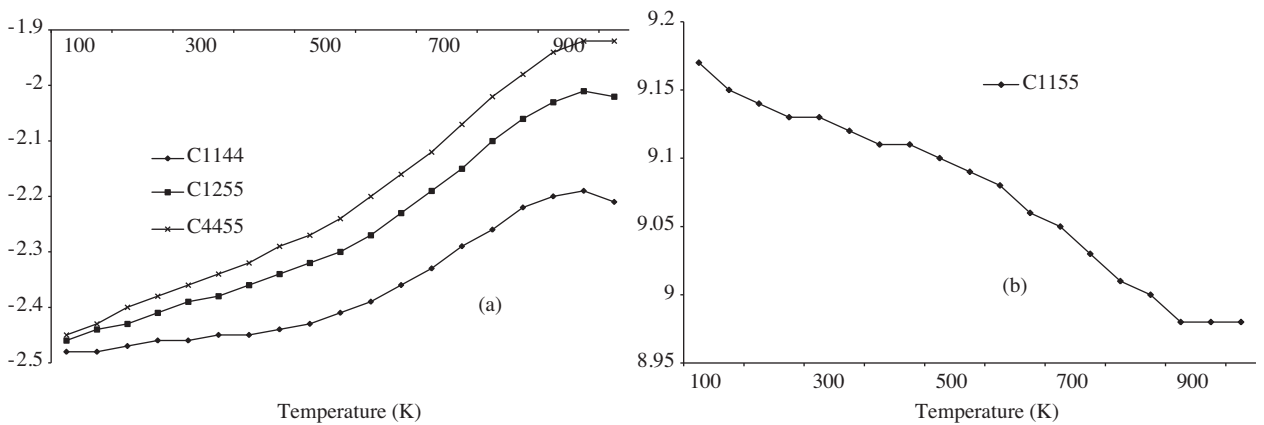**Figure 8.** Temperature variation of FOEC for KI ($\times 10^{11}$ N/m^2).

Figure 9. (a) Temperature variation of FOECs for KI ($\times 10^{10}$ N/m^2). (b) Temperature variation of C_{1155} for KI ($\times 10^{10}$ N/m^2).
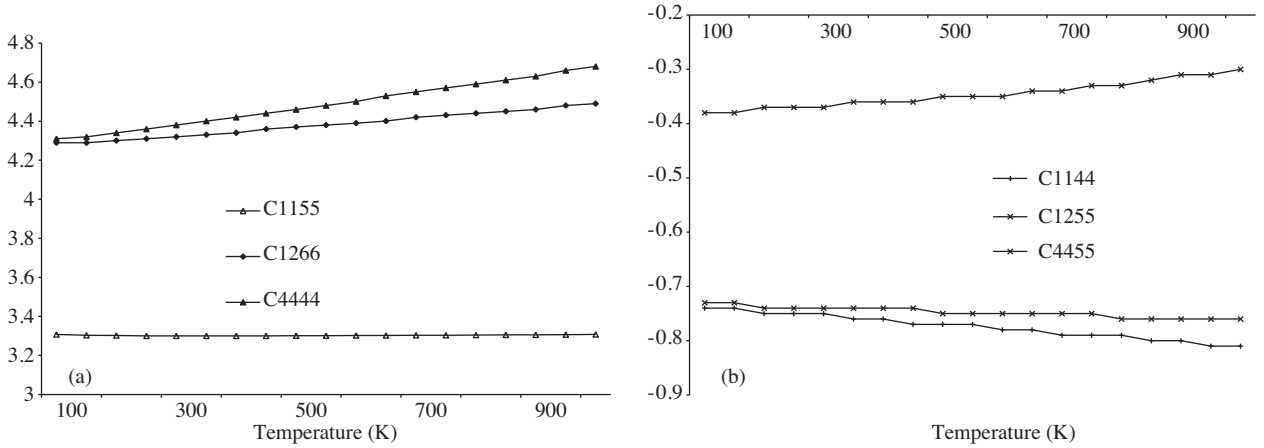
Figure 10. (a) Temperature variation of the selected FOECs for KF ($\times 10^{11}$ N/m^2). (b) Temperature variation of the selected FOECs for KF ($\times 10^{11}$ N/m^2).
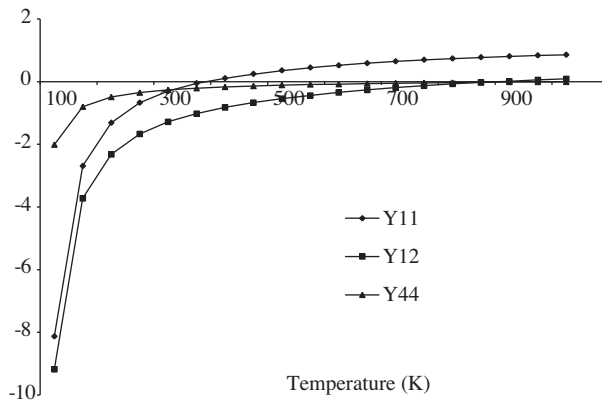
Figure 11. Temperature variation of Partial Contractions (in $\times 10^{12}$) for KI.

Recent extension of ultrasonic techniques to high pressure and high frequencies renewed interest in the higher order coefficients of non- linear elasticity. Much theoretical work has been done on the temperature dependence of the elastic constants of ionic crystals [49–53]. An investigation into the higher order elastic constants and their pressure derivatives provides useful information on the inter-atomic forces, inter-ionic potentials and on anharmonic properties of crystalline solids. This is why recently [38–41, 45, 46, 49–54] there have been several attempts to determine the elastic constants of higher order, particularly for alkali halide crystals, using theoretical [7, 8] as well as experimental techniques. The FOPDs and SOPDs of the SOECs of potassium halides are presented in Table 10 along with experimental [26, 55, 56] and theoretical [47, 48] data. On comparison, one may state that the present results are in well agreement at a great extent. Calculated results of first and second order pressure derivatives of second order elastic constants at different temperatures are reported in Figures 12, 13 and 14. An important aspect of the present investigation is the calculation of second order pressure derivatives of SOECs at different temperatures. Experimental values of SOPD are available corresponding to 300 K. The good agreement between theoretical and experimental values supports the validity of the present work.

The FOPDs of the TOECs of potassium halides are presented in Table 11 along with theoretical [47]

data. On comparison, one may state that the present results are in well agreement at a great extent. Calculated results at different temperatures are reported in Figure 15.
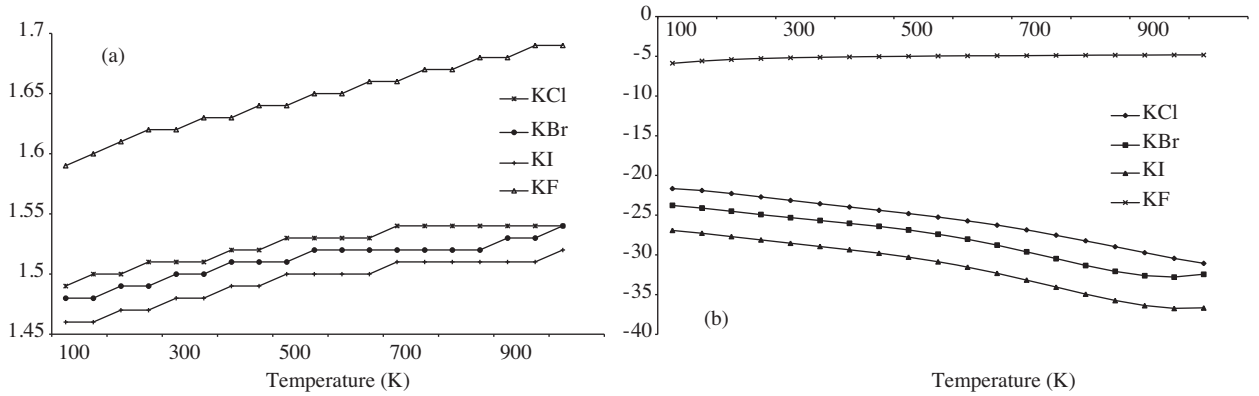

Figure 12. (a) Temperature variation of the first order pressure derivative of C_{12}. (b) Temperature variation of the first order pressure derivative of $C_{44}(\times 10^{-2})$.
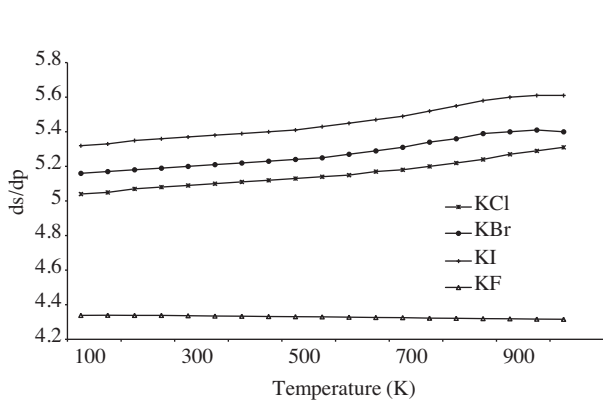

Figure 13. Temperature variation of ds/dp.
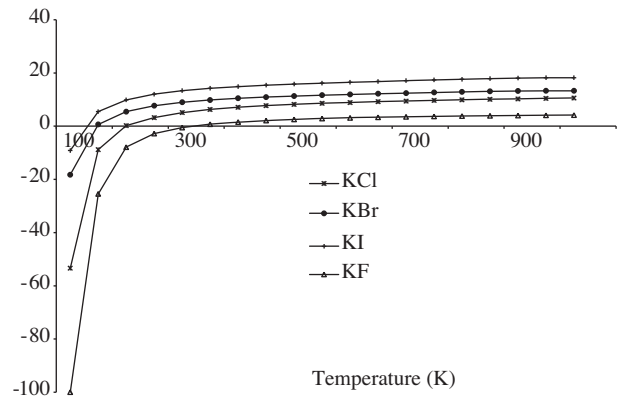
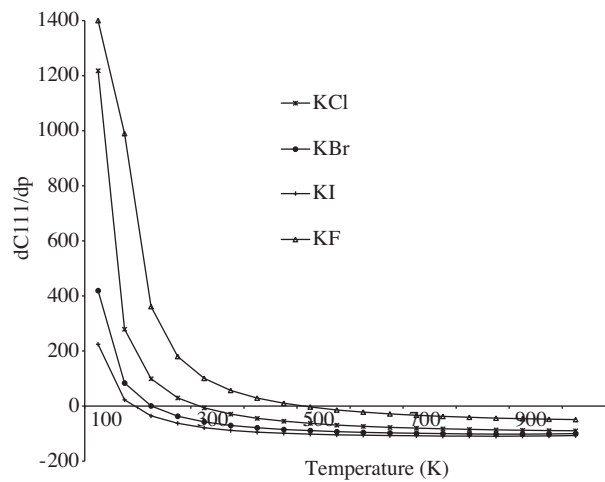**Figure 14.** Temperature variation of $d^2 C_{11}/dp^2$ (10^{-10}).

Figure 15. Temperature variation of FOPD of a TOEC.

5. Conclusion

The extensive investigations of second-, third- and fourth- order elastic constants and their pressure derivatives carried out in present study appear to be important in revealing the anharmonic elastic properties of solids. It may thus be concluded that the "deformation-mechanism" used in present model provides much better interpretation of the crystal properties in general. The cases discussed in present study are overall in good agreement with theoretical and experimental results, which shows the validity of present theory. These data are also useful for the interpretation of the anomalous elastic behavior of cyanides, halides and similar systems. The new data may provide a further chance to improve the theoretical models developed recently for the interpretation of the behavior of elastic constants in higher temperature region. But as the non-availability of experimental data, a detailed discussion of these properties may be left for a later investigation when the main effects are better understood. We have thus presented a simple method to study the elastic properties of solids under varying conditions of temperatures. The results obtained are encouraging. Due to the simplicity of the method, it can be applied to the more complicated solids, like minerals of geophysical importance and applications. The results on different types of solids at deferent temperatures and composition are in progress.

References

[1] K. M. Raju, *Acta Physica Polonica A*, **118**, (2010), 600.

[2] K. M. Raju, Kailash and R. K. Srivastava, *Physics Procedia*, **3**, (2010), 927.

[3] O. Kilian and G. Allan and L. Wirtz, *Phys. Rev. B,* **80**, (2009), 245208.

[4] P. F. Yuan and Z. J. Ding, *Physica B,* **403**, (2008), 1996.

[5] K. M. Raju, R. K. Srivastava and Kailash, *Pramana – J. Phys.*, **69**, (2007), 445.

[6] Kailash and K. M. Raju, *Ind. J. Theo. Phys.*, **54**, (2006), 237.

[7] K. M. Raju, R. K. Srivastava, A. Kumar and S. Devi, *Physica B*, **405**, (2010), 4855.

[8] K. M. Raju, *Bulga. J. Phys.,* **37**, (2010), 115.

[9] M. Lach-hab, D. A. Papaopoulos and M. J. Mehl, *J. Phys. Chem. Solids,* **63**, (2002), 833.

[10] B. N. Onwvagba, *Solid State Commun.*, **89**, (1994), 289 .

[11] K. Walasek and K. L. Walasek, *Phys. Rev. B*, **49**, (1994), 9937.

[12] S. Lehri and J. Shankar, *Phys. Stat. Sol.(b)*, **141**, (1987), 97.

[13] U. C. Shrivastava, *Phys. Stat Sol. (b)*, **100**, (1980), 641.

[14] S. Haussühl, J. Eekstein, K. Rocker and F. Wall Sofen, *Acta Crystall.*, **A33**, (1977), 847.

[15] S. Haussühl, *Solid State Commun.*, **13**, (1973), 147.

[16] S. K. Sateza and C. H. Wang, *J. Chem. Phys.*, **70**, (1979), 4437.

[17] F. Birch, *Phys. Rev.*, **71**, (1947), 809.

[18] K. Brügger, *Phys. Rev. A,* **133**, (1964), 1604.

[19] G. Leibfried and H. Hahn, *Z. Phys.*, **150**, (1958), 197.

[20] G. Leibfried and W. Ludwig, *Solid State Physics*, vol. 12, (Academic Press, New York. 1961).

[21] M. Börn and J. M. Mayer, *Z. Phys.*, **71**, (1932), 1.

[22] C. Kittel, *Introduction to Solid State Physics*, (John Wiley, New York. 1981).

[23] P. B. Ghate, *Phys. Rev.*, **139**, (1965), A1966; *Physics Stat. Sol. (b)*, **14**, (1966), 325.

[24] G. R. Barch and Z. P. Chang, *J. Appl. Phys.*, **39**, (1968), 3276.

[25] Z. P. Chang and G. R. Barsch, *J. Phys. Chem. Solids*, **32**, (1971), 27.

[26] G. R. Barsch and H. E. Shull, *Phys. Stat Sol. (b)*, **43**, (1971), 637.

[27] J. Chandra, R. Kumar and B. R. K. Gupta, *High Temperatures-High Pressures*, **37**, (2002), 335.

[28] R. K. Singh, *Phys. Rep.,* **85**, (1982), 259.

[29] R. K. Singh and S. P. Sanyal, *Physica B,* **132**, (1985), 201.

[30] C. E. Sims, G. D. Barrera and N. L. Allan, *Phys. Rev. B,* **57**, (1998), 11164.

[31] Sir C. V. Raman and D. Krishnamurti, *Proc. Ind. Acad. Sci.,* **A42**, (1955), 111.

[32] CRC Hand Book of Chemistry & Physics, (CRC Press, Florida. 1977) p. 58.

[33] American Institute of Physics Hand Book (Mc-Graw Hill, New York. 1981).

[34] A. A. Botaki, I. N. Gyrbu and A. V. Sharko, *Sov . Phys. Solid State*, **13**, (1972), 3096.

[35] J. K. Galt, *Phys. Rev.*, **73**, (1948), 1460.

[36] V. K. Garg, D. S. Puri and M. P. Verma, *Phys. Stat. Sol. (b)*, **82**, (1977), 325.

[37] R. K. Varshney and J. Shankar, *Phys. Stat. Sol. (b)*, **61**, (1985), 129.

[38] Y. Teng, S. Zhu, F. Zhang, M. Li, F. Wang and W. Wu, *Physica B*, **358**, (2005), 77.

[39] T. H. Kwon, *Philosophical Magazine*, **B68**, (2005), 663.

[40] V. N. Cimmelli and K. Frischmuth, *Physica B*, **355**, (2005), 147.

[41] R. Terki, H. Feraoun, G. Bertrand and H. Aourag, *Phy. Stat. Sol. (b)*, **242**, (2005), 1054.

[42] E. Guilliorit, C. Bacon and B. Hosten, *J. Acoust. Soc. Am.*, **122**, (2002), 65.

[43] O. A. Kapustina, *Acoust. Phys.*, **46**, (2000), 164 .

[44] P. Kielczynski, W. Pajewski and M. Szalew, *IEEE Trans. Ultra. Ferro. Freq. Control*, **46**, (1999), 233.

[45] Z. H. Fang, *Physica B*, **357**, (2005), 433.

[46] W. C. Hughes and L. S. Cain, *Phy. Rev. B,* **53**, (2005), 5774.

[47] J. Shanker, J. P. Singh and V. P. Gupta, *Phys. Stat. Sol. (b)*, **103**, (1981), 573.

[48] V. K. Garg, D. S. Puri and M. P. Verma, *Phy. State. Sol. (b)*, **82**, (1977), 481

[49] Y. Gudkov, A. Lonchakev, V. Sokolov, I. Zheustouskikh and N. Gruzdev, *Phys. Stat. Sol. (b)*, **242**, (2005), 30 .

[50] R. P. M. Krishna and A. Chatterjee, *Physica B*, **358**, (2005), 191.

[51] L. Lelovsky, G. Gonzalcz and I. N. Volovicher, *Phys. Stat. Sol. (b)*, **242**, (2005), 971 .

[52] M. Zhao and Q. Jiang , *Mate. Chem. Phy.*, **87**, (2004), 1.

[53] R. A. Shukor and C. T. Vui, *Physica B*, **357**, (2005), 253.

[54] J. R. Drabble and R. E. B. Strathen, *Proc. Phys. Soc.*, **92**, (1967), 1090.

[55] R. W. Roberts and C. S. Smith, *J. Phys Chem. Solids*, **31**, (1970), 619.

[56] M. H. Norwood and C. V. Briscoe, *Phys. Rev.*, **112**, (1958), 45.