A theoretical study on the thermal and elastic properties of $(KCN)_x(RbCN)_{1-x}$

Shemim S S [1], Fergy John[2]

[1]Dept of Physics, T K M College of Engineering, Kollam, Kerala, India
[2]Department of Physics, St Gregorious College, Kottarakkara, Kerala

Crystalline solids have a finite regular arrangement of atoms in space which is never perfect due to the vibrational motion of the atoms about their equilibrium position and their rotational motion to a greater extent. This paper attempts to understand the crystal interactions of the crystal $(KCN)_x(RbCN)_{1-x}$ which is an orientationally disordered alkali cyanide by studying its dynamical properties. The interatomic potential model of Extended Three Body Force Shell Model is used for calculating the elastic constants of second order and the thermal and cohesive properties of this mixed alkali cyanide for different compositions of x such as 0.15, 0.50, 0.70, 0.90 and 1 for a temperature range of 315 K to 395 K. The calculated values of these mechanical properties indicate that this potential model which integrates the effect of translational – rotational coupling in the frame work of Three Body Force Shell Model is mechanically stable one. In addition, the results reveal that these properties depend more on temperature than their composition and are in excellent agreement with the available experimental results.

Keywords: Second order elastic constants; Cohesive energy; Thermal properties; ETSM.

1. Introduction

The study of the dynamic properties of orientationally disordered materials (ODM's) such as, alkali cyanides and their mixed crystals is an unresolved problem in condensed matter Physics. Singh and Gaur [1] showed that ODM's are important because they are translationally ordered but, orientationally disordered. Even though a number of experimental studies have been performed on them, only a very few theoretical studies were conducted so far to explain the properties of these materials. These studies performed using two body potential failed to explain the low temperature anomalous behaviour of their elastic properties. Thus, it became imperative to develop an interaction potential which explains such properties successfully, and the Extended Three body force Shell Model (ETSM) was formulated as shown in Refs. [2, 3].

The Rigid Shell Model was modified with the introduction of three body interaction which resulted in Three Body Force Shell Model (TSM). This model explains the dynamic as well as static properties of various ionic, covalent and molecular solids. TSM was further modified by introducing Translational- Rotational (TR) coupling effect and the new model was termed as ETSM. This model has been successful in predicting the mechanical properties of ODM's. The computation of anharmonic elastic, cohesive and thermal properties of the mixed crystal of $(KCN)_x(RbCN)_{1-x}$ can be performed using the potential model of ETSM as shown by Singh and Gaur [1].

The effect of TR coupling results in the reduction of elastic constants in ODM's. Bell and Michel [4] found that this is because of the change in the orientational probability function due to strain which results in reduction of the free energy of the crystal. This could be due to the change to a highly ordered state as a result of phase transition. Also, this reduction in elastic constant depends highly on temperature.

The crystal interactions are assessed from the cohesive and thermal properties of the crystal. Cohesion in a system can be estimated from the cohesive energy (Φ) of the material. The cohesion for a material is negative, if the constituent atoms can gain energy by reacting to form a compound (solid or molecule).The complete crystal interactions can be extracted only by examining the thermodynamic properties such as Debye temperature (θ_D), Restrahlen frequency (υ), Molecular force constant (f), Gruneisen parameter (γ) and ratio of volume thermal expansion coefficient to specific heat at constant volume (α_v/c_v).

1. Methodology and Theory

The potential model of ETSM is a combination of energies arising from the effects of the following forces as given in Refs. [2, 5-7],

- Long- range Coulomb forces between ions
- Three body interaction due to the charge transfer mechanism
- Short range Van der Waals forces
- Overlap repulsion represented by Hafemeister and Flygare potential [5] and
- TR coupling.

The ionic interaction potentials [8-13] are considered in the ETSM as,

$$\Phi = \Phi_c + \Phi_{TBI} + \Phi_{vdW} + \Phi_{SR} + \Phi_{TR}$$

$$= \frac{-1}{2}\sum_{kk'} \frac{Z_k Z_{k'}}{|r_{kk'}|} e^2 + \frac{-1}{2}\sum_{kk'k} \frac{Z_k Z_{k'}}{|r_{kk'}|} e^2 f(r_{kk''}) - \sum_{kk'} c_{kk'} r_{kk'}^{-6} - \sum_{kk'} d_{kk'} r_{kk'}^{-8} + \sum_{kk'} b\beta_{kk'} e^{\frac{r_k + r_{k'} - r_{kk'}}{\rho}} + \Phi_{TR} \quad (1)$$

The terms in the equation being;

i. long-range coulomb interaction energy
ii. long-range three body interaction energy
iii. Van der Waals dipole-dipole interaction
iv. Van der Waals dipole- quadrapole interaction
v. Short-range overlap repulsion, which is considered up to the second neighbour ion and $\beta_{kk'}$ is the Pauling coefficient, b is the hardness parameter and ρ is the range parameter.
vi. ϕ_{TR} is the interaction potential due to the TR coupling effect.

The equation for the Pauling coefficient $\beta_{kk'}$ is given as,

$$\beta_{kk'} = 1 + \frac{Z_k}{n_k} + \frac{Z_{k'}}{n_{k'}} \quad (2)$$

where, n_k *and* $n_{k'}$represents the number of valence electrons and Z_k *and* $Z_{k'}$represents the valency of the ions.

2. Results and Discussion

The three model parameters contained in the potential model of ETSM are; b, the hardness parameter, ρ, the range parameter and the function $f(r)$ which is the long range three body interaction parameter. The term, r is the interionic separation at equilibrium and they are used

to compute the second- order elastic constants (SOEC's) of the mixed crystal as explained by Thakur et Al [14]. The cohesive energy of the crystal can be obtained using Equation (1). The equations given in Refs. [8-13,26] were used to calculate the thermodynamic properties such as, Debye temperature (θ_D), Restrahlen frequency (υ), molecular force constant (f), and Gruneisen parameter (γ).

The input data for pure KCN and RbCN sourced from Refs. [2, 15-20,26] are tabulated in Table 1. From these the model parameters of $(KCN)_x(RbCN)_{1-x}$ are calculated. Table 2 presents the model parameters for $(KCN)_x(RbCN)_{1-x}$ calculated from the above for a temperature range of 315 K $\leq T \leq$ 395 K for compositions x = 0.15, 0.50, 0.70, 0.90 and 1.The SOEC's of the crystal such as C_{11}, C_{12} and C_{44} for this temperature range and compositions were calculated using the model parameters considering the effect of TR Coupling and were plotted graphically in Fig.1, Fig. 2 and Fig. 3 respectively. The cohesive and thermal properties of the crystal in the present study for the above concentrations and temperatures were calculated and the results are tabulated in Table 3.

From Fig. 1 to Fig. 3, it is clear that C_{11} has a quasilinear behaviour for all compositions whereas, C_{12} decreases with increase in temperature. The comparison of the computed results with the experimental data given in Refs. [16, 17] for the concentration x=1 shows good agreement. Comparison for other concentrations could not be carried out due to the unavailability of experimental data. The role of shear elastic constant is significant in mixed crystals at specific temperature and concentration. Anomalous behaviour in the values of C_{44} with variation of temperature are observed and these values indicate excellent agreement with the data obtained from ultrasonic techniques by Garland et al [22]. The coupling of CN^- ions is the cause for the lowering of C_{44} at low temperature range. This dependence on temperature can be accounted to the collective behaviour of the coupled impurity.

A decrease with temperature and an increase with concentration of x is shown by the values of cohesive energy ($\boldsymbol{\Phi}$) and molecular force constant (f). A similar trend is also observed for Restrahlen frequency (υ_0) and Debye temperature (θ_D). An increasing pattern with temperature is exhibited by the values of compressibility (β), Gruneissen parameter (γ) and α_v/c_v which could potentially be due to the increased interionic separation. But the values of compressibility and Gruneissen parameter is decreasing with concentration whereas, the values of α_v/c_v is also increasing with concentration. The interesting factor in these results are its congruity to the

available experimental results given in Refs. [23-25] for pure crystals at room temperature.

3. Conclusion

The theory of ETSM has been utilized in calculating the elastic and thermodynamic properties of an alkali cyanide mixed crystal which belongs to the class of ODM's. The values of shear elastic constant C_{44} is seen to be reduced at low temperatures which reflects the collective behaviour of the coupled impurity. The computed values of SOEC's were compared with the available experimental results which shows an excellent agreement. In general, the elastic constants of solids decrease with increase in temperature. But for the mixed crystal used in this study, the elastic constants are found to increase with the decrease in temperature. A good comparison was found between the calculated values of the mixed crystal and the experimental values available for pure KCN of the parameters such as cohesive energy, compressibility and molecular force constant.

Even though, the comparison of other obtained results is limited until the report of experimental data on them, they can be used as a lead to the experimental studies in future. Thus, it can be inferred that the TR coupling plays a major role in the mechanical properties of ODM's at very low temperature ranges. In addition, it can also be concluded that the potential model of ETSM is an effective model in explaining the elastic and thermal properties of mixed alkali cyanides which are ODM's.

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Figure 1: The graphical comparison of the variation of second order elastic constant C_{11} of $(KCN)_x(RbCN)_{1-x}$ for different compositions (x = 0.15, 0.50, 0.70, 0.90 and 1) and for the temperature range of 315 K ≤ T ≤ 395 K and the experimental values (at x=1) for the same temperature range.

Figure 2: The graphical comparison of the variation of second order elastic constant C_{12} of $(KCN)_x(RbCN)_{1-x}$ for different compositions (x = 0.15, 0.50, 0.70, 0.90 and 1) and for the temperature range of 315 K ≤ T ≤ 395 K and the experimental values (at x=1) for the same temperature range.

Figure 3: The graphical comparison of the variation of second order elastic constant C_{44} of $(KCN)_x(RbCN)_{1-x}$ for different compositions (x = 0.15, 0.50, 0.70, 0.90 and 1) and for the temperature range of 315 K ≤ T ≤ 395 K and the experimental values (at x=1) for the same temperature range.

Table 1**:** Input data for $(KCN)_x(RbCN)_{1-x}$[2]

Table 2. The model parameters for $(KCN)_x$ $(RbCN)_{1-x}$ for different compositions (x = 0.15, 0.50, 0.70, 0.90 and 1) and for the temperature range of 315 K ≤ T ≤ 395 K.

Table 3. Thermal and cohesive properties of $(KCN)_x$ $(RbCN)_{1-x}$ for different compositions (x = 0.15, 0.50, 0.70, 0.90 and 1) and for temperature range 315 K ≤ T ≤ 395 K and experimental value at 300 K at x=1.

TABLE 1. Input data for $(KCN)_x(RbCN)_{1-x}$

Properties	KCN (x= 1)	RbCN (x = 1)
$r_o(A^o)$	3.26	3.42
$c_{11}(10^{11}$dynes cm$^{-2})$	1.92	1.75
$c_{12}(10^{11}$dynes cm$^{-2})$	1.20	1.04
$c_{44}(10^{11}$dynes cm$^{-2})$	1.14	0.17
$\alpha_+(A^o)^3$	1.30	2.10
$\alpha_-(A^o)^3$	1.80	1.80
ε_0	5.720	4.50
ε_α	1.990	1.77
C	678.41	1164.50
D	277.49	502.86
c+-	79.79	137.28
c++	63.22	181.60
c--	105.25	105.25
d+-	39.56	72.36
d++	24.26	83.76
d--	61.56	61.56

TABLE 2. The model parameters for $(KCN)_x$ $(RbCN)_{1-x}$ for different compositions for the temperature range of 315K ≤ T ≤ 395K.

x	*T*(K)	Model Parameters			
		r (A^o)	*b*(10^{-12} ergs)	ρ(A^o)	*f(r)*
0.15	315	3.402	3.418	0.348	1.388
	325	3.404	3.424	0.348	1.381
	335	3.406	3.430	0.349	1.374
	345	3.408	3.436	0.350	1.360
	355	3.409	3.442	0.350	1.360
	365	3.411	3.449	0.350	1.354
	375	3.413	3.456	0.350	1.348
	385	3.414	3.463	0.351	1.341
	395	3.416	3.470	0.351	1.334
0.50	315	3.342	3.213	0.338	1.401
	325	3.343	3.217	0.338	1.396

	335	3.345	3.222	0.339	1.391
	345	3.345	3.228	0.339	1.385
	355	3.348	3.236	0.339	1.379
	365	3.349	3.244	0.340	1.373
	375	3.351	3.251	0.340	1.367
	385	3.353	3.258	0.340	1.361
	395	3.355	3.266	0.340	1.355
0.70	315	3.312	3.015	0.326	1.414
	325	3.313	3.020	0.326	1.410
	335	3.15	0.025	0.326	1.405
	345	3.317	0.031	0.327	1.400
	355	3.319	3.037	0.327	1.394
	365	3.321	3.043	0.327	1.388
	375	3.323	3.046	0.328	1.382
	385	3.325	3.050	0.328	1.376
	395	3.327	3.053	0.329	1.370
0.90	315	3.221	2.841	0.325	1.512
	325	3.222	2.846	0.325	1.508
	335	3.223	2.851	0.325	1.504
	345	3.225	2.856	0.326	1.500
	355	3.227	2.861	0.236	1.494
	365	3.229	2.866	0.326	1.488
	375	3.231	2.872	0.327	1.482
	385	3.233	2.877	0.327	1.476
	395	3.235	2.883	0.327	1.470
1.0	315	3.202	2.731	0.323	1.153
	325	3.203	2.734	0.323	1.508
	335	3.204	2.738	0.323	1.503
	345	3.206	2.742	0.324	1.497
	355	3.208	2.746	0.324	1.492
	365	3.209	2.750	0.324	1.487
	375	3.211	2.755	0.325	1.482
	385	3.212	2.760	0.325	1.477
	395	3.213	2.765	0.325	1.472

TABLE 3. Thermal and cohesive properties of $(KCN)_x (RbCN)_{1-x}$ for temperature range $315K \leq T \leq 395K$.

x	T (K)	Φ (KJ mol^{-1})	β (10^{-12} dyne^{-1}cm^2)	f (10^4 Dyne cm^{-1})	υ_0 (THz)	θ_D (K)	α_v/c_v (10^3J)	γ
	315	-602.58	6.321	2.624	4.269	203.08	1.734	5.238
	325	-602.01	6.335	2.621	4.266	202.87	1.737	5.243
	335	-601.62	6.348	2.617	4.264	202.72	1.740	5.248
	345	-601.16	6.351	2.614	4.261	202.60	1.742	5.253
0.15	355	-600.82	6.363	2.611	4.258	202.46	1.745	5.257
	365	-600.34	6.375	2.608	4.255	202.31	1.748	5.261
	375	-599.72	6.389	2.605	4.252	202.18	1.751	5.266
	385	-599.41	6.391	2.602	4.249	202.87	1.754	5.271
	395	-598.76	6.402	2.598	4.246	201.91	1.757	5.275
	315	-608.42	6.018	2.718	4.451	213.67	1.742	5.178
	325	-608.20	6.024	2.715	4.449	213.54	1.745	5.182
	335	-607.91	6.032	2.711	4.446	213.45	1.748	5.186
	345	-607.44	6.046	2.707	4.443	213.33	1.750	5.180
0.50	355	-606.82	6.053	2.704	4.441	213.21	1.753	5.194
	365	-606.35	6.064	2.701	4.439	213.08	1.756	5.198
	375	-605.73	6.075	2.697	4.436	212.92	1.759	5.202
	385	-605.25	6.082	2.694	4.434	212.81	1.762	5.206
	395	-604.66	6.091	2.691	4.431	212.69	1.765	5.210
	315	-619.36	5.521	2.831	4.829	234.47	1.761	5.121
	325	-618.88	5.534	2.828	4.827	234.86	1.764	5.125
	335	-618.52	5.545	2.825	4.824	234.21	1.767	5.129
	345	-618.21	5.556	2.822	4.821	234.08	1.770	5.133
0.70	355	-617.93	5.568	2.819	4.819	233.96	1.773	5.137
	365	-617.62	5.577	2.816	4.816	233.82	1.775	5.141
	375	-617.18	5.585	2.813	4.813	233.70	1.778	5.144
	385	-616.81	5.591	2.809	4.810	23.58	1.781	5.147
	395	-616.42	5.603	2.806	4.809	233.45	1.784	5.151
	315	-625.44	5.438	2.961	5.018	248.66	1.765	5.038
	325	-624.90	5.446	2.958	5.016	248.52	1.767	5.042
	335	-624.51	5.453	2.955	5.013	248.40	1.769	5.046
	345	-624.25	5.461	2.952	5.010	248.28	1.771	5.050
0.90	355	-623.88	5.472	2.949	5.009	248.17	1.773	5.054
	365	-623.54	5.485	2.945	5.005	248.05	1.775	5.058
	375	-623.12	5.487	2.942	5.003	247.91	1.777	5.062
	385	-622.80	5.503	2.939	5.000	247.78	1.779	5.066
	395	-622.51	5.512	2.936	4.997	247.65	1.781	5.070
	315	-628.86	5.326	3.012	5.137	254.82	1.773	5.021
	325	-628.55	5.337	3.009	5.134	254.71	1.775	5.025
	335	-628.04	5.349	3.006	5.131	254.58	1.778	5.029
	345	-627.78	5.358	3.003	5.129	254.47	1.780	5.033
1	355	-627.61	5.361	3.000	5.126	254.36	1.782	5.037
	365	-627.22	5.373	2.997	5.123	254.25	1.785	5.041
	375	-626.68	5.387	2.994	5.120	254.17	1.778	5.045
	385	-626.37	5.397	2.991	5.117	254.05	1.790	5.049

	395	-625.71	5.408	2.988	5.115	253.94	1.792	5.053
	300 (expt)	-674.00	6.96	2.82	4.11	197.0	-	-

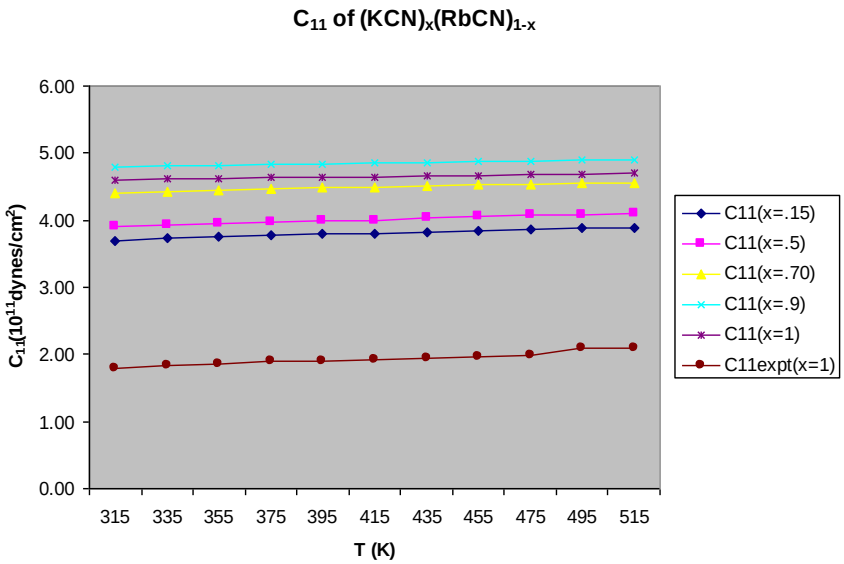

FIGURE 1. *(1) C_{11} of $(KCN)_x(RbCN)_{1-x}$*

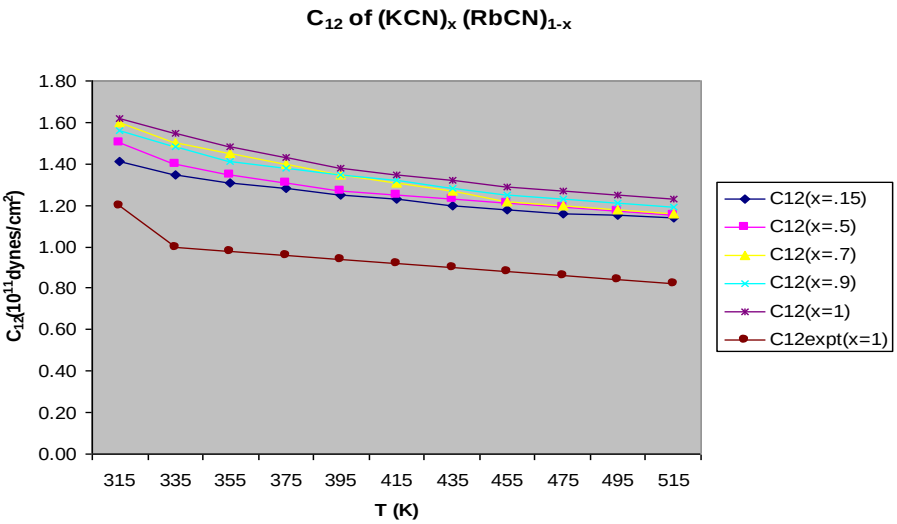

FIGURE 2. *C_{12} of $(KCN)_x(RbCN)_{1-x}$*

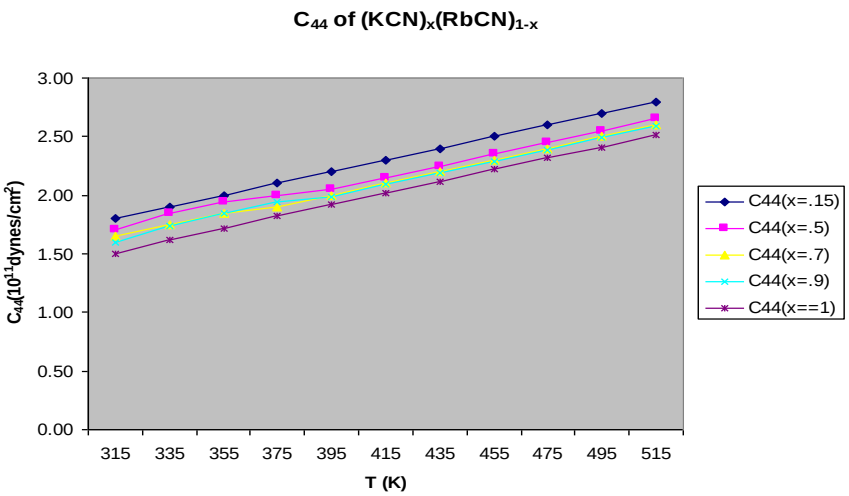

FIGURE 3.C_{44} *of* $(KCN)_x(RbCN)_{1-x}$