

Thermoelastic and Cohesive Properties of (KCN)_x(KBr)_{1-x}

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Abstract–The motivation for the present work was gained from the recent publication on cohesive and thermoelastic properties of (KCN)_x(KCl)_{1-x} using Extended Three Body Force Shell Model (ETSM). The thermal and elastic properties of (KCN)_x(KBr)_{1-x} are investigated by means of the same model which incorporates the effect of coupling between the translation modes and the orientation of the cyanide molecules. The motion of constituent atoms or molecules or the nature of binding forces of a crystal can be investigated by studying the mechanical properties of pure and mixed crystals like, anharmonic elastic properties. We have chosen different compositions at different temperatures to show that anharmonic elastic properties are temperature dependent rather than composition dependent and the purpose of study is to test the mechanical stabilities of the potential. Also, the thermodynamic properties such as molecular force constant (f), Reststrahlenfrequency, cohesive energy, Debye temperature and Gruneisen parameter have also been discussed.

Keywords – Elastic constants, Cohesive energy, Thermodynamic properties

1. INTRODUCTION

In the past few years, the cohesive and thermoelastic properties of orientationally disordered alkali metal cyanides have been of interest to the experimental as well as theoretical workers on this field. The lattice mechanics of many ODMs have been reported satisfactorily by means of ETSM. This model which was designed by incorporating Translational-Rotational coupling effect in the framework of Three Body Force Shell Model was found to be excellent in explaining the static, dynamic, dielectric and optic properties of ODMs. Inspired by the great success of ETSM [1] in explaining these properties of ODMs we thought it appropriate to extend the investigation to thermoelastic and cohesive behaviour of

(KCN)_x(KBr)_{1-x} which belongs to the mixed alkali halide-cyanide family.

When the Br⁻ ion of an alkali halide system is replaced by a CN⁻ ion, a (KCN)_x(KBr)_{1-x} system is generated. Here, the substitution of the spherical Cl⁻ ions by the dumb-bell shaped CN⁻ ions strongly

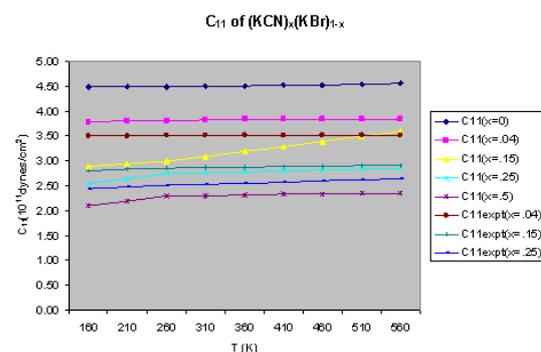


Figure 1. The variation of C_{11} with temperature for (KCN)_x(KBr)_{1-x}

lower the transition temperature of the system. This mixed system shows glassy state at very low temperature and over a wide range of concentration. This system which exhibits rich (X, T) phase diagram [2], above a critical concentration of $x_c = 0.08$, undergo structural change from cubic phase to monoclinic or orthorhombic phases at room temperature [2]. The structural changes result in linear TR coupling orientational degree of freedom of the cyanide molecules and the translational modes. Also, the requirement of application of ETSM to (KCN)_x(KBr)_{1-x} evolved from the fact that the K⁺ ions and the CN⁻ ions has larger ionic size difference which makes the three-body interactions (TBI) more effective in this crystal. The formulation of ETSM is given in 2. We present the results and related discussions about the thermoelastic and cohesive properties in section 3. Concluding remarks are given in Section 4.

II .ESSENTIAL FORMULATION

The formalism of the Extended Three Body Force Shell Model has been derived from the following interatomic interaction [3-8]

$$\Phi = \frac{e^2}{2} \sum_k \sum_{k'} Z_k Z_{k'} r_{kk'}^{-1} [1 + \sum_{kk'} f(r_{kk'})] - \sum_{kk'} c_{kk'} r_{kk'}^{-6} - \sum_{kk'} d_{kk'} r_{kk'}^{-8} + b \sum_{kk'} \beta_{kk'} \exp(r_k + r_{k'} - r_{kk'} / \rho) + \phi^{TR} \quad (1)$$

Here, the first term is attractive long range (LR) coulomb interactions energy and the second term is the three body interaction potential. The third and fourth term represents the contributions of van der Waals (vdW) attraction for the dipole-dipole interaction and dipole-quadrupole interactions and the fifth term is short range (SR) overlap repulsive energy represented by the Hafemeister–Flygare type (HF) interaction extended up to the second neighbor. ϕ^{TR} is the contribution due to translational rotational coupling. In expression (1), other symbols involved are the same as those defined in our earlier papers [3-8].

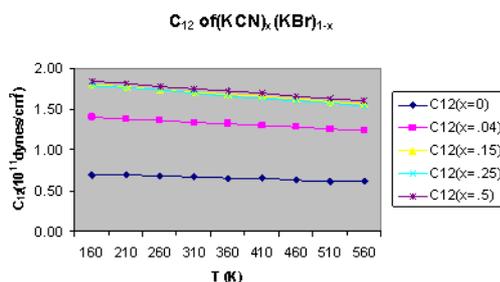


Figure 2. The variation of C_{12} with temperature for $(KCN)_x(KBr)_{1-x}$

b_i and ρ_i are the hardness and range parameters for the i^{th} cation–anion pair ($i = 1, 2$) respectively and $\beta_i^{kk'}$ is the Pauling coefficient [9] given by

$$\beta_i^{kk'} = 1 + (Z_k / N_k) + (Z_{k'} / N_{k'}) \quad (2)$$

Z_k ($Z_{k'}$) and N_k ($N_{k'}$) are the valence and the number of electrons in the outermost orbit of the k (k') ion respectively. The contributions of van der Waals (vdW) attraction for the dipole-dipole interaction are determined by using the Slater–Kirkwood Variational (SKV) method [10]. The model parameters, hardness (b) and range (ρ) are determined from the equilibrium condition.

$$\left[\frac{d\phi}{dr} \right]_{r=r_0} = 0 \quad (3)$$

and the bulk modulus

$$B = 1/9 K r_0 \left[\frac{d^2\phi}{dr^2} \right]_{r=r_0} \quad (4)$$

where K is the crystal-structure-dependent constant

and r_0 is the equilibrium nearest neighbour distance. The expressions for calculating the thermodynamic properties like Debye temperature (θ_D), Restrahlen frequency (ν), molecular force constant (f), and Gruneisen parameter (γ) are taken from our earlier papers [3-8]. The present model (ETSM) described above for the $(KCN)_x(KBr)_{1-x}$ contains three model parameters (b , ρ and f), which are used to determine the second-order elastic constants (SOECs) of $(KCN)_x(KBr)_{1-x}$.

III. RESULTS AND DISCUSSION

We have obtained the model parameters (b , ρ and f) as a function of temperature using input data (Table 1) taken from Ref. [11-12] and the van der Waals coefficients. The model parameters computed for $(KCN)_x(KBr)_{1-x}$ for the concentrations $x=0, 0.04, 0.15, 0.25, 0.5, 0.7, 0.85$ and 0.95 are given in Table 2. Using the model parameters we have calculated the second order (SOECs) elastic constants of $(KCN)_x(KBr)_{1-x}$ at $160K \leq T \leq 560K$ for the composition $x=0.04, 0.25, 0.5, 0.7, 0.95$ and are plotted in Figures 1-3. The values of c_{11} increases with increase in temperature and c_{12} show quasilinear dependence on temperature. Due to lack of experimental results the values of c_{11} and c_{12} could not be compared. Our calculated results on shear elastic constant c_{44} (Figure 3) are in good agreement with the measured values obtained by Kwiecien and Garland [13]. Also a gradual increase in c_{44} with increase in temperature is observed. It is interesting to note that a softening of c_{44} with lowering of temperature is observed which might be due to the effective coupling of CN^- ions which indicates a phase transition at lower temperature or the collective behaviour of coupled impurity. The values of c_{44} are found to be 100 times lesser than the values of c_{11} and c_{12} in these compounds.

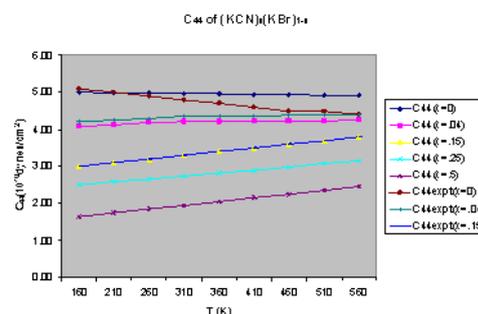


Figure 3. The variation of C_{44} with temperature for $(KCN)_x(KBr)_{1-x}$

The thermophysical properties of $(KCN)_x(KBr)_{1-x}$ cohesive energy ϕ , compressibility β , molecular force constant f and Restrahlen frequency ν_0 , the Debye temperature θ_D and

Grüneisen parameter γ , α_v / c_v are calculated for concentrations $x = 0.5, 0.65, 0.7, 0.85$ and 0.95 for temperature range $160\text{K} \leq T \leq 560\text{K}$ and are listed in Table 3. From Table 3 it is clear that cohesive energy ϕ , is decreasing with increase in temperature but is increasing with increase in concentration of CN⁻ ions. It is in close resemblance to the experimental values observed at room temperature [14]. The negative values of cohesive energy show that the stability of these compounds is intact. The Reststrahlen frequency ν_0 and the Grüneisen parameter decrease with increase in temperature. Thus, the Grüneisen parameter is temperature dependent and its decrease with increase in temperature for various compositions is due to the increase in interatomic separation [15].

The calculated values of compressibility β by ETSM are found to be increasing with increase in temperature and are closer with the available experimental data [16-17]. The Debye temperature of a crystal is a parameter which is involved in many phenomena associated with lattice vibrations. Our values of Debye temperature θ_D are compared with the experimental values [18] of Debye temperature obtained by the method of Seitoff and Ahlborn [19] and are found to be in good agreement. The values of molecular force constant f are closer to the reported value of 2.82×10^4 dynes/cm respectively for pure KCN crystals [14] at 300K. The thermophysical properties calculated by us for a wide range of temperature and different compositions as mentioned above follow the same trend as reported earlier for a narrow range of temperature [20].

IV .CONCLUSION

The elastic and thermodynamic properties of the orientationally disordered $(\text{KCN})_x(\text{KBr})_{1-x}$ mixed crystal are investigated with the help of ETSM. Our calculated results on shear elastic constant c_{44} are in fairly good agreement with the available experimental data. Also, the values of cohesive energy, compressibility and molecular force constant obtained from ETSM are in good agreement with the available experimental values of these parameters. Our comments on the other results are restricted until the report of experimental data on them but these results will serve as a guide to the experimental workers in future. A successful description of mechanical properties achieved for such complicated $(\text{KCN})_x(\text{KBr})_{1-x}$ can be considered remarkable in view of the inherent simplicity of the ETSM and its less parametric nature.

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