Third order anharmonicity in NaCN

A. K. Choudhary[a] and Kailash[b]

[a]Department of Physics, Atarra P. G. College, Atarra, Banda, U.P., India
[b]Department of Physics, BN PG College, Rath, Hamirpur, U.P., India

_____

ABSTRACT

Sodium Cyanide crystal shows many interesting properties which arise from the molecular character of the CN ion group. Higher order elastic constants of Sodium Cyanide crystal in orientationally disordered crystalline (ODIC) phase have been evaluated by a method based on Börn model of ionic solids. NaCN exhibit NaCl-type face centered cubic crystal structure above critical temperature 288K. Starting from the nearest neighbor distance and hardness parameter the second and third order elastic constants of NaCN have been computed at elevated temperatures (up to the nearest melting point).The computed values of higher order elastic constants have been used to calculate anharmonic property related other constants like first order pressure derivatives of third order elastic constants.

Key words: Cyanide, FCC, Higher Order Elastic Constants, Pressure Derivatives, Anharmonic Properties
_____

INTRODUCTION

Elastic constants are one of the fundamental mechanical and the thermodynamic properties of any substance. 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 second order elastic constants(SOECs), Gru¨neisen numbers and temperature derivatives of SOECs are directly related to SOECs and third order elastic constants(TOECs). In the last few decades, considerable interest has been taken in the investigation of anharmonic properties of materials of various kinds [1–10]. In this present work formulations have been developed for quantifying anharmonic properties such as higher order elastic constants of materials which possess face centered cubic (FCC) crystal structure 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. The model we have used has been proved to be highly successful in predicting the elastic properties of alkali halides. The special interest in NaCN lies in the fact that this exhibits the NaCl like structure above critical temperature 288K. It is of interest to test the applicability of our present model to Sodium Cyanide (NaCN).

NaCN is an ionic crystal with a pseudo cubic (NaCl, Fm3m) high temperature phase. It undergoes an order-disorder transition from a cubic (Fm3m) structure with the CN⁻ ion distributed randomly along [1 1 1] direction to an orthorhombic (Immm) structure with the CN⁻ ions along one of the cubic [1 1 0] direction [11,12].Since the discovery by Haussuhl [13] of the anomalous behavior of the C_{44} elastic constant in the orientationally disordered(ODIC) crystalline phase of KCN,the elastic properties of this material and of NaCN [13-18] have been the subject of many theoretical and experimental investigations.

The present work is concerned with the formulation to evaluate the TOECs and the FOPDs of the TOECs; using long- and short-range potentials starting from the nearest-neighbor distance and hardness parameter. Section 2 deals

with the brief description of the theory. In Section 3, the theory is tested for NaCN. The results thus obtained are widely discussed in Section 4.

FORMULATION

The elastic energy density for a crystal of a cubic symmetry can be expanded up to quartic terms as shown below [19];

$$U_0 = U_2 + U_3 + U_4 = [1/2!]\, C_{ijkl}\, \alpha_{ij}\, \alpha_{kl} + [1/3!]\, C_{ijklmn}\, \alpha_{ij}\, \alpha_{kl}\, \alpha_{mn} + [1/4!]\, C_{ijklmnpq}\, \alpha_{ij}\, \alpha_{kl}\, \alpha_{mn}\, \alpha_{pq} \qquad (1)$$

Where C_{ijkl}, C_{ijklmn} and $C_{ijklmnpq}$ are the SOECs, TOECs and FOECs in tensorial form; α_{ij} are the Lagrangian strain components; The SOECs, TOECs and FOECs are as given below:

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

$$C_{ijklmnpq} = C_{IJKL} = (\partial^4 U / \partial\alpha_{ij}\partial\alpha_{kl}\partial\alpha_{mn}\partial\alpha_{pq})_{\alpha=0} \qquad (2)$$

C_{IJ}, C_{IJK} and C_{IJKL} are the SOECs, TOECs and FOECs in Brügger's definition and voigt notations [20].

The free energy density of a crystal at a finite temperature T is

$$U_{Total} = U_0 + U^{vib}, \quad U^{vib} = [KT / NV_c]\sum_{i=1}^{3sN} \ln 2 Sinh(\hbar\omega_i / KT) \qquad (3)$$

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 consists of two parts as follows:

$$C_{IJ} = C_{IJ}^0 + C_{IJ}^{vib}, \quad C_{IJK} = C_{IJK}^0 + C_{IJK}^{vib} \text{ and } C_{IJKL} = C_{IJKL}^0 + C_{IJKL}^{vib} \qquad (4)$$

The first part is the strain derivative of the internal energy U_o 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 0 has been introduced to emphasize that the static elastic constants correspond to 0 K.

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

$$U_0 = [1/2V_c]\sum_{v=1}^{s} \sum_{\substack{m\neq o \\ u\neq v}} Q_{uv}(R_{uv}^{mo}) = \Sigma' Q_{uv}(R)/2V_c \qquad (5)$$

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 potentials.

$$Q_{uv}(r_0) = \pm(e^2 / r_0) + A\exp(-r_0 / q) \qquad (6)$$

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

$$A = 0.29126q(z^2 e^2 / r_0^4)/[\exp(-r_0 / q) + 2\sqrt{2}\exp(-r_0 \sqrt{2} / q)] \qquad (7)$$

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 e_{ab} as follows:

$$(R_{uv}^{mo})^2 - (r_{uv}^{mo})^2 = 2 Y_{uvi}^{mo} Y_{uvj}^{mo} e_{ab} = 2 Z_{uv}^{mo} \qquad (8)$$

351

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 Eq.(8). The internal energy U_0 given by Eq. (5) can be expanded in terms of Z_{uv}^{mo}, which will yield cubic terms as given below:

$$U_3 = [1/2V_c]\sum'[Z^3 D^3 Q(R)/3!]_{R=r} = [1/12V_c][e_{ab}e_{cd}e_{mn}\sum' Y_i Y_j Y_k Y_l Y_m Y_n D^3 Q(R)]_{R=r}$$
(9)

With reference to Eqs. (3) and (4) and comparison of Eqs. (1) and (9), one may obtain the static elastic constants. For a central force model, there are only three independent TOECs 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 cubic terms are as below:

$$U_3 = [1/V_c 3!]\sum'\sum_,'\sum_{''}'[Z'Z''Z(D'D''D)U^{vib}]_{Z=0} = [1/6V_c]e_{ab}e_{cd}e_{mn}f_{ijklmn} \qquad (10)$$

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

On comparison Eqs. (1) and (10); one determines the vibrational elastic constants. Vibrational contributions to TOECs are shown as a combination of ε_n's and η_n's which are evaluated by taking crystal's symmetry into account and the expressions for ε_n and η_n are presented below. By adding the vibrational elastic constants to the static elastic constants, one may get TOECs at any temperature for monovalent FCC crystals.

Expression for the TOECs for fcc Crystals

$C_{111} = 10.2639\,\alpha - \alpha_3 - 2\alpha_4 + \varepsilon_3\eta_1^3 + \varepsilon_2\,\eta_2\eta_1 + \varepsilon_1\eta_5$,

$C_{112} = 1.208625\,\alpha - \alpha_4 + \varepsilon_1\eta_1^3 + \varepsilon_2\eta_1\,(2\eta_3 + \eta_2) + \varepsilon_1\eta_6$,

$C_{123} = 0.678375\,\alpha + \varepsilon_3\eta_1^3 + 3\varepsilon_2\eta_1\eta_3$,

$C_{144} = 0.678375\,\alpha + \varepsilon_2\eta_1\eta_3$,

$C_{166} = 1.208625\,\alpha - \alpha_4$,

$C_{456} = 0.678375\,\alpha + \varepsilon_2\eta_1\eta_3 + \varepsilon_1\eta_6$,

Where; $\quad \alpha = z^2 e^2/r_0^4$, $\quad \alpha_1 = (1/r_0 + 1/q)\,Q(r_0)/\,qr_0$, $\quad \alpha_2 = (\sqrt{2}/2r_0 + 1/q)\,Q(r_0\sqrt{2})/\,qr_0$

$\quad \alpha_3 = (3/r_0^2 + 3/qr_0 + 1/q^2)\,Q(r_0)/q$, $\quad \alpha_4 = (3\sqrt{2}/r_0^2 + 6/qr_0 + 2\sqrt{2}/q^2)\,Q(r_0\sqrt{2})/4q$

$\varepsilon_1 = \varepsilon_0\xi; \qquad \varepsilon_2 = \varepsilon_0[(X/\xi_1) + \xi]/2; \qquad \varepsilon_3 = \varepsilon_0[(2X^2\xi/3\xi_1) + (X/\xi_1) + \xi]/48;$

$\varepsilon_4 = -\varepsilon_0[(X^3\xi_2/2\xi_1) + (X^3/6\xi_1^2) + (X^2\xi/\xi_1) + (5X/4\xi_1) + (5\xi/4)]/144;$

$\varepsilon_0 = \hbar\omega_0/8r_0^3; \qquad X = \hbar\omega_0/2KT; \qquad \omega_0^2 = (1/m_1 + 1/m_2)/qr_0\eta_0;$

$\xi = \operatorname{Coth} X; \xi_1 = \operatorname{Sinh}^2 X$

Expression for η_n's for fcc Crystals

$\eta_0 = 1/[(q_0 - 2)(Q(r_0) + 2(q_0 - \sqrt{2})Q(r_0\sqrt{2}))$, $q_0 = r_0/q$;

$\eta_1 = 2[(2 + 2q_0 - q_0^2)Q(r_0) + 2(\sqrt{2} + 2q_0 - \sqrt{2}q_0^2)Q(r_0\sqrt{2})]\eta_0$;

$\eta_2 = 2(-6 - 6q_0 - q_0^2 + q_0^3)Q(r_0)q_0 + 2\eta_3$;

$\eta_3 = (-3\sqrt{2} - 6q_0 - \sqrt{2}q_0^2 + 2q_0^3)Q(r_0\sqrt{2})\eta_0$;

$\eta_4 = 2(-210 - 210q_0 - 75q_0^2 - 5q_0^3 + 4q_0^4 + q_0^5)Q(r_0)\eta_0 + 2\eta_7$;

$\eta_5 = 2(-30 - 30q_0 - 9q_0^2 + q_0^3 - q_0^4)Q(r_0)\eta_0 + 2\eta_6$;

$\eta_6 = [(15/\sqrt{2}) + 15q_0 - (9/\sqrt{2})q_0^2 - q_0^3 - \sqrt{2}q_0^4]Q(r_0\sqrt{2})\eta_0$;

$\eta_7 = [-(105/2\sqrt{2}) - (105/2)q_0 - (75/2\sqrt{2})q_0^2 - (5/2)q_0^3 + 2\sqrt{2}q_0^4 + q_0^5]Q(r_0\sqrt{2})\eta_0$

EVALUATION

The theory for the calculation of different anharmonic properties of the substances possessing FCC crystal structures is given in the preceding section 2. The TOECs for NaCN is evaluated from 300K to an elevated temperature (near melting point). Throughout this temperature range NaCN exhibits FCC crystal structure. Selecting a few data obtained in this study, the values of TOECs at room temperature are given in Tables 2. The FOPDs of TOECs have been evaluated utilizing data of TOECs and SOECs and the results are shown in Tables 3. 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 [6] of the nearest-neighbor distance (r0) and hardness parameter (q) are given in Table 1.

RESULTS AND DISCUSSION

The TOECs in 10^{11}dyne/cm^2 at room temperature for NaCN are given in Tables 2. The FOPDs of the TOECs are presented in Table 3. The temperature variation of anharmonic properties TOECs and FOPDs of TOECs for NaCN are represented graphically in Fig 1 – 4. There are six third order elastic constants. Among the calculated third-order elastic constants of this material, 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}.

For NaCN, the values of C_{111}, C_{112} and C_{166} are negative in nature, while C_{123}, C_{144} and C_{456} are positive in nature. The values of C_{111}, C_{123}, C_{144} and C_{166} increase, the values of C_{112} decrease as temperature increases, C_{456} remaining constant. The temperature variations of TOECs are given in Fig. 1, 2.

The values of dC_{111}/dp, dC_{112}/dp, dC_{123}/dp, dC_{144}/dp, dC_{166}/dp increase as temperature increases, and the values of dC_{456}/dp decrease as temperature increases.

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 along with other physical properties may provide further critical data for testing the machines for non-destructive-testing. These elastic constants are used to compute ultrasonic parameters such as ultrasonic velocities, thermal relaxation time etc [21- 23]. The variation of elastic constants [24-27] with respect to pressure can reveal many important features of the short range forces at high pressure. The ultrasonic studies [28, 29] can provide interesting information on the specificities of ion-solvent interaction related to the structure of the solute and the reciprocal effects which arises in the solvent. The data obtained in present investigation will be helpful to those workers who are engaged in studying the temperature variation of anharmonic properties of solids at higher temperatures [30, 31].

Table 1: The nearest neighbour distance (r$_0$) and hardness parameter (q) in 10^{-8} cm and SOECs in 10^{11} dyne/cm^2 of NaCN at room temperature

MP(K)	r$_0$	q	C11	C12	C44
836.7	2.0721	0.266	16.066	5.186	5.523

Table 2: The TOECs of NaCN in 10^{11} dyne/cm^2 at room temperature

C111	C112	C123	C144	C166	C456
-164.238	-46.178	10.651	9.406	-21.93	8.489

Table 3: The FOPDs of TOECs of NaCN at room temperature

dC111	dC112	dC123	dC144	dC166	dC456
-5.342	9.423	2.252	0.973	2.131	**2.287**
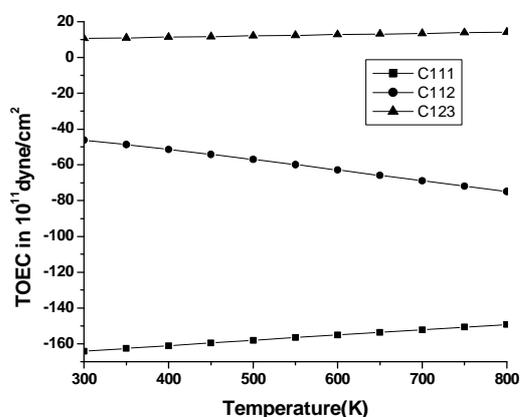
Fig.1. Temperature variation of TOEC for NaCN
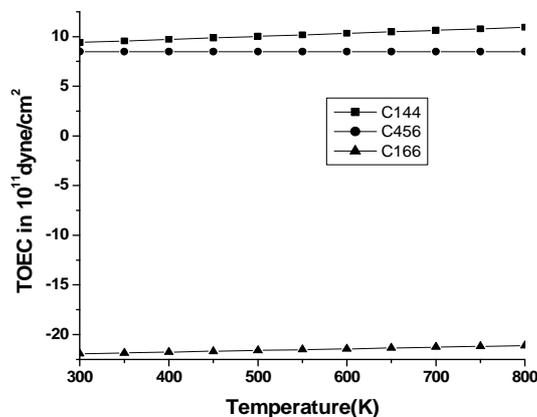
Fig.2.Temperature variation of TOEC for NaCN
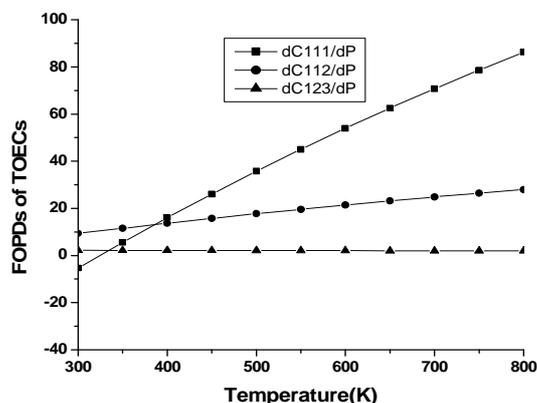
Fig. 3. Temperature variation of FOPDs for NaCN
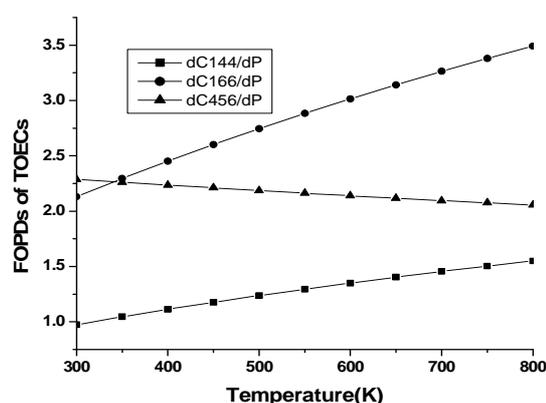
Fig. 4. Temperature variation of FOPDs for NaCN

REFERENCES

[1] I. Ohno, K. Harada, C. Yoshitomi, *Phys. Chem. Minerals* **2006**, 33, 1.

[2] C. Falter, *Phys. Stat. Sol. B,* **2005**, 242, 30.

[3] S. Kwon, J. Kim, *Mining Tech.: IMM Trans. A,* **2005**, 114, 89.

[4] B.P. Singh, H. Chandra*, Physica B,* **2005**, 358, 1.

[5] Kailash, S.K. Kor**,** *Physica B,* **1987**, 145, 209.

[6] Kailash**,** *Acta Phys. Pol. A,* **1996**, 89, 75.

[7] Kailash, K.S. Kushwaha, S.K. Shrivastava, K. Raju, *J. Pure Appl.Ultra.,* **2005**, 27, 29.

[8] S.K. Shrivastava, A. Kailash, K.M. Raju, *Ind. J. Phys.***,** **2005**, 79, 547.

[9] M. Nastar, W. William, *Phys. Rev. B,* **1995**, 31, 6896.

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

[11] A Cimino, G S Parry and A R Ubbelohde, *Proc. R. Soc. London ,* **1959**, A252, 445.

[12] J M Rowe, D. Hinks, D. L. Price, S Susman , J. Rush, *J. Chem. Phys.,* **1973**, 58, 2039.

[13] S. Haussu¨ hl, *Solid State Commun.,* **1973**, 13, 147.

[14] Krasser, Buchenau and Haussu¨ hl, *Solid State Commun.,* **1976**, 18, 287.

[15] M. Boissier, R Vacher, D. Fontaine and R. M. Pick, *J. Physique,* **1978**, 39, 205

[16] S. Haussu¨ hl, J. Eekstein, K. Rocker, F. Sofen, *Acta Crystallogr.,* **1977**, A33, 847.

[17] D. Sahu, S.D. Mohanti, *Phys. Rev. B,* **1982**, 26, 2981.

[18] S. Haussu¨ hl, *Solid State Commun.,* **1979**, 32, 181.

[19] Ghate P. B., *Phys. Rev.,* **1965**, 139, A1666.

[20] K. Brugger, Phys. Rev. A, **1964**, 133, 1604**.**

[21] Awasthi O. N. and Pundhir V. K., *Ind. J. Pure Appl. Phys.,* **2007**, 45, 434.

[22] Singh D. and Pandey D. K., Pramana*,* **2009**, 32, 389.

[23] Singh D., Pandey D. K. and Yadawa P. K., *Cent. J. Phys***, 2009**, 7, 198.

[24] Arya B.S., Aynyas M. and Sanyal S. P., *Ind. J. Phys.,* **2009**, 83, 153.

[25] Rukmangad A., Aynyas M. and Sanyal S. P., *Ind. J. Pure Appl. Phys.*, **2009**, 47, 114.

[26] Rao C. S. and Reddy C. E., *Ind. J. Pure Appl. Phys.*, **2009**, 47, 54.

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

[28] Udo K., Friecter E. and Karl L., *Measur. Sc. Tech.,* **2008**, 19, 62001.

[29] Thirumaran S. and Sabu K. J., *Ind. J. Pure Appl. Phys.,* **2009**, 47, 87.

[30] Kailash, Raju K. M. et al., Physica *B*, **2007**, 390, 270.

[31] Upadhyay A. K. and Sharma B. S., *Ind. J. Pure Appl. Phys.,* **2009**, 47, 362.