

Second Order Elastic Constants of $(\text{CsCN})_x(\text{CsX})_{1-x}$, (X= Cl, Br and I) mixed crystals

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Abstract: We have applied an Extended Three-Body Force Shell Model (ETSM) to investigate the elastic properties of mixed alkali cyanide-alkali halide crystal $(\text{CsCN})_x(\text{CsX})_{1-x}$ (X= Cl, Br and I) for $x=0, 0.28, 0.59$ and 0.96 at different temperature. This model includes the effect of coupling between the translational and rotational motion of cyanide molecules. The static shear elastic constant c_{44} obtained by us shows an anomalous behaviour as a function of temperature. We have also reported the c_{11} and c_{12} of $(\text{CsCN})_x(\text{CsX})_{1-x}$ (X= Cl, Br and I) mixed crystal.

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1. Introduction

Mixed crystals of the type $\text{A}(\text{CN})_x\text{X}_{1-x}$, where A is an alkali metal ion (K, Rb, Na, Cs etc.) and X is a halogen ion (Br or Cl) have been a subject of extensive research during recent years. The $(\text{CsCN})_x(\text{CsX})_{1-x}$ (X= Cl, Br and I) mixed crystals offer a useful system for understanding the importance of the translational-rotational coupling in orientationally disordered crystal. The TR coupling has turned out to be responsible for important effects in these orientationally disordered crystals. In mixed crystals, it is possible to vary the impact of translational rotational coupling by changing the substitutional disorder [1]. It influences the elastic as well as the phonon properties at finite wave vector, which may lead to an orientational glass state or even to lattice instability [2, 3]. In particular, CN^- orientational modes are strongly coupled with transverse acoustic (TA) lattice translational modes and the c_{44} shear elastic constant softens drastically [4].

Elastic constants of crystals and their temperature dependence are of interest in themselves as well as they provide much insight into the inter-atomic forces of solids [5]. The rapid decrease of c_{44} in pure CsCN has been shown to arise from a strong coupling between the orientation of CN^- ion and TA phonon of the crystal [6]. The shear elastic constant for pure crystal is small and varies rapidly with the temperature whereas it becomes more interesting to study the effect of temperature on the elastic soft mode of the replaced ion [7]. Several theoretical models have been proposed to describe the orientational ordering in mixed crystals [8-11] but a completely satisfactory description is still not available.

We have developed an Extended Three-Body Force Shell Model (ETSM) by including the effect of coupling between the translational and rotational modes of CN^- molecules [12, 13]. This model has successfully been applied to study the static, dynamic, dielectric, optical and anharmonic properties of pure ionic crystals. In the present work, we extend the application of the ETSM to calculate the second order elastic

constant (SOECs) for mixed $(\text{CsCN})_x(\text{CsX})_{1-x}$ (X= Cl, Br and I) for $x=0, 0.28, 0.59$ and 0.96 at different temperature.

2. Essential Formalism

The interaction potential used to derive the framework of the present ETSM can be expressed as [14-16]

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

where the first two terms represent the long range Coloumb and Three Body Interaction [13]; the third and fourth terms are the van der Waals(vdW) interaction due to dipole-dipole(d-d) and dipole-quadrupole(d-q) attractions, the fifth term represents the Hafemeister Flygare [14] type short-range overlap repulsion extended up to second neighbour ions, $\beta_{kk'}$ are the Pauling coefficient [15, 16]; ρ and b are the range and hardness model parameters, respectively as defined earlier [17-19]

$$\left[\frac{d\phi(r)}{dr} \right]_{r=r_0} = 0 \quad (2)$$

and the bulk modulus

$$B = \frac{1}{9Kr_0} \left[\frac{d^2\phi(r)}{dr^2} \right]_{r=r_0} \quad (3)$$

ϕ^{TR} is the contribution due to TR coupling effects [20] Where r is the nearest neighbour (nn) separation and r_0 is the equilibrium nn separation. K as the crystal structure constant. The TR coupling effect has been taken through elastic constant.

The temperature dependent Second Order Elastic Constants (SOECs) are determined with the help of following equations:

$$c_{11} = -4.388T\beta B_T + \frac{e^2}{4r_0^4} \left[A_1 - 4.388B_1 + \frac{A_2}{2} + 4.888B_2 + 9.3204r_0 f'(r_0) \right] + \delta c_{11}^{TR} \quad (4)$$

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$$c_{12} = 1.194T\beta B_r + \frac{e^2}{4r_0^4}[-1.194B_1 + \frac{A_2}{4} - 1.444B_2 + 9.3204r_0 f'(r_0)] + \delta c_{12}^{TR} \quad (5)$$

$$c_{44} = 2.194T\beta B_r + \frac{e^2}{4r_0^4}[-1.194B_2 + \frac{A_2}{4} - 1.444B_2] + \delta c_{44}^{TR} \quad (6)$$

$$\text{where } T\beta B_r = \frac{e^2}{4r_0^4} [1.165\epsilon\{\epsilon + 12f(r)\} + B_1 + B_2]$$

and A_1, A_2, B_1, B_2 are the short range force parameters; $f(r)$ and $rf'(r)$ are the TBI parameters. The parameter $f(r)$ and its derivatives are calculated from the knowledge of elastic constants and the relation $f = f_0 \exp(-r/\rho)$. The SOECs are obtained from equation (4) to (6) incorporated by TR coupling. The TR coupling constants are given by,

$$\delta c_{11}^{TR} = c_{11}^0 - \frac{8}{r_0} A_{eff}^2 \chi_{11}(T) \quad (7)$$

$$\delta c_{12}^{TR} = c_{12}^0 + \frac{4}{r_0} A_{eff}^2 \chi_{11}(T) \quad (8)$$

$$\delta c_{44}^{TR} = c_{44}^0 - \frac{2}{r_0} B_{eff}^2 \chi_{44}(T) \quad (9)$$

where A_R, B_R are the short range repulsion and A_Q, B_Q are the quadrupole contributions to the translational-rotational coupling and $\chi_{ij}(T)$ is the rotational susceptibility [20].

3. Result and Discussion

The input data for $(\text{CsCN})_x(\text{CsCl})_{1-x}$, $(\text{CsCN})_x(\text{CsBr})_{1-x}$ and $(\text{CsCN})_x(\text{CsI})_{1-x}$ [21-27] at different temperature are obtained from pure CsCN, CsCl, CsBr and CsI by the well known Vegard's law [21]. To calculate r_0 at different composition at $x=0, 0.28, 0.59$ and 0.96 as

$$r_0[(\text{MCN})_x(\text{MX})_{1-x}] = xr_0[(\text{MCN})] + (1-x)r_0[(\text{MX})] \quad (10)$$

Where x and $1-x$ are concentration dependent parameters for the host and substituted ions respectively. To obtain data at different temperature, we have used the thermal expansion relation,

$$I_T = I_0(1 + \alpha T) \quad (11)$$

The calculated values of the input data for various concentrations are given in Table 1-3 where all the symbols have the usual meanings as explained earlier.

Table 1: Input data and vdW coefficient for $(\text{CsCN})_x(\text{CsCl})_{1-x}$ at room temperature.

Properties	$(\text{CsCN})_x(\text{CsCl})_{1-x}$			
Concentration	$x=0$	$x=0.28$	$x=0.59$	$x=0.96$
$r_0(\text{\AA})$	3.571	3.602	3.635	3.676
r_+	1.903	1.903	1.903	1.903
r_-	1.648	1.682	1.72	1.765
$c_{11}(10^{11}\text{dyn cm}^{-2})$	3.640	3.209	2.731	2.162
$c_{12}(10^{11}\text{dyn cm}^{-2})$	0.920	1.026	1.144	1.285
$c_{44}(10^{11}\text{dyn cm}^{-2})$	0.800	0.688	0.564	0.416
$\alpha_+(\text{\AA})^3$	1.140	1.5198	2.438	3.252
$\alpha_-(\text{\AA})^3$	4.130	2.2876	2.755	1.893

Table 2: Input data and vdW coefficient for $(\text{CsCN})_x(\text{CsBr})_{1-x}$ at room temperature.

Properties	$(\text{CsCN})_x(\text{CsBr})_{1-x}$			
Concentration	$x=0$	$x=0.28$	$x=0.59$	$x=0.96$
$r_0(\text{\AA})$	3.720	3.709	3.696	3.682
r_+	1.903	1.903	1.903	1.903
r_-	1.809	1.798	1.786	1.772
$c_{11}(10^{11}\text{dyn cm}^{-2})$	3.097	2.818	2.509	2.139
$c_{12}(10^{11}\text{dyn cm}^{-2})$	0.903	1.014	1.137	1.284
$c_{44}(10^{11}\text{dyn cm}^{-2})$	0.750	0.652	0.544	0.414
$\alpha_+(\text{\AA})^3$	1.140	1.756	2.438	3.252
$\alpha_-(\text{\AA})^3$	4.130	3.478	2.755	1.893

Table 3: Input data and vdW coefficient for $(\text{CsCN})_x(\text{CsI})_{1-x}$ at room temperature

Properties	$(\text{CsCN})_x(\text{CsI})_{1-x}$			
Concentration	$x=0$	$x=0.28$	$x=0.59$	$x=0.96$
$r_0(\text{\AA})$	3.956	3.879	3.793	3.691
r_+	1.903	1.903	1.903	1.903
r_-	2.048	1.970	1.884	1.781
$c_{11}(10^{11}\text{dyn cm}^{-2})$	2.434	2.340	2.237	2.113
$c_{12}(10^{11}\text{dyn cm}^{-2})$	0.636	0.822	1.028	1.273
$c_{44}(10^{11}\text{dyn cm}^{-2})$	0.632	0.567	0.495	0.409
$\alpha_+(\text{\AA})^3$	1.140	1.756	2.438	3.252
$\alpha_-(\text{\AA})^3$	4.130	3.478	2.755	1.893

Using the above input data, we have calculated the model parameters of these systems. The model parameters viz. interatomic separation (r), hardness parameter (b), range parameter (ρ) and three body interaction parameter $rf(r_0)$ were calculated for various temperature. The values for these four model parameters along with corresponding inter atomic separation at different concentration $x=0, 0.28, 0.59$ and 0.96 are given in Tables 4-5.

Table 4: Model parameters for $(\text{CsCN})_x(\text{CsX})_{1-x}$ ($X = \text{Cl, Br and I}$) at $x=0, 0.28, 0.59$ and 0.96)

T(K)	r_0			ρ
	$x=0$	$x=0.28$	$x=0.59$	$x=0.96$
300	3.619	3.65	0.359	0.347
300	3.725	3.726	0.356	0.359
300	3.961	3.896	0.228	0.399
	$x=0.59$	$x=0.96$	$x=0.59$	$x=0.96$
300	3.684	3.725	0.354	0.357
300	3.727	3.729	0.349	0.355
300	3.824	3.738	0.399	0.399

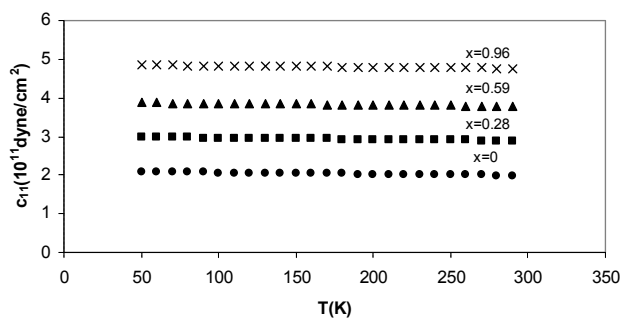
Table 5: Model parameters for $(\text{CsCN})_x(\text{CsX})_{1-x}$ ($X = \text{Cl, Br and I}$) at $x=0, 0.28, 0.59$ and 0.96)

T(K)	b		$f(r)$	
	$x=0$	$x=0.28$	$x=0$	$x=0.28$
300	0.26	0.397	-0.006	-0.017
300	0.253	0.392	-0.0062	-0.0173
300	0.105	0.37	-0.0002	-0.0185
	$x=0.59$	$x=0.96$	$x=0.59$	$x=0.96$
300	0.564	0.771	-0.031	-0.048
300	0.557	0.769	-0.0332	-0.0487
300	0.592	0.845	-0.0367	-0.0559

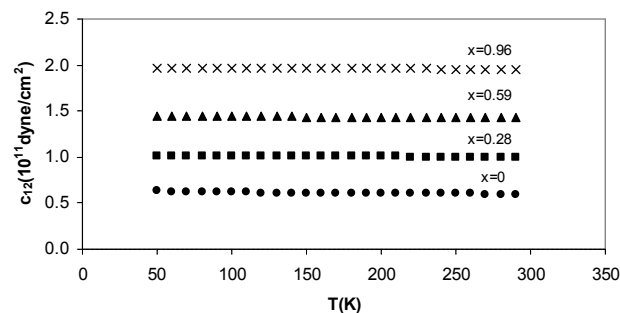
4. Second Order Elastic Constants

So far we have considered the softening of elastic constants due to translational-rotational coupling in ideal periodic crystals. In mixed crystal with substitutional disorder, it is possible to vary the importance of TR coupling by changing

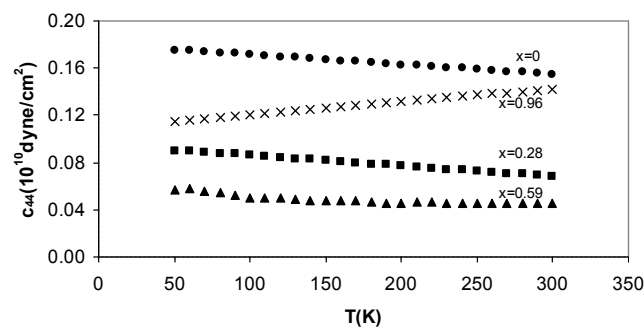
the substitutional disorder. The most prominent example of this category of mixed crystals are the alkali metal halide cyanides. $\text{CsCN}_x\text{X}_{1-x}$. Here, X is a halogen. Depending on the nature of the substitutional ion and on the concentration, these system exhibit very rich phase diagrams. A theoretical explanation in terms of TR coupling has been given by ETSM. Elastic constants in orientationally disordered CsCN - CsX mixed crystals are reduced (or softened) by the translation- rotation coupling at the zone center. If this coupling results in a phase transition to a more ordered state, then the softening of the corresponding elastic constant is strongly and anomalously temperature dependent, decreasing as the temperature is reduced towards T_c , but even in orientationally disordered phases where the phase transition does not occur at the zone center, elastic constants may still be significantly softened by translation- rotation coupling that are not involved in the phase transition. In this section we will compute the second order elastic constants of $(\text{CsCN})_x(\text{CsCl})_{1-x}$, $(\text{CsCN})_x(\text{CsBr})_{1-x}$ and $(\text{CsCN})_x(\text{CsI})_{1-x}$ for different temperature range, for the concentrations $x=0, 0.28, 0.59$ and 0.96 . The translational-rotational coupling of the CN^- ion is taken into account. The TR coupling is applied on the lines of Sahu and Mahanti[22]. We have calculated c_{11} , c_{12} and c_{44} at different concentration and temperature with the help of equations 4-6. The results obtained from ETSM for c_{11} , c_{12} and c_{44} are shown in Fig. 1-3 for $(\text{CsCN})_x(\text{CsCl})_{1-x}$, $(\text{CsCN})_x(\text{CsBr})_{1-x}$ and $(\text{CsCN})_x(\text{CsI})_{1-x}$ respectively. On inspection of Fig. (1)-(3), the c_{11} and c_{12} changes slightly with the increase in temperature and the behaviour of these two constants changes when composition of cyanide decreases more and more and shows quasilinear behaviour. If we exclude the TR coupling effect, their behaviour were similar to that of alkali halides for the whole range of concentration. The experimental values of c_{11} , c_{12} and c_{44} for mixed CsCN are not available to compare our theoretical results. However, one can easily find that the difference $c_{11}-c_{12}$ decreases at higher concentration of CN^- and low temperatures, indicating change towards stability. The shear elastic constants c_{44} of $(\text{CsCN})_x(\text{CsCl/Br})_{1-x}$ plays a significant role in explaining the unusual behaviour at a particular temperature and composition. Our c_{44} results show the deviation of c_{44} from straight lines for $(\text{CsCN})_x(\text{CsX})_{1-x}$ ($X=\text{Cl, Br and I}$) mixed crystals. This deviation might be due to the difference in ionic radii of CN^- and Br^- . Besides, the c_{44} shows softening at lower temperature side. This softening might be due to the effective coupling of CN^- ion and the temperature dependence of c_{44} reflects the collective behaviour of coupled impurity.



(a)

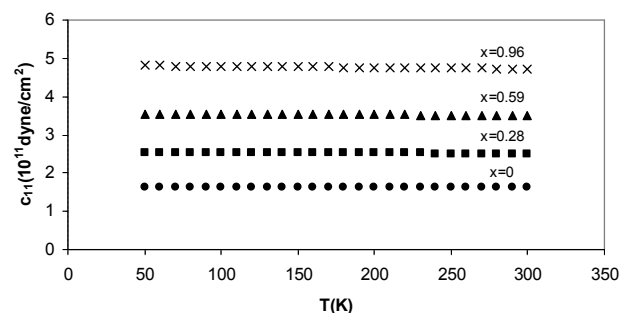


(b)

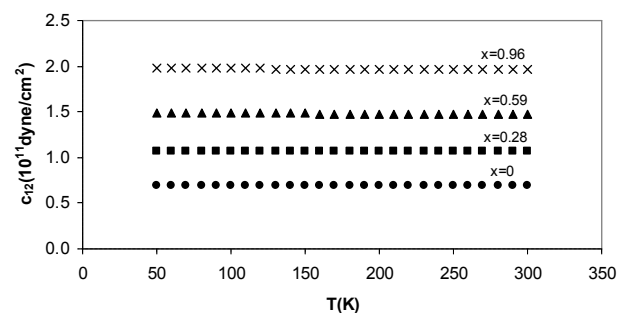


(c)

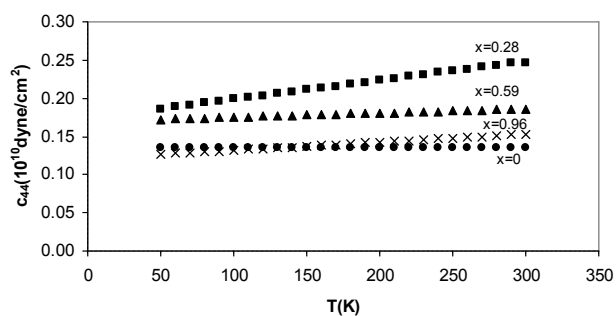
Figure 1: Second order elastic constants for $(\text{CsCN})_x(\text{CsCl})_{1-x}$ mixed crystals. (a) c_{11} , (b) c_{12} and (c) c_{44} where (●), (■), (▲) and (×) represents the variation of c_{ij} at $x=0, 0.28, 0.59$ and 0.96



(a)

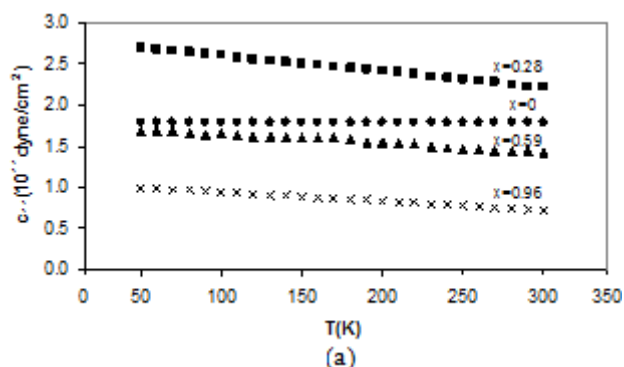


(b)

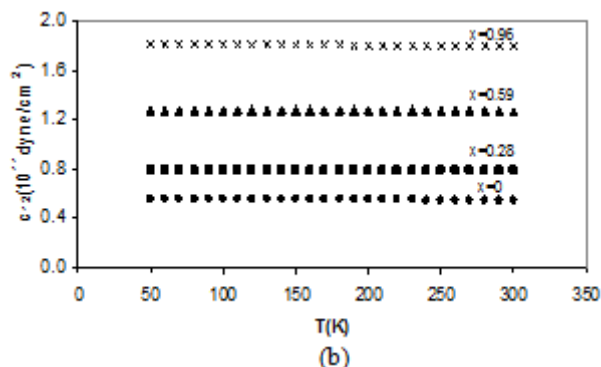


(c)

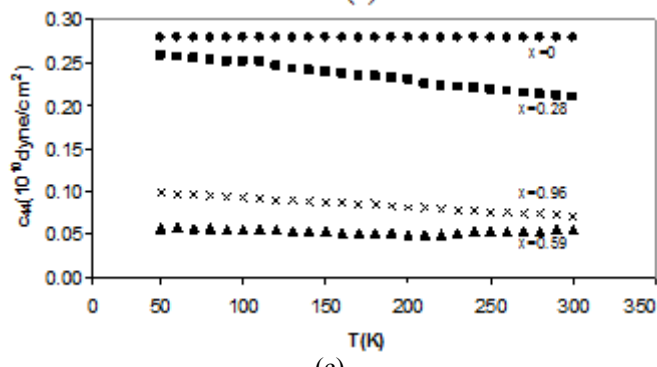
Figure 2: Second order elastic constants for $(\text{CsCN})_x(\text{CsBr})_{1-x}$ mixed crystals. (a) c_{11} , (b) c_{12} and (c) c_{44} where $(\bullet)$, $(\blacksquare)$, $(\blacktriangle)$ and $(\times)$ represents the variation of c_{ij} at $x=0, 0.28, 0.59$ and 0.96



(a)



(b)



(c)

Figure 3: Second order elastic constants for $(\text{CsCN})_x(\text{CsI})_{1-x}$ mixed crystals. (a) c_{11} , (b) c_{12} and (c) c_{44} where $(\bullet)$, $(\blacksquare)$, $(\blacktriangle)$ and $(\times)$ represents the variation of c_{ij} at $x=0, 0.28, 0.59$ and 0.96

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