PRAMANA
— journal of
physics

Vol. 63, No. 2
August 2004
pp. 413–417

Static and dynamic properties of KCN_xCl_{1-x}

JYOTSNA GALGALE, NUPINDER KAUR, PREETI SINGH,
MANIK MANAKE, N K GAUR and R K SINGH*
Department of Physics, Barkatullah University, Bhopal 462 026, India
*M.P. Bhoj Open University, Bhopal 462 016, India
E-mail: surela@sancharnet.in

Abstract. An extended three-body force shell model (ETSM) has been applied to investigate the static and dynamic properties of KCN_xCl_{1-x} for the composition $x = 0.56$ and 1.0 at 300 K. The phonon dispersion curves computed by us are compared with the single crystal neutron diffraction data. The unusual features of these curves are the upward curvature seen in some of the acoustic branches. This is a result of K-dependent softening of the phonon due to translation–rotation coupling. The transverse acoustic branch is more soft near the zone centre.

Keywords. Phonon dispersion curves (PDCs); cohesive energy; compressibility; neutron diffraction.

PACS Nos 62.20; 62.60Dc; 65.40.-f; 65.90.+i

1. Introduction

Potassium cyanide which exists in several crystallographic phases depend on temperature and pressure. 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 [1,2]. When a dumb-bell shaped CN^- replaces Cl^- in KCl system a mixed system KCN_xCl_{1-x} is obtained. The mixed system of this type shows glassy state at very low temperature and over a wide range of concentration [3]. This feature is brought about by the dumb-bell shaped CN^- ion forming elastic quadrupoles, which determine the anomalous dynamic and static properties.

There are several theories in which this transition is associated with soft mode instability for the translational mode that is coupled to CN^- rotational modes [4–6]. This compound exhibits several interesting and anomalous temperature-dependent behaviour [7–9]. It is of interest to study the effect of temperature on the elastic soft mode of replacing CN^- ion by chloride ion. The motivation for the present work was gained from the publication on single crystal neutron diffraction of KCN_xCl_{1-x} [10,11] as a function of temperature with changing concentration. It shows softening of TA modes. Also it shows elastic C_{44} soft mode behaviour and orientational ordering.

Earlier, we have developed an extended three-body force shell model (ETSM) [12] by incorporating the effect of coupling between the translational modes and the orientations of cyanide $(CN)^-$ molecules. This ETSM has been successfully applied for the description of lattice mechanical properties of orientationally disordered materials [12–18]. Looking to its success, we thought it pertinent to apply ETSM for the prediction of PDCs of KCN_xCl_{1-x}. The necessity of the application of ETSM to KCN_xCl_{1-x} may also be emphasized from the fact that the K^+ and CN^- ions have larger ionic size difference which consequently leads to more pronounced effect of three-body interaction (TBI) [19] responsible for the large Cauchy discrepancy (C_{12}–C_{44}). This ETSM has been found to reveal satisfactory description of the PDCs of KCN_xCl_{1-x} and larger Cauchy discrepancy (C_{12}–C_{44}). The essential theory of ETSM is given in §2. The result and discussion have been presented in the §3.

2. Essential theory of ETSM

The interaction potential used to derive the framework of the present ETSM can be expressed as [17,18]

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

The first two terms represent the long-range Coulomb and three-body interaction (TBI) [19]. The third and fourth terms are vdW coefficients due to dipole–dipole and dipole–quadrupole $(d-q)$ interactions. The fifth term is Hafemeister and Flygare (HF) type short-range (SR) overlap repulsion [19] extended up to the second neighbour ion with $\beta_{kk'}$ as the Pauling coefficient, ρ and b are the range and hardness parameters [16,17], ϕ^{TR} is the contribution due to translational–rotational coupling [4–7].

3. Results and discussion

There are four potential parameters $b, \rho, f(r_0), r_0 f'(r_0)$ and four-model parameters (d_1, d_2, Y_1, and Y_2) in the ETSM framework. Here d and Y are the distortion polarizabilities and shell charge parameters; we have determined the values of translational–rotational coupling coefficients on the lines given in our earlier paper [16,17]. Using the input data for pure KCN and KCl taken from [20], we have obtained the mixed values at different composition by applying the Vegard law [21]. The input data is specified in the table 1. The values of these translational–rotational coupling coefficients and model parameters are given in table 2. We have used vdW coefficients reported in our earlier paper [12].

Using the model parameters we have calculated the cohesive energy (ϕ), compressibility (β), molecular force constant (f) and Restrahalen frequency (ν_0) and

Table 1. Input data for KCN_xCl_{1-x} at $x = 0.56$ and $x = 1.0$.

Properties	$x = 0.56$	$x = 1.0$
r_0 (Å)	3.21[a,b]	3.26[d]
C_{11} (10^{11} dyn cm^{-2})	6.15[a,c]	1.92[e]
C_{12} (10^{11}dyn cm^{-2})	1.93[a,c]	1.20[e]
C_{44} (10^{11}dyn cm^{-2})	0.35[a,c]	0.14[e]
α_+ $(A^0)^3$	1.33[a,b]	1.30[f]
α_- $(A^0)^3$	2.48[a,b]	1.80[g]

a – [12]; b – [26]; c – [27]; d – [22]; e – [23]; f – [24]; g – [25].

Table 2. TR coupling coefficient and model parameters of KCN_xCl_{1-x} at $x = 0.56, 1.0$.

TR coupling coefficient	$x = 0.56$	$x = 1.0$	Model parameters	$x = 0.56$	$x = 1.0$
A_R (10^{-4} dyn)	0.60	−0.098	b (10^{-12} erg)	0.022	0.389
B_R (10^{-4} dyn)	−0.14	0.403	ρ (Å)	0.122	0.345
A_Q (10^{-4} dyn)	0.29	0.578	$f(r_0)$	0.004	−0.009
B_Q (10^{-4} dyn)	−0.23	−0.472	$r_0 f'(r_0)$	0.118	0.089
χ_{44} (10^{12} dyn cm^{-1})	−1.87	1.220	d_1	0.058	0.197
χ_{11} (10^{12} dyn cm^{-1})	4.38	−3.680	d_2	0.354	0.287
			Y_1	−2.940	−1.258
			Y_2	−0.230	−1.372

Table 3. Static properties of KCN_xCl_{1-x} for $x = 0.56$ and $x = 1.0$.

Conc. (x)	Φ (kJ mol^{-1})	β (10^{-12} dyn cm^{-2})	f (10^4 dyn cm^{-1})	ν_0 (THz)
0.56	−685.259	2.04	9.42	10.11
1.0	−689	6.39	3.06	5.47
Expt. (ref. [20])	(−6.74)	(6.95)	(2.82)	(4.11)

listed them in table 3. Our results are closer to experimental values therein [20] available for $x = 1.0$, i.e., pure KCN. The static properties at $x = 0.56$ could not be compared due to lack of experimental data. Also we have computed the PDCs for KCN_xCl_{1-x} for $x = 0.56$, 1.0 at 300 K and depicted them in figures 1 and 2 along with ultrasonic measurement and neutron diffraction data [10,11] for the symmetry directions. An inspection of figure 1 reveals that agreement between ultrasonic measurement data [10] (available only for [q 0 0] direction of TA modes) and our theoretical results are closer for $KCN_{0.56}Cl_{0.44.}$ The present result also shows softening of transverse acoustic mode along the [q 0 0] and [q q 0] directions.

We have shown the PDCs of KCN_xCl_{1-x} (at $x = 1.0$) with the measured neutron diffraction data [2,11] in figure 2. Our results are closer to the measured data and shows softening in TA modes. The upward curvature seen in some of the acoustic branches might be the K-dependent softening of phonon due to translation–rotation

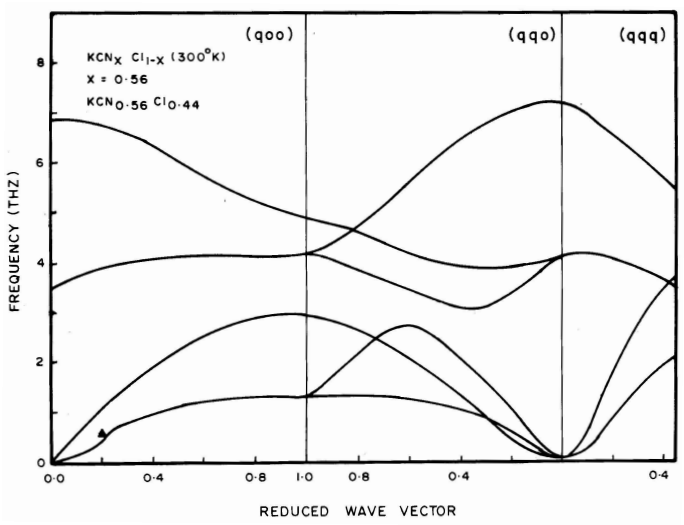

Figure 1. Phonon dispersion curves of KCN_xCl_{1-x} at $x = 0.56$ obtained from ETSM. The full triangles are the data obtained from ultrasonic measurement [10].

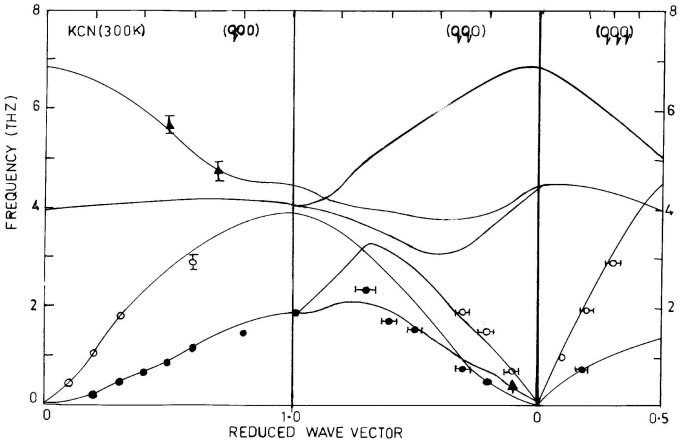

Figure 2. Phonon dispersion curves of KCN_xCl_{1-x} at $x = 1.0$ obtained from ETSM. The circles and triangles are neutron diffraction data [2] and full triangles are from ref. [11].

coupling. The transverse acoustic branches are more soft near the zone centre. This is not surprising as the present model is capable of taking proper account of elastic (Cauchy violation), dielectric (polarizabilities) and translational–rotational coupling in orientationally disordered KCN_xCl_{1-x}. The results on KCN_xCl_{1-x} at different temperatures and composition are in progress.

Acknowledgement

The authors are thankful to the University Grants Commission, New Delhi for providing financial support under the SAP programme.

References

[1] A Cimino, G S Parry and A R Ubbelohde, *Proc. R. Soc. London* **A252**, 445 (1959)
[2] J M Rowe, D G Hinks, D L Price, S Susman and J J Rush, *J. Chem. Phys.* **58**, 2039 (1973)
[3] Wiotte *et al*, *Phys. Rev.* **B43**, 12751 (1991)
[4] K H Michel and J Naudts, *Phys. Rev. Lett.* **B39**, 212 (1977); *J. Chem. Phys.* **67**, 547 (1977)
[5] D Sahu and S D Mahanti, *Solid State Commun.* **47**, 297 (1983); *Phys. Rev.* **B29**, 340 (1984)
[6] D Sahu, *J. Chem. Phys.* **85**, 5251 (1988)
[7] R M Lynderbell and K H Michel, *Rev. Mod. Phys.* **66**, 721 (1994)
[8] S Haussuhl, J Eckstein, K Recher and F Wallrafen, *Acta Crystallogr.* **A33**, 18 (1979)
[9] S Haussuhl, *Solid State Commun.* **32**, 181 (1979)
[10] C W Garland, J K Kwiecien and J C Damein, *Phys. Rev.* **B25**, 5818 (1982)
[11] J M Rowe, J J Rush, E Prince and J J Chesser, *Ferroelectrics* **16**, 107 (1977)
[12] R K Singh and N K Gaur, *Physica* **B150**, 385 (1988)
[13] R K Singh and N K Gaur, *Z. Phys.* **B75**, 127 (1989)
[14] N K Gaur, R K Singh and S K Singh, *Ind. J. Pure Appl. Phys.* **29**, 183 (1990)
[15] N K Gaur, J Galgale, M Manke and R K Singh, *J. Lumin.* **94–95**, 755 (2001)
[16] J Galgale, N K Gaur and R K Singh, *J. Lumin.* **94–95**, 713 (2001)
[17] J Galgale, M Manke, R K Singh and N K Gaur, *Indian J. Phys.* **A76**, 341 (2001)
[18] N K Gaur, N Kaur, J Galgale, M Manke and R K Singh, *Mod. Phys. Lett.* **B17**, 1391 (2003)
[19] R K Singh, *Phys. Rep.* **85**, 259 (1982)
[20] Manik Manake, Ph.D. Thesis (Bhopal University, Bhopal, India, 2000)
[21] L Vegard, *Z. Phys.* **5**, 17 (1920)
[22] H D B Jenkins and D F C Morris, *Mol. Phys.* **33**, 663 (1977)
[23] S Haussuhl, *Solid State Commun.* **13**, 147 (1973); *Acta Crystallogr.* **A30**, 455 (1974)
[24] J R Tessman, A H Khan and W Shockley, *Phys. Rev.* **92**, 890 (1953)
[25] K D Ehrhardt, W Press, J Lefebvre and S Haussuhl, *Solid State Commun.* **34**, 580 (1980)
[26] D Roy and A K Ghosh, *Phys. Rev.* **B3**, 3510 (1971)
[27] K V Namjoshi, S S Mitra and J F Vetelino, *Phys. Rev.* **B3**, 4398 (1971)