

Non linear Behaviour of Cyanides Crystals using Ultrasonic Techniques

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Abstract

The aim of this work is to evolve a theory for obtaining anharmonic properties of alkali cyanides using long-range Coulomb and short-range Börn Mayer potentials starting from nearest-neighbour distance and hardness parameter. An attempt has been made to evaluate higher order elastic constants and related physical properties of alkali cyanides such as LiCN, NaCN, KCN and RbCN at different temperature ranges. The computed values of SOECs, TOECs and FOECs have been used to estimate the FOPDs of SOECs and TOECs, SOPDs of SOECs and partial contractions. While evaluating the properties, it is assumed that the crystal structure does not change during temperature variation. A comparison has been made the available theoretical and experimental data.

Introduction

Most considerable interest has been made for obtain the information of elastic constants and acoustical properties of numerous kinds of materials. During last decades various researchers have strengthened the field of Ultrasonics by their theoretical and experimental research design. In the current scenario, several investigators are still working in the study of linear and non-linear properties of different material having different type of crystal structures [1-3]. The study of higher order elastic constants in different solids provides the utile information about the nature of short-range repulsive forces. The study of non-linear properties of particular crystal can be studied by obtaining the information of short-range potential [4,5]. The anharmonic properties plays an inimitable role in the study of solids that how the rock form. The efforts for appraising anharmonic properties have been made for monovalent rock salt structured materials [6]. Elastic properties of divalent compounds are also equally high-priority because they relate to the numerous fundamental solid-state phenomena like as phonon spectra, atomic potential and equation of state [7]. If the value of second order elastic constant and density at a particular temperature are known for any substance, one may acquire ultrasonic velocities for longitudinal and shear mode which give a significant information about its anharmonic properties [8,9]. Elastic properties are associated thermodynamically with thermal expansion, specific heat, pressure derivative, Debye temperature and Grüneisen parameters [10-12]. In the previous year some successful researches are done by different researchers for the study of different solids. Chinmayee Tripathy et al [13] investigated different elastic or ultrasonic properties of lanthanum pnictides (LnPn) in different temperature ranges. Alpana Tiwari et al [14] have formulated temperature dependence elastic constants of second and higher order of NH₄Cl like a function of temperature for 240K to 440K temperature range. S. K. Shrivastava et al [15] have investigated the ultrasonic wave propagation and elastic properties of calcium oxides in high temperature. Liu Y, et al [16] have evaluated elastic properties of magnesium-based composites using longitudinal and shear wave velocities.

Information about higher order elastic constants is very important for studying the nature of short-range potential in crystals at different temperature. This information is easily obtained through the study of non-linear properties of particular crystals. A formulation has been developed for quantifying anharmonic properties such as higher order elastic constants of solids which possess phase centred cubic (FCC) crystal structure initiating from fundamental physical parameters such as nearest neighbour distance & hardness

parameter assuming long- and short-range potential at different temperature. The elastic energy density for a crystal can be expressed as higher series of strain with the help of Taylor’s series expansion. The second order elastic constant, third order elastic constant and fourth order elastic constant are the coefficient of quadratic, cubic and quartic terms. Several physical properties and crystal anharmonicities such as specific heat at elevated temperature, thermal expansion, temperature dependency of acoustic velocity at attenuation, first order pressure dependence (FOPDs) of second order elastic constant (SOECs), temperature dependence of second order elastic constants and Grüneisen parameter are directly concerned to SOECs and TOECs. The computed values of SOECs, TOECs and FOECs have been used to estimate the FOPDs of SOECs and TOECs, SOPDs of SOECs and partial contractions. The present work is chiefly focussed on the study of temperature variation of higher order elastic constants and their pressure derivatives up to an elevated temperature up to near melting point for alkali cyanides (LiCN, NaCN, KCN, RbCN) crystals using Börn-Mayer and Coulomb potential initiating from nearest neighbour distance and hardness parameters.

FORMULATION

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

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

Where 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 [18] and Voigt notations.

The SOECs, TOECs and FOECs are as given below:

$$\begin{aligned}
 C_{ijkl} &= C_{ij} = (\partial^2 \tilde{U} / \partial x_{ij} \partial x_{kl})_{x=0} \\
 C_{ijklmn} &= C_{IJK} = (\partial^3 \tilde{U} / \partial x_{ij} \partial x_{mn} \partial x_{kl})_{x=0}
 \end{aligned}$$

and

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

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

$$\begin{aligned}
 U_{Total} &= U_0 + U^{vib} \\
 U^{vib} &= KT/NV_c \sum_{i=1}^{3sN} \ln 2 \sinh (\hbar \omega_i / KT)
 \end{aligned}
 \tag{3}$$

Where U_0 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.

An elastic constant can be separated into two parts as follows;

$$\begin{aligned}
 C_{ij} &= C_{ij}^0 + C_{ij}^{vib} \\
 C_{IJK} &= C_{IJK}^0 + C_{IJK}^{vib} \\
 C_{IJKL} &= C_{IJKL}^0 + C_{IJKL}^{vib}
 \end{aligned}
 \tag{4}$$

The first part is the strain derivative of the internal energy U_0 and is known as “static” elastic constant and the second part is the strain derivative of the vibrational free energy U^{vib} and is called “Vibrational” elastic constant. The superscript “O” has been introduced to emphasize that the static elastic constants correspond to 0K.

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

$$U_0 = [1/2V_c] \sum_{v=1}^s \sum Q_{uv} (R_{uv}^{m0}) = \sum Q_{uv} (R) / 2V_c
 \tag{5}$$

$$\begin{matrix} m \neq 0 \\ u \neq v \end{matrix} \quad \left| \quad \right| \quad \left| \quad \right|$$

Where R_{uv}^{mo} is the distance between the v-th ion in the o-th cell and the u-th ion in the m-th 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.

$$Q_{uv}(r_o) = \pm (e^2/r_o) + A \exp(-r_o/q) \tag{6}$$

Where e is the electric charge, ± sign apply to like and unlike ions respectively, r_o is the nearest-neighbour distance, q is hardness parameter and A is

$$A = -0.29126q (e^2/r_o^4) / [\exp(-r_o/q) + 2 \sqrt{2} \exp(-r_o\sqrt{2}/q)] \tag{7}$$

It is assumed that the crystal is deformed homogeneously.

When the crystal is deformed homogeneously, the distance between (v,o) and (u, m) ion in the deformed and non-deformed states, R_{uv}^{mo} and r_{uv}^{mo} , are related to the Lagrangian strains x_{ij} as follows

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

Where Y_{uvi}^{mo} is the i-th Cartesian component of the vector r_{uv}^{mo} , the definition of the quantity Z_{uv}^{mo} is also 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:

$$\begin{aligned} U_2 &= [1/2V_c] \sum' [Z^2 D^2 Q(R)/2!]_{R=r} = [1/4V_c] [X_{ij} X_{kl} \sum' Y_i Y_j Y_k Y_l D^2 Q(R)]_{R=r} \\ U_3 &= [1/2V_c] \sum' [Z^3 D^3 Q(R)/3!]_{R=r} = [1/12V_c] [X_{ij} X_{kl} X_{mn} \sum' Y_i Y_j Y_k Y_l Y_m Y_n D^3 Q(R)]_{R=r} \\ U_4 &= [1/2V_c] \sum' [Z^4 D^4 Q(R)/4!]_{R=r} = [1/48V_c] [X_{ij} X_{kl} X_{mn} X_{pq} \sum' Y_i Y_j Y_k Y_l Y_m Y_n Y_p Y_q D^4 Q(R)]_{R=r} \end{aligned} \tag{9}$$

Where, $D = d/(RdR)$

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

$$\begin{aligned} U_2 &= [1/V_c 2!] \sum' \sum' [Z Z (D' D) U^{vib}]_{Z=0} = [1/2V_c] X_{ij} X_{kl} f_{ijkl} \\ U_3 &= [1/V_c 3!] \sum' \sum' \sum' [Z Z' Z (D' D' \Delta) U^{vib}]_{Z=0} = [1/6V_c] X_{ij} X_{kl} X_{mn} f_{ijklmn} \\ U_4 &= [1/V_c 4!] \sum' \sum' \sum' \sum' [Z Z' Z'' Z''' (D' D'' D''' D) U^{vib}]_{Z=0} \\ &= [1/24V_c] X_{ij} X_{kl} X_{mn} X_{pq} f_{ijklmnpq} \end{aligned} \tag{10}$$

Where, $f_{ijkl} = \sum' \sum' [Y_i Y_j Y_k' Y_l' (D' D) U^{vib}]_{R=r}$
 $f_{ijklmn} = \sum' \sum' \sum' [Y_i Y_j Y_k' Y_l' Y_m' Y_n' (D'' D' D) U^{vib}]_{R=r}$

and $f_{ijklmnpq} = \sum' \sum' \sum' \sum' [Y_i Y_j Y_k' Y_l' Y_m' Y_n' Y_p' Y_q' (D''' D'' D' D) U^{vib}]_{R=r}$

Here the abbreviations $Z_u' v' m'o \rightarrow Z'$ [$d/\{R_u' v' m'o dR_u' v' m'o\} \rightarrow D'$], etc. Are used on comparison Equations (1) and (10), one can determine the vibrational elastic constants. 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 formulated conveniently by taking crystals symmetry [22] into account and the expressions for g_n and F_n are tabulated in Tables-3 & 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 crystal.

The FOPDs of SOECs are conserved with SOECs and TOECs, the FOPDs of TOECs and SOPDs of SOECs are directly related to the SOECs, TOECs and FOECs. 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.

The values [27,28,30] of the nearest neighbour distance (r_o) and hardness parameter (q) are given in Table-10. Thermal expansion coefficients (α) [28-30,32] for different solids are taken into account as,

$$r = r_o(1+\alpha T), \text{ where } \alpha = A_1 + A_2 T + A_3 T^2 + A_4 T^3 + A_5 T^4, \quad \alpha = A_n T^{n-1} \tag{11}$$

equations for α are computed using curve fitting and A_1, A_2, A_3 are shown in Table-11

Table 1
Expression for the SOECs, TOECs and FOECs at 0K for Alkali Cyanides.

$$\begin{aligned}
 C_{11}^0 &= -1.56933G + G_1 + 2G_2 \\
 C_{12}^0 &= C_{44}^0 = 0.347775G + G_2 \\
 C_{111}^0 &= 10.2639G - G_3 - 2G_4 \\
 C_{112}^0 &= C_{166}^0 = 1.208625G - G_4 \\
 C_{123}^0 &= C_{144}^0 = C_{456}^0 = 0.678375G \\
 C_{1111}^0 &= -80.71455G + G_5 + 2G_6 \\
 C_{1112}^0 &= C_{1155}^0 = 4.43205G + G_6 \\
 C_{1122}^0 &= C_{1266}^0 = C_{4444}^0 = 5.615925G + G_6 \\
 C_{1123}^0 &= C_{1144}^0 = C_{1255}^0 = C_{1456}^0 = C_{4455}^0 = -1.584975G
 \end{aligned}$$

Where;

$$\begin{aligned}
 G &= e^2/r_0^4 \\
 G_1 &= (1/r_0 + 1/q) Q (r_0)/qr_0 \\
 G_2 &= (\sqrt{2}/2r_0 + 1/q) Q (r_0\sqrt{2})/qr_0 \\
 G_3 &= (3/r_0^2 + 3/qr_0 + 1/q^2) Q (r_0)/q \\
 G_4 &= (3\sqrt{2}/r_0^2 + 6/qr_0 + 2\sqrt{2}/q^2) Q (r_0\sqrt{2})/4q \\
 G_5 &= (15/r_0^3 + 15/qr_0^2 + 6/q^2 r_0 + 1/q^3) r_0 Q (r_0)/q \\
 G_6 &= (15\sqrt{2}/4r_0^3 + 15\sqrt{2}qr_0^2 + 3\sqrt{2}/q^2 r_0 + 1/q^3) r_0 Q (r_0\sqrt{2})/2q
 \end{aligned}$$

Table 2
Expression for Vibrational Contribution to the SOECs, TOECs and FOECs for Alkali Cyanides.

$$\begin{aligned}
 C_{11}^{vib} &= g_1 F_1^2 + g_1 F_2 \\
 C_{12}^{vib} &= g_2 F_1^2 + g_1 F_5 \\
 C_{44}^{vibn} &= g_1 F_5 \\
 C_{111}^{vib} &= g_3 F_1^3 + g_2 F_2 F_1 + g_1 F_3 \\
 C_{112}^{vib} &= g_1 F_1^3 + g_2 F_1 (2F_5 + F_2) + g_1 F_6 \\
 C_{123}^{vib} &= g_3 F_1^3 + 3 g_2 F_1 F_5 \\
 C_{144}^{vib} &= g_2 F_1 F_5 \\
 C_{166}^{vib} &= g_2 F_1 F_5 + g_1 F_6 \\
 C_{456}^{vib} &= 0 \\
 C_{1111}^{vib} &= g_4 F_1^4 + 6g_3 F_1^2 F_2 + 3g_2 F_2^2 + 4g_2 F_1 F_3 + g_1 F_4 \\
 C_{1456}^{vib} &= 0 \\
 C_{1112}^{vib} &= g_4 F_1^4 + 3g_3 F_1^2 (F_5 + F_2) + 3g_2 F_5 F_2 + g_2 F_1 (3F_6 + F_3) + g_1 F_7 \\
 C_{1122}^{vib} &= g_4 F_1^4 + 2g_3 F_1^2 (2F_5 + F_2) + g_2 (2F_5^2 + F_2^2) + 4g_2 F_1 F_2 + g_1 F_7 \\
 C_{1123}^{vib} &= g_4 F_1^4 + g_3 F_1^2 (5F_5 + F_2) + g_2 F_1 (2F_5 + F_2) + 2g_2 F_1 F_6 \\
 C_{1144}^{vib} &= g_3 F_1^2 F_5 + g_2 F_5 F_2 \\
 C_{4444}^{vib} &= 3g_2 F_5^2 + g_2 F_7 \\
 C_{1155}^{vib} &= g_3 F_1^2 F_5 + g_2 F_5 F_2 + 2g_2 F_1 F_6 + g_1 F_7 \\
 C_{4455}^{vib} &= g_3 F_5^2 \\
 C_{1255}^{vib} &= g_3 F_1^2 F_5 + g_2 F_5^2 + g_2 F_1 F_6 \\
 C_{1266}^{vib} &= g_3 F_1^2 F_5 + g_2 F_5^2 + 2g_2 F_1 F_6 + g_1 F_7
 \end{aligned}$$

Table 3
Expressions for g_n 's for Alkali Cyanides.

g_1	=	$g_0 S$;
g_2	=	$g_0 [(X/S_1) + S]/2$;
g_0	=	$\hbar\omega_0/8r_0^3$;
g_3	=	$g_0 [(2X^2 S/3S_1) + (X/S_1) + S]/48$;
X	=	$\hbar\omega_0 / KT$;
g_4	=	$-g_0 [(X^3 S^2/3S_1) + (X^3/6S_1^2) + (X^2 S/S_1) + (5X/4S_1) + (5S/4)]/144$;
ω_0	=	$(1/M^+ + 1/M^-)/qr_0 F_0$;
S	=	$\text{Coth } X$; $S_1 = \text{Sinh}^2 X$.

Table 4
Expressions for F_n 's for Alkali Cyanides.

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

Table 5
Expressions for the FOPDs of the SOECs and TOECs for Alkali Cyanides.

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
Expressions for the SOPDs of the SOECs and for Partial Contraction of the FOECs for Alkali Cyanides.

$d^2 C_{11}/dP^2$	=	$[(1 + 3C_P) C_{11} + (4 + 3C_P) (C_{111} + 2C_{112}) + C_{1111} + 4C_{1112} + 2C_{1122} + 2C_{1123}] C_0^2$;
$d^2 C_{12}/dP^2$	=	$[(1 + 3C_P) C_{12} + (4 + 3C_P) (2C_{112} + C_{123}) + 2C_{1122} + 5C_{1123}] C_0^2$;
$d^2 C_{44}/dP^2$	=	$[(1 + 3C_P) C_{44} + (4 + 3C_P) (C_{144} + 2C_{166}) + C_{1144} + 2C_{1166} + 4C_{1244} + 2C_{1266}] C_0^2$;
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}	=	$C_{1144} + 2C_{1166} + 4C_{1244} + 2C_{1266}$;

Table 7

The Melting points and the SOECs and TOECs in 10^{10} Newton/m² at room temperature for Alkali Cyanides.

Crystal	Melting Point, K	C ₁₁	C ₁₂	C ₄₄	C ₁₁₁	C ₁₁₂	C ₁₂₃	C ₁₄₄	C ₁₆₆	C ₄₅₆	Ref
LiCN	-	15.16	12.523	13.10	-190.3	-50.89	17.077	18.947	-52.46	18.682	-
NaCN	836.70	3.775	1.305	1.195	-4.755	-13.230	4.465	4.680	-13.430	4.613	-
		2.530a	1.444a	0.330a	-	-9.720b	-6.760b	2.410b	-2.700b	-1.440b	31a,34b
		5.749	-	0.750	16.220b	-	-	-	-	-	33
KCN	907.50	0.464	1.113	1.100	-32.91	-14.87	8.705	3.272	-9.486	3.276	-
		1.916a	1.197a	0.140a	-12.92b	-5.51b	-10.09b	1.63b	-2.70b	-0.79b	32a,34b
		5.115	-	0.470	-	-	-	-	-	-	33
RbCN	820.00	9.799	2.457	2.848	-149.10	-10.14	2.598	4.729	-11.59	4.636	-
		4.022	-	0.411	-	-	-	-	-	-	33
		1.747	1.040	0.165	-	-	-	-	-	-	29

Table 8

FOECs in 10^{10} Newton/m² at room temperature of Alkali Cyanides.

Crystal	C ₁₁₁₁	C ₁₁₁₂	C ₁₁₂₂	C ₁₁₂₃	C ₁₁₄₄	C ₁₁₅₅	C ₁₂₅₅	C ₁₂₆₆	C ₁₄₅₆	C ₄₄₄₄	C ₄₄₅₅
LiCN	-6785	-10658	-10627	-10931	-44.25	234.1	-44.09	274.1	-43.65	275.6	-43.77
NaCN	662.5	-1390	-1384	-1513	-20.28	104.3	-20.08	123.9	-19.83	124.9	-19.88
KCN	1113	-829.5	-829.7	-909.8	-13.68	66.35	-13.49	81.46	-13.31	82.32	-13.34
RbCN	1304	-547.5	-550.6	-611.7	-11.16	51.85	-10.98	65.26	-10.83	66.01	-10.85

Table 9

The FOPDs and SOPDs (in 10^{-11} Newton/m²) of the SOECs and partial contractions (in 10^{12} Newton/m²) of Alkali Cyanides.

Crystal	Y ₁₁	Y ₁₂	Y ₄₄	dC ₁₁ /dP	dC ₁₂ /dP	dC ₄₄ /dP	ds/dP	dk/dP	d ² C ₁₁ /dP	d ² C ₁₂ /dP	d ² C ₄₄ /dP	Ref
LiCN	-945	-972.2	-207.5	5.89	2.17	0.81	1.54	3.83	-5.39	-4.58	-1.16	-
NaCN	-97.35	-121.94	-25.30	8.11	1.98	0.36	2.39	4.26	-0.79	-1.79	0.30	-
				5.55	5.98	-0.36	-	-	-	-	-	34
KCN	-52.01	-74.06	15.32	9.26	1.76	0.15	3.57	4.51	0.11	-1.89	-0.29	-
				4.43	5.90	-0.11	-	-	-	-	-	34
RbCN	-32.1	52.5	-9.82	9.84	1.69	0.06	3.90	4.64	1.13	-1.67	-0.20	-
				4.46	5.38	-0.125	-	-	-	-	-	34

Table 10

The nearest neighbour distance (r_0) and hardness parameter (q) (10^{-10}m) FOPDs of the TOECs at room temperature of Alkali Cyanides.

Crystal	r_0	Q	dC_{111}/dP	dC_{112}/dP	dC_{123}/dP	dC_{144}/dP	dC_{166}/dP	dC_{456}/dP
LiCN	1.7013	0.265	765	804	815	-1.31	269	2.86
NaCN	2.0721	0.266	119	189	199	-1.24	64.5	2.49
KCN	2.2892	0.267	62.9	151	159	-1.21	52.0	2.33
RbCN	2.4104	0.268	19.2	117	125	-1.20	40.8	2.26

Table 11

Numerical Coefficient for Alkali Cyanides.

Coefficient	A_1	A_2	A_3	A_4	A_5
NaCN	20.1891	0.1850	-	-	-
KCN	204.078	-0.2426	-	-	-

Results and Discussion

The Non-linear properties of Alkali Cyanides are shown in Table no. 7-11. The elastic constant and pressure derivatives are evaluated at different temperatures. These values are calculated using nearest neighbour distance and hardness parameter. The second, third, fourth order elastic constant and pressure derivatives starting from room temperature upto their melting points are shown in Table-7. This complete study is based on such concepts that FCC crystal structure does not change when temperature varies upto their melting points. The numerical coefficient or thermal coefficients are also evaluated using equation no 11. The knowledge of higher order elastic constants gives the information about non-linear properties of the crystals and ie. thermal conductivity, thermo elastic constants and thermal expansion. As we know that the elastic constants of solids decrease with temperature while NaCl like structure, the elastic constant increases with temperature. This effect is known as anomalous temperature dependency of elastic constants in solids. In the present theory this anomalous behaviour of temperature is discussed.

The third order elastic constants provide interactions of ultrasonic vibrations with thermal phonons harmonic generator and equation of state. The knowledge of third order elastic constants also provide essential data for testing under non-destructive mechanism. The third order elastic constants play an important role for explaining anharmonic phenomena in solids. The values of third order elastic constants are evaluated according to Table-7 and these values are in well agreement with these workers who also calculated the same values experimentally. The temperature variations of third order elastic constants in Alkali Cyanides are calculated by taking thermal expansion coefficient. The elastic constants are sensitive to the temperature and these constants have divergence at 300K while not same for other Alkali Cyanides. This effect is found due to the largest molecular weight of Iodine.

The importance of fourth order elastic constants of crystals same as the third order elastic constants. In other words, we can say with the help of third and fourth order elastic constants, the non-linearity of the substance can be studied. The fourth order elastic constants are calculated and presented in Table-8 since the experimental data for fourth order elastic constants are not available so the comparison could not be made. Higher order pressure derivatives provide useful data on the inter-atomic forces, inter-ionic potential and anharmonic properties of solids. The theoretical data of second order pressure derivate are calculated and presented in Table-9. which are in well agreement with the experimental data available for the present work. Fourth order pressure derivatives and thermal coefficients are also evaluated at different temperatures shown in Table-10 & 11.

On the view of above discussion, the present study is in good agreement with theoretical and experimental data and hence validation of present theory. The reported results are very helpful for the

researchers who are working in the field of ultrasonic velocities. These data are also explained to interpret the anomalous elastic behaviour of Cyanides at higher temperatures.

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