Elastic properties of KCN_xCl_{1-x}

P. SINGH*, N. K. GAUR
Department of Physics, Barkatullah University, Bhopal, 462 026 India

In the present paper we have applied an Extended Three-Body Force Shell Model (ETSM) to investigate the elastic properties of mixed alkali cyanide-alkali halide crystal KCN_xCl_{1-x} for x= 0.41, 0.56, 1.0 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 anamolous behaviour as a function of temperature and followed the same trend as observed experimentally. We have also reported the c_{11} and c_{12} of KCN_xCl_{1-x} mixed crystal.

(Received April 20, 2009; accepted May 25, 2009)

Keywords: Elastic Constants, Cohesive energy, Elastic constants, Elastic softening, Mixed crystals, Translational-rotational coupling

1. Introduction

Mixed crystals of the type $A(CN)_xX_{1-x}$, where A is an alkali metal ion (K, Rb, Na etc.) and X is a halogen ion (Br or Cl) have been a subject of extensive research during recent years. The KCN_xCl_{1-x} 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 KCN 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), third order elastic constant (TOECs) and their pressure derivatives for mixed KCN_xCl_{1-x} (x=0.41, 0.56, 1.0) at 100K≤ T≤ 300K. An investigation of these higher order elastic constants and their pressure derivatives provides useful information about their inter-atomic forces and anharmonic properties.

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-quadrapole(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

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

ϕ^{TR} is the contribution due to TR coupling effects [20] Where r is the nearest neighbour (nn) sepration and r_o is the equilibrium nn separation. K as the crystal structure constant (=1.4142 for NaCl structure). 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:

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

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

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

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

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 χ_{ij} (T) is the rotational susceptibility [20]. The temperature dependent TOECs are obtained as

$$c_{111} = 32.237Tb\beta_T + \frac{e^2}{4r_0^4}[-32.231B_1 - 34.48B_2 + \frac{4C_1 - 12A_1 + C_2 - 3A_2}{4} + 13.4599B_1 + 89.305r_0 f'(r_0)] \quad (10)$$

$$c_{112} = -4.15Tb\beta_T + \frac{e^2}{4r_0^4}[4.151B_1 + 4.52B_2 + \frac{C_2 - 3A_2}{8} + 4.6608r_0^2 f''(r_0) - 18.640r_0 f'(r_0)] \quad (11)$$

$$c_{166} = -6.151Tb\beta_T + \frac{e^2}{4r_0^4}[4.151B_1 + 4.52B_2 + \frac{C_2 - 3A_2}{8} - 3.5377B_{21} - 5.56r_0 f'(r_0)] \quad (12)$$

$$c_{123} = 2.332Tb\beta_T + \frac{e^2}{4r_0^4}[-2.332(B_1 + B_2) + 16.692r_0 f'(r_0)] \quad (13)$$

$$c_{144} = 2.332Tb\beta_T + \frac{e^2}{4r_0^4}[-2.332(B_1 + B_2) + 5.564r_0 f'(r_0)] \quad (14)$$

$$c_{444} = 2.332Tb\beta_T + \frac{e^2}{4r_0^4}[-2.332(B_1 + B_2)] \quad (15)$$

where all the parameters are same as defined earlier. Using these equations, we have calculated elastic constants (SOECs and TOECs) and pressure derivatives at x = 0.41, 0.56, 1.0 for the temperature range 100K ≤ T≤300K.

3. Result and discussion

Using the input data for pure KCN and KCl [21-23] we have obtained the mixed values at different composition by applying Vegards law [24] to calculate inter-atomic separation(r_0) for x = 0.41, 0.56, 1.0 at different temperatures [25] and listed them in Table 1.

Table 1. Input data for KCN_xCl_{1-x} mixed crystals.

Properties	$KCN_{0.41}Cl_{0.59}$	$KCN_{0.56}Cl_{0.44}$	$KCN_{1.0}Cl_{0.0}$
r_0 (Å)	3.195	3.212	3.260
c_{11} (10^{11} dyn/cm^2)	3.175	6.147	1.910
c_{12} (10^{11} dyn/cm^2)	0.904	1.927	1.190
c_{44} (10^{11} dyn/cm^2)	0.429	0.356	0.140
α_+(Å)	1.317	1.313	1.300
α_-(Å)	2.418	2.310	1.800

The values of vdW and TR coupling coefficient are used from our earlier papers [17-19]. The TR coupling coefficients are incorporated in elastic constant on the lines of Sahu and Mahanti [20], this takes proper account of the Cauchy discrepancy which is very large in KCN_xCl_{1-x}. These values were further used to calculate the model parameters ρ, b and f(r). The values of model parameters ρ, b and f(r) along with corresponding inter atomic separation are given in Table 2.

Table 2. Model Parameters for KCN_xCl_{1-x} at different composition and temperature.

Concentration (x)	Model parameters at 300 K			
	r (Å)	B (10^{12}erg)	ρ (Å)	f (r)
0.41	3.254	0.451	0.342	-0.010
0.56	3.254	0.438	0.328	-0.012
1.0	3.272	0.624	0.346	-0.023

We have calculated the SOECs (c_{11}, c_{12} and c_{44}) for x=0.41, 0.56, 1.0 at 100K ≤ T≤ 300K and depicted them in Fig. 1, 2 and 3 respectively. Fig. 1 and 2 the increase in temperature for all the composition x=0.41, 0.56 and 1.0 and behaviour of these two constants change when composition of cyanide ion decreases more and shows quasilinear behaviour. Our values of c_{11} and c_{12} at x=1 i.e pure KCN are closer to the available experimental values [21]. The SOECs c_{11} and c_{12} at x=0.41 and 0.56 could not be compared due to lack of experimental data on them. Here, it is interesting to note that c_{12} decrease sharply at higher concentration of CN^- for the lower temperature range which indicate the change towards instability.

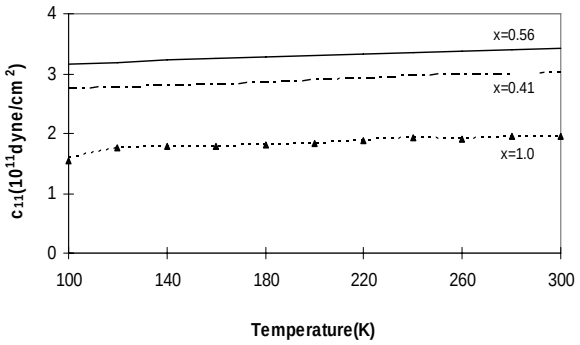

Fig. 1. Variation of present second order elastic constant c_{11} with temperature for KCN_xCl_{1-x} at x=0.41, 0.56 and 1.0 are shown by (– · –), (–) and (– – –) respectively. The solid triangle (▲) represents the experimental data [20] at xw=1.0.

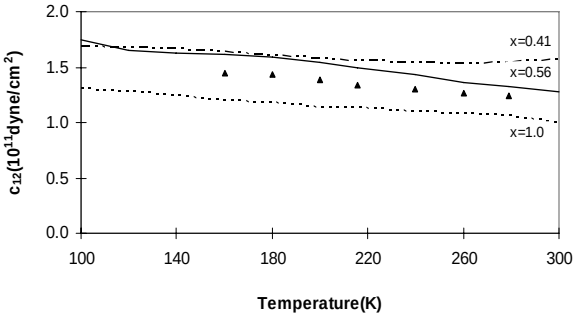

Fig. 2. Variation of present second order elastic constant c_{12} with temperature for KCN_xCl_{1-x} at x=0.41, 0.56 and 1.0 are shown by (– · –), (–) and (– – –) respectively. The solid triangle (▲) represents the experimental data [20] at x=1.0.

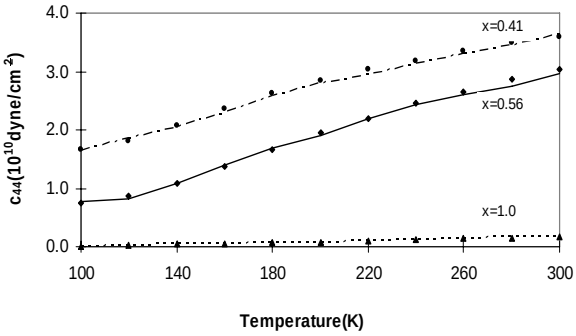

Fig. 3. Variation of present second order elastic constant c_{44} with temperature for KCN_xCl_{1-x} at x=0.41, 0.56 and 1.0 are shown by (– · –), (–) and (– – –) and experimental data [28] shown by circle (●), square (■) and triangle (▲) for x=0.41, 0.56 and 1.0 respectively.

Table 3. Values of TOECs (10^{12} dyne/cm^2) of KCN_xCl_{1-x} as a function of temperature at x=0.41, 0.56 and 1.0.

T(K)	c_{111}			c_{112}			c_{116}		
	x=0.41	x=0.56	x=1.0	x=0.41	x=0.56	x=1.0	x=0.41	x=0.56	x=1.0
100	-1.708	-1.801	-1.666	-0.679	-0.796	-1.135	-0.243	-0.222	-0.222
120	-1.704	-1.794	-1.658	-0.678	-0.793	-1.309	-0.243	-0.221	-0.220
140	-1.692	-1.784	-1.651	-0.675	-0.788	-1.303	-0.242	-0.220	-0.219
160	-1.684	-1.777	-1.643	-0.673	-0.786	-1.297	-0.241	-0.219	-0.218
180	-1.681	-1.768	-1.636	-0.667	-0.785	-1.291	-0.240	-0.218	-0.217
200	-1.674	-1.762	-1.628	-0.662	-0.780	-1.285	-0.239	-0.217	-0.216
220	-1.672	-1.753	-1.621	-0.659	-0.777	-1.279	-0.239	-0.216	-0.215
240	-1.653	-1.747	-1.613	-0.659	-0.776	-1.273	-0.231	-0.215	-0.214
260	-1.650	-1.742	-1.606	-0.658	-0.773	-1.268	-0.233	-0.215	-0.214
280	-1.636	-1.734	-1.599	-0.657	-0.773	-1.262	-0.234	-0.214	-0.213
300	-1.608	-1.664	-1.591	-0.654	-0.738	-1.256	-0.231	-0.195	-0.212
(Expt.)			(-1.29)			(-0.24)			(-0.26)

Table 3. (Continuation).

T(K)	c_{123}			c_{144}			c_{456}		
	x=0.41	x=0.56	x=1.0	x=0.41	x=0.56	x=1.0	x=0.41	x=0.56	x=1.0
100	0.239	0.273	0.474	0.186	0.200	0.309	0.159	0.164	0.227
120	0.239	0.272	0.472	0.185	0.199	0.308	0.158	0.163	0.226
140	0.238	0.271	0.469	0.184	0.198	0.306	0.157	0.162	0.225
160	0.237	0.269	0.467	0.184	0.198	0.305	0.157	0.162	0.224
180	0.236	0.269	0.465	0.184	0.197	0.304	0.155	0.161	0.223
200	0.234	0.267	0.463	0.184	0.196	0.302	0.155	0.161	0.222
220	0.234	0.267	0.461	0.182	0.195	0.301	0.154	0.159	0.221
240	0.233	0.266	0.459	0.182	0.195	0.299	0.154	0.159	0.220
260	0.233	0.265	0.457	0.180	0.194	0.298	0.154	0.159	0.219
280	0.231	0.265	0.455	0.179	0.194	0.297	0.153	0.158	0.217
300	0.229	0.251	0.453	0.177	0.180	0.295	0.151	0.145	0.217
(Expt.)			(0.11)			(0.23)			(0.23)

Expt.-[28-30]

The shear elastic constant (c_{44}) plays significant role in explaining the anomalous behaviour of mixed crystals KCN_xCl_{1-x} at particular temperature and concentration. Fig. 3 shows the deviation from the straight line for KCN_xCl_{1-x}, this deviation might be due to the difference of ionic radii of $CN^-(Cl^-)$. In addition, it is interesting to note that c_{44} shows softening at lower temperature side. This softening might be due to the effective combining of CN^- ions and temperature dependence of c_{44} reflects collective behaviour of the coupled impurity. The entire range of temperature investigated matches very well with the trend shown by Garland et. al [26]. We conclude that overall agreement between the experimental and our theoretical values of c_{11}, c_{12} and c_{44} are fairly good.

We have calculated the TOECs for mixed KCN_xCl_{1-x} at different temperature and concentration probably for the first time. The TOECs obtained at concentration x=0.41, 0.56, 1.0 in the temperature range 100K ≤ T≤ 300K are listed in Table 3. It is found that with the decrease in temperature all the TOECs (i.e. C_{111}, C_{112},, C_{116} ,C_{123}, C_{144} and C_{456}) increases. This variation may be due to the decrease in inter-atomic separation with temperature. It is found that at room temperature, the thermal effects are important and their contribution to SOECs and TOECs are significant [27, 28]. The variation of TOECs for both the compositions (x=0.41, 0.56) follow the same trend while at x=1.0 the values of TOECs are being slightly higher. Therefore, it can be said that TOECs is more of temperature dependent rather than composition dependent for atleast in the temperature range of present study. We have also calculated the pressure derivatives of SOECs and TOECs listed at T=300K in Table 4. Our results on pressure derivatives of elastic modulii are found in good agreement with the experimental data [29, 30] except dc_{44}/dp.

Table 4. Values of pressure derivatives of SOECs and TOECs of KCN_xCl_{1-x} at 300K for x=0.41, 0.56 and 1.0.

Properties	At 300K		
	x=0.41	x=0.56	x=1.0
dk / dp	4.7445	4.9751	$4.861(4.46)^{expt.}$
ds /dp	4.3987	4.6570	$4.419(5.90)^{expt.}$
dc_{44} / dp	-0.8550	-0.9233	$-1.109(-0.11)^{expt.}$
dc_{111}/dp	-307.37	-353.78	-197.71
dc_{112}/dp	-11.217	-13.680	-10.923
dc_{123}/dp	3.487	3.959	3.525
dc_{144}/dp	0.3409	0.4040	0.0318
dc_{166}/dp	1.7361	1.8024	2.152
dc_{456} / dp	1.7673	1.6349	1.293

Here, it is interesting to note that the Cauchy relation, which are believed to be almost fulfilled with alkali halides are severely violated by the cyanides in SOECs. The relation is $c_{12}=c_{44}$ in SOECs; the transverse constant c_{12} is much larger than c_{44} i.e the Cauchy relation in the sense $c_{12}>>c_{44}$ behave in certain respect like fluid [29], where $c_{11}=c_{12}$ and c_{44} is almost zero. Therefore, this is not unexpected, as ETSM framework is capable to account for the effect of Cauchy violation (elastic properties) and TR coupling for the elastic, thermal and cohesive properties of present system KCN_xCl_{1-x}.

References

[1] J. F. Berret, A. F. Farkadi, M. Boissner, J. Pelous, Phys. Rev. B. **39**, 13451 (1989).
[2] R. M. Lynden –Bell, K. H. Michel, Rev. Mod. Phys. **66**, 721 (1994).
[3] P. Zielenski, K. H. Michel, Phys. Rev. B. **46**, 4806 (1992).
[4] J. Z. Kwiecien, R.C. Leung, C.W. Garland, Phys. Rev. B. **23**, 4419 (1981).
[5] S. C. Kim, T. H. Kwon, J. Phys. Chem. Solids. **53**, 539 (1992).
[6] K. H. Michel, J. Naudts, Phys. Rev. Lett. **39**, 212 (1977).
[7] J. O. Fossum, C. W. Garland, Phys. Rev. Lett. **60**, 592 (1988).
[8] J. M. Rowe, J. J. Rush, D. G.Hinks, S. Susman, Phys. Rev. Lett. **43**, 1158 (1979).
[9] A. Loidl, R. Feile, K. Knorr, R. Renker, J. Daubert, D. Durand, J. B. Suck, Z. Phys. B. **38**, 253 (1980).
[10] K. H. Michel, J. M. Rowe, Phys. Rev. B. **22,** 1417 (1980).
[11] V. Yu. Topolov, Z. Phys. **B100**, 27 (1996).
[12] R. K. Singh, N. K. Gaur, Physica B. **150**, 385 (1988).
[13] R. K. Singh, N. K. Gaur, Z. Phys. **75**, 127 (1989).
[14] D. W. Hafemeister, W. H. Flygare, J. Chem. Phys. **43**, 795 (1965).
[15] P. Singh, N. K. Gaur, R. K. Singh, Phys. Stat. Sol.(b). **244**, 3099 (2007); Phys. Lett. A. **371**, 349 (2007).
[16] N. Kaur, R. Mohan, N. K.Gaur, R. K. Singh, Physica C. **451**, 24 (2007).
[17] N. K. Gaur, N. Kaur, J. Galgale, M. Manke, R. K. Singh, Mod. Phys. Lett. B. **17**, 1391 (2003).
[18] J. Galgale, N. Kaur, P. Singh, M. Manke, N. K. Gaur, R. K. Singh, Pramana. **63**, 413 (2004).
[19] N. K. Gaur, P. Singh, E. G. Rini, J. Galgale, R. K. Singh, Pramana. **63**, 419 (2004).
[20] D. Sahu, S. D. Mahanti, Phys. Rev. B. **26**, 2981 (1982).
[21] S. Haussuhl, Solid Stat. Commun.,**13**, 147 (1973); Acta Cryst. A. **33,** 847 (1977) .
[22] K. D. Ehrhardt, W. Press, J. Lefebvrae, S. Haussuhl, Solid Stat. Commun. **34**, 591 (1980).
[23] J. R. Tessemann, A. H. Khan, W. Schockley, Phys. Rev. **92**, 890 (1953).
[24] L. Vegards, Z. Phys. **5**, 17 (1921).
[25] M. Kumar, S. S. Bedi, Phys. Status. Solidi (b). **188**, 645 (1995).
[26] C. W. Garland, J. Z. Kwiecien, J. C. Damien, Phys. Rev. B. **25**, 5818 (1982).
[27] K. H. Michel, T. Theuns, Phys. Rev. B. **40**, 5761 (1988).
[28] V. K. Garg, D. S. Puri, M. P. Verma, Phys. Stat. Sol.(b). **80**, 63 (1977).
[29] S. Haussuhl, Solid Stat. Commun. **32**, 181 (1979).
[30] S. Haussuhl, W. Michaels, Acta. Cryst. A. **35**, 240 (1979)

*Corresponding author: preetisingh2006@gmail.com