



## **STATIC AND THERMO-ELASTIC PROPERTIES OF ALKALI CYANIDE CRYSTALS**

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### **ABSTRACT**

*In the present paper authors have made an attempt to analyse the thermo-elastic properties of alkali cyanide crystals by estimating the values of their cohesive energy, Bulk-modulus and their pressure derivatives, Debye-temperature and Gruneisen parameter. A modified form of the three-body force shell model has been employed to calculate these values. The model used in the present study consists of long-range Coulomb and three-body interactions, short-range overlap repulsion of HZ-type, and van der Waals interactions. The van der Waals interaction coefficients are determined using the Kirkwood-Muller theory. Results obtained are compared with the available experimental data. A good agreement is found.*

### **INTRODUCTION**

The existing literature shows that the study on various physical properties of alkali cyanide crystals has been of considerable interest as they undergo a structural phase transition at low temperature<sup>(1-6)</sup>. At ordinary temperature, sodium, potassium and rubidium cyanides crystallize in NaCl-structure but below room temperature sodium and potassium cyanide crystals crystallize in orthorhombic structures while rubidium cyanide in monoclinic structure<sup>(3,5,7)</sup>. Another interesting phenomena in them are anomalous softening of C44<sup>(8,9)</sup> and unusual features in the phonon dispersion relations<sup>(6,10)</sup>. One of the most striking features of alkali-cyanides is the fact that these crystals also do not satisfy the Cauchy relation between second order or higher-order elastic constants like the simple alkali halides.

Although there have been some experimental investigations on thermoelastic or thermodynamic behaviour of alkali cyanide crystals<sup>(3,6)</sup>. The theoretical studies of this system have been quite scarce in past years. Recently Rana et al<sup>(11)</sup> have studied the static and thermodynamical properties of these cyanide crystals within the frame work of three body force shell model. However, their model is too simple to account for real interactions operative in cyanide crystals. There are three main drawbacks in the model adopted by them.

1. The repulsive hardness parameter (P) in the Born-Mayer exponential form which plays the significant role in describing the repulsive potential was assumed by Rana et al<sup>(11)</sup> to have a common value for cation-anion, cation-cation and anion-anion interactions. This assumption which has been considered by these workers is not justified in view of the fact that the behaviour of outermost electrons of different ion pairs responsible for overlap repulsion is not expected to be the same. Recent quantum mechanical<sup>(12,13)</sup> as well as phenomenological studies<sup>(14-17)</sup> on ionic crystals suggest that the repulsive stiffness between anion-anion is significantly different from that between cation-cation or cation-anion.

2. Rana et al<sup>(11)</sup> used the van der Waals potentials derived from the Slater-Kirkwood variational theory<sup>(18-19)</sup>. It has been noted<sup>(20)</sup> that the van-der Waal coefficient's determined from Slater-Kirkwood theory are about one-third in magnitude as compared to those calculated from Kirkwood-Muller theory<sup>(21-22)</sup> in the case of ionic solids. The larger values of van der waal energies calculated from Kirkwood-Muller formulae have been shown to yield cohesive energies in better agreement with experimental values<sup>(18)</sup>.
3. Although three-body interaction have been taken into account by Rana et al, but the three-body charge transfer parameter is actually determined by them using the values of second order elastic constants (SOEC) as input data. Since SOE constants are directly related to bulk- modulus and its pressure derivatives to predicted, the agreement obtained by Rana et al is rather forced and their method does not reveal a critical examinations of inter-ionic force model used.

In the present paper, we consider the overlap repulsive interaction of Hafemeister- Zarht<sup>(23)</sup> type in which the inter-ionic forces are corroborated by quantum mechanical results. The different values of hardness parameters between cation- anion, cation- cation and anion- anion are calculated from the overlap integrals<sup>(24)</sup>. The van der waals coefficients are determined using the kirkwood- Muller<sup>(21-22)</sup> theory which predicts about three times larger values of van der waal coefficients as compared to those obtained by Rana et al using Slater- Kirkwood formulae.

We have also considered Lindquist's three- body potential<sup>(25)</sup> in order to take account for Cauchy breakdown. The three- body potential parameters are estimated from over- lap integrals<sup>(24)</sup> using Cochram formula<sup>(26)</sup> unlike the previous worker<sup>(11)</sup>. The interionic potential thus developed is used to calculate cohesive energies, bulk- modulus and its pressure derivatives and Guneisen parameters of NaCN, KCN and RbCN crystals. A brief theory of model and calculated results are given in section 2. Section 3 deals with discussion of results achieved in the present investigation.

## THEORY AND METHOD OF CALCULATION

Within the frame work of the interionic-force model as developed in the present study, the potential energy of the alkali cyanide crystals corresponding to the lattice separation ( $r_{ij}$ ) can be written as follows:

$$\phi(r) = \frac{1}{2} \sum_{i,j} \frac{Z_i Z_j}{r_{ij}} e^2 + \sum_{i,j,k} \frac{Z_i Z_j}{r_{ij}} e^2 f(r_{ik}) + \phi^R(r) + \phi^V(r) \quad \dots(1)$$

In equation (1) the first and second terms are respectively the long-range coulomb and three-body interaction energies. In second term  $f(r_{ik})$  is a charge-transfer parameter determine from Cochran relation<sup>(26)</sup>. Third term represents the HZ-form of short-range overlap repulsion between nearest as well as between next nearest neighbour ions. Fourth term is due to dipole-dipole and dipole-quadrupole vander Waals interactions. The HZ-form of overlap repulsion and van der Waals short range attraction are different as follows:

$$\phi^R(r) = N b \left[ \frac{\beta_{ij}}{r_{ij}} \exp\left(\frac{r_i + r_j + r_k}{\rho_{ij}}\right) + N' \left[ \frac{\beta_{ii}}{r_{ii}} \exp\left(\frac{2r_i - r_{ij}}{\rho_{ii}}\right) + \frac{\beta_{jj}}{r_{jj}} \exp\left(\frac{2r_j - r_{ij}}{\rho_{jj}}\right) \right] \right]$$

and

$$\phi^V(r) = - \sum_{i,j} \frac{C}{r_{ij}^6} - \sum_{i,j} \frac{D}{r_{ij}^8} \quad \dots(2)$$

Where  $\beta_{ij}$  is Pauling coefficient,  $r_1$  and  $r_j$  are the radii of cation and anion respectively.  $r_{ij}$  is the separation between cation and anion,  $b$  is repulsive strength parameter.  $\rho_{ij}$ ,  $\rho_{ii}$ ,  $\rho_{jj}$  are the hardness parameters between nearest as well as between next nearest neighbour ions.  $C$  and  $D$  being the van der waals coefficients calculated using the theory of kirkwood-Muller<sup>(21, 22)</sup>. The strength parameter  $b$  is estimated using the crystal equilibrium condition i. e.

$$\frac{d\phi(r)}{dr} / r = r_0 = 0 \quad \dots(4)$$

In order to test the validity and effectiveness of the interionic potential as described by equation (4), we have calculated the of isothermal bulk modulus ( $B_T$ ), pressure derivatives of bulk- modulus ( $\frac{dB_T}{dP}$ ), Gruneisen- parameter ( $\gamma_G$ ) and Debye temperature ( $\theta_D$ ) for NaCN, KCN and RbCN crystals. The expressions used for the calculations of bulk modulus and its pressure derivative are as follows:

$$B_T = \frac{1}{18r_0} \cdot d^2\phi \frac{r}{dr^2} \quad \dots(5)$$

and

$$\frac{dB_T}{dP} = 1 - \frac{d^3\phi(r)/dr^3}{5B_T} \quad \dots(6)$$

The well known relations used for the calculation of Gruneisen-parameter ( $\gamma_G$ ) and Debye temperature ( $\theta_D$ ) are

$$(\gamma_G) = -\frac{r_0}{6} \cdot \frac{d^3\phi(r)/dr^3}{d^2\phi(r)/dr^2} \quad \dots(7)$$

$$(\theta_D) = \frac{h}{k} \left( \frac{5r_0 B_T}{\mu} \right) \quad \dots(8)$$

where  $h = h / 2\pi k$  is the Boltzmann constant and  $\mu$  is the reduced mass.

The calculated values of cohesive energy, bulk-modulus and its pressure derivative are reported in Table II, Gruneisen- parameter and Debye-temperature are listed in Table III. The calculated values of model parameter used for the calculations of these quantities are mentioned in Table I.

## DISCUSSION

It is evident from Table I that calculated values of cohesive energy and bulk modulus are in excellent agreement with the experimental data. Our calculated values are in better agreement with experimental data as compared to those of Rana et al<sup>(11)</sup>. The clearly indicates that the interionic potentials and parameter considered in the present study prove superior to previous studies<sup>(11)</sup>. The better agreement in results for these crystals further confirms the findings of Jenkins and Morris<sup>(27)</sup> that the effective radius of CN – ion should be smaller than those of Pauling's radius<sup>(29)</sup> and the rmdynamical radius<sup>(30)</sup> for the calculations of cohesive energy and bulk modulus of these crystals. Since the experimental values of pressure derivatives of bulk modulus, Gruniesen parameter and Debye temperature are not available so for in the case of alkali crystals, the calculated results for them could not be compared with experimental data. However, our calculated values of these quantities are of academic interest at present and they may stimulate the experimental investigations in future.

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**Table I. Calculated values of model parameters**

Properties	NaCN	KCN	RbCN
F (r)	0.0324	0.0365	-0.0255
B ( $10^{-9}$ ergs)	6.1201	8.3205	8.3680
P + - ( $10^{-8}$ cm)	0.307	0.316	0.325
P + + ( $10^{-8}$ cm)	0.189	0.170	0.178
P - - ( $10^{-8}$ cm)	0.436	0.416	0.385
C ( $10^{-60}$ ergs cm <sup>6</sup> )	689.65	1702.18	2710.68
D ( $10^{-76}$ ergs cm <sup>8</sup> )	251.08	859.85	1418.70

**Table II. Values of cohesive energy (in K Cal/ mol), bulk modulus ( $10^{11}$  dyne/cm<sup>2</sup>) and the pressure derivatives of bulk modulus**

Crystals	$\emptyset$ (r)	B <sub>T</sub>	$\frac{dB_T}{dp}$
NaCN	-173.24 (-173.57)*	1.805 (1.807)**	3.612 (4.330)***
KCN	-152.65 (-153.33)	1.421 (1.437)	3.856 (4.679)
RbCN	-150.89 (-151.90)	1.246 (1.276)	4.107 (4.783)

\* Experimental values [27, 28]

\*\* Values calculated from the relation ( $\frac{C_{11} + 2C_{12}}{3}$ ).

\*\*\* Calculated by Rana et al (11).

**Table III. Values of Gruneisen- parameters and Debye- temperature**

Crystal	$\gamma_G$	$\theta_D$
NaCN	1.856 (1.665)*	289.62 (276.01)*
KCN	2.135 (1.839)	246.58 (229.52)
RbCN	2.305 (1.891)	212.12 (195.03)

\* Calculation by Rana et al [11]