Third Order Elastic Constant Pressure derivatives of Caesium Cyanide

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Abstract

In this paper we have evaluated the pressure derivatives of third order elastic constants in the CsCN material. An extended three body force shell model (ETSM), which incorporates the effects of translational– rotational (TR) coupling, three body interactions (TBI) and anharmonicity, has been applied. The pressure derivatives of TOECs, dc_{111}/dp, dc_{112}/dp, dc_{166}/dp, dc_{111}/dp dc_{123}/dp and dc_{456}/dp show increasing trend with increasing temperature. However their values could not be compared due to lack of experimental data.

Introduction

The alkali-cyanides are the molecular crystals which undergo various structural phase transitions depending on temperature and pressure. At room temperature the molecules CN^- are orientationally disordered due to their dumb-bell shape but lower temperature leads to a partial full ordering of the $[CN^-]$ molecule. A crystal that contains molecules or molecular ions is more complex than one that contains atoms or atomic ions only because the individual species have orientation as well as position. This allows the existence of new types of phases, liquid crystals and orientationally disordered crystals. In a normal crystal both the positions and orientations of the molecules from which, crystal is made, are ordered. In a liquid there is neither translational nor orientational order. Between the crystal and liquid phases it is possible to find partially ordered phases, either liquid crystals in which most or all the translation order is destroyed but orientational order remains, or orientationally disordered crystals in which there is translational order without orientational disorder.

The alkali-cyanides have long been considered as model cases of a large group of ionic crystals with general composition $M^+(XY)^-$, which shows interesting collective phenomenon due to interactions between the $(XY)^-$ radicals[1].

The cyanide ion is non-spherical but it can attain effective spherical symmetry by rotation in certain crystals. At ordinary temperature NaCN, KCN and RbCN crystallize with the rock salt structure (space group O_h^5, Fm3m) whereas CsCN crystallize with the cesium chloride structure (space group O_h^1, Pm3m). The unit cell lengths of the NaCN, KCN and RbCN are a_0=5.893, 6.527 and 6.82 Å respectively [2-5]and of the CsCN is a_0=7.36 Å.

The rapid rotation of CN^- molecular ion at high temperature and atmospheric pressure, the alkali-cyanides show pseudocubic structure similar to those of alkali-halides[6-9].

The CN^- ion is of particular interest since it possesses an electric dipole and quadrupole moment at the same time. Under cooling conditions, collective ordering of the CN^- ions induces transitions into different orientationally ordered phases. In the elastically ordered phases, the CN^- ions are aligned

close to the six directions of the original cubic cell but remain disordered in terms of the direction of their permanent dipole moment [10].

The ellipsoidal CN⁻ molecules are oriented independently in their lattice cells and because of the different orientations from cell to cell, the translational symmetry of the cyanide crystal is destroyed and the crystal is said to be disordered. This disorder in the crystal is responsible for various properties in alkali-cyanides and their mixed crystals. In this chapter, we shed light on the properties of pure cesium cyanides.

Cesium Cyanide

Ionic molecular solids undergo a series of structural phase transitions and show anomalous the rmoelastic properties, which are intimately connected, with the orientational, spin and orbital degrees of freedom of the ionic molecular species. The cesium cyanide possess cesium chloride structure with a space group Pm3m (pseudo cubic high temperature phase), in which the CN⁻ elastic dipoles are in disordered orientations. At 193K, CsCN transform discontinuously into a trigonal (R3m) structure. The (CN⁻) ions are aligned along the threefold axis, corresponding to what were the (111) axis in the cubic phase. The space group of the low temperature phase implies that the cyanide ions are still disordered with respect to head and tail. As no further phase transformation was found down to 14K, the crystal exists in a non-equilibrium state where the electric ordering is suppressed by high hindering barriers leading to long relaxation times for 180^0 flips. This situation is strongly suggestive for a frozen- in state at the lowest temperature[11].

The special interest in CsCN lies in the fact that it exhibits the CsCl structure different from NaCN, KCN, RbCN and it can be expected, that the reorientational dynamics differ significantly from those of the rock salt-type structure. The description of structure is discussed in introductory chapter.

The study of mechanical properties of alkali cyanide crystals continues to be the subject of increasing interest for both theoretical and experimental workers mainly because of anomalous behaviour in elastic and dynamic properties. In this chapter, we have reported the results obtained from ETSM.
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 of different types. In the present work, we extend the application of the ETSM to calculate the pressure and temperature derivatives of pure CsCN at different temperature.

Essential Formalism

The interaction potential used to derive the framework of the present ETSM can be expressed as [14-21]

$$\phi = -\frac{e^2}{2}\sum_{kk'} Z_k\,Z_{k'}\,r_{kk'}^{-1}\left[1+\sum_{kk'}f_k\left(r_{kk'}\right)\right]-\sum_{kk'}c_{kk'}\,r_{kk'}^{-6}$$

$$-\sum_{kk'}d_{kk'}\,r_{kk'}^{-8}-b\sum_{kk'}\beta_{kk'}\exp\left\{\frac{r_k+r_{k'}-r_{kk'}}{\rho}\right\}+\phi^{TR}$$

(1)

where the first two terms represent the long range Coloumb and Three Body Interaction; 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 HafemeisterFlygare type short- range overlap repulsion extended up to second neighbour ions, $\Box_{kk'}$ are the Pauling coefficient; $\Box\Box$and b are the range and hardness model parameters, respectively as defined earlier [22-24]

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

and the bulk modulus

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

ϕ^{TP} is the contributiondue to TR coupling effects [25]

Where r is the nearest neighbour (nn) sepration and r_o is the equilibrium nn separation. K as the crystal structure constant. The TR coupling effect has been taken through elastic constant.

Pressure Derivatives of TOECs

Pressure derivatives of TOECs is given below,

$$\frac{dc_{111}}{dP} = -\frac{1}{3K}[-3c_{11} - 6c_{12} + 3c_{111} + c_{1111} + 2c_{1112}] \tag{4}$$

$$\frac{dc_{112}}{dP} = -\frac{1}{3K}[c_{11} + 2c_{12} + 3c_{112} + c_{1112} + c_{1122} + 2c_{1123}] \tag{5}$$

$$\frac{dc_{166}}{dP} = -\frac{1}{3K}[-c_{11} - 2c_{12} + 3c_{166} + c_{1166} + 2c_{1244}] \tag{6}$$

$$\frac{dc_{123}}{dP} = -\frac{1}{3K}[-c_{11} - 2c_{12} + 3c_{123} + 3c_{1123}] \tag{7}$$

$$\frac{dc_{144}}{dP} = -\frac{1}{3K}[c_{11} + 2c_{12} + 3c_{144} + c_{1144} + 2c_{1244}] \tag{8}$$

$$\frac{dc_{456}}{dP} = -\frac{1}{3K}[-c_{11} - 2c_{12} + 3c_{456} + 3c_{1456}] \tag{9}$$

where $K = \frac{c_{11} + 2c_{12}}{3}$

Computation of Model Parameters

We have applied ETSM for studying the various properties of cesium cyanide. The values of input data are given in Table 4.1.

Table 4.1 Input data, TR coupling coefficients and Anharmonicity coefficients for CsCN at room temperature.

Properties	Values	TR coupling coefficient	Values
r_0 (Å)	3.68[a]	A_R $(10^{-4}$dyn)	-0.098
$c_{11}(10^{11}$dyn cm$^{-2})$	2.11[b]	B_R $(10^{-4}$dyn)	0.403
$c_{12}(10^{11}$dyn cm$^{-2})$	1.18[b]	A_Q $(10^{-4}$dyn)	0.578
$c_{44}(10^{11}$dyn cm$^{-2})$	0.40[b]	B_Q $(10^{-4}$dyn)	-0.472
α_+(Å^3)	3.34[c]	χ_{44} $(10^{12}$dyn. cm$^{-1})$	0.122[g]
α_- (Å^3)	1.80[d]	χ_{11} $(10^{12}$dyn. cm$^{-1})$	-3.68[g]
ε_∞	2.36[f]	Anharmonicity coefficient	Values
		γ_{11} $(10^9$ δψv.cm^{2}K)	0.120

	γ_{12} (10^9 $\delta\psi v.\chi\mu^2 K$)	0.048
	γ_{44} (10^9 $\delta\psi v.\chi\mu^2 K$)	0.106

a-[13], b-[14], c-[15], d-[16], e-[extrapolated values obtained from r_0 versus ε_0 for alkali cyanides], f-[obtained from Lorentz-Lorentz relation] and g-[17].

Here r_0 is the equilibrium interionic distance; c_{11}, c_{12}, c_{44} are the elastic constants; v_{TO} is the zone center vibration frequency; α_+, α_- are the electronic polarizabilities; ε_0 and ε_∞ are the dielectric constants; A_R, B_R, A_Q, B_Q, χ_{44}, χ_{44} are TR coupling coefficients and γ_{11}, γ_{12} and γ_{44} are anharmonicity coefficients. The values of van der Waal coefficients for CsCN are directly taken from the ref[12] and listed in Table 4.2.

Table 4.2 van der Waal coefficients for CsCN ($c_{kk'}$ and $d_{kk'}$ are in the units of 10^{-60} erg.cm^6 and 10^{-76} erg.cm^8 respectively)

Compound	CsCN
C	2780.21
D	1235.67
$c_{kk'}$	211.09
c_{kk}	426.14
$c_{k'k'}$	105.25
$d_{kk'}$	114.63
d_{kk}	211.96
$d_{k'k'}$	615.60

There are three model parameters in ETSM i.e. hardness parameter (b), range parameter (ρ) and TBI parameter f (r). The first two terms, hardness and range parameters are the short-range overlap repulsive parameters and give the nearest and next nearest neighbour interactions expressed by Hafemeister-Flygare[14] type potential. The function f(r) is the long-range TBI parameter. The higher order derivatives of f(r) are obtained from the expression[19],

$$f(r) = f_0 \, exp\left(\frac{-r}{\rho}\right) \tag{4.1}$$

The interionic separation at different temperature is obtained by the linear thermodynamic expression,

$$I_T = I_0(1 + \alpha T) \tag{4.2}$$

with usual notations. 'α' the linear thermal expansion coefficient and T is temperature for CsCN are taken from the ref[26]. Using the input data and vdW, we have computed b, ρ, f(r) at different temperature for CsCN.

The values of model parameter ρ (Å), b (10^{-13}ergs), f (r) (10^{-2}) and r (Å) obtained for various temperature ranges are listed in Table 4.3.

Table 4.3 Model parameters for CsCN at 50K ≤ T ≤ 300K

T(K)	r_0	ρ	b	$f(r_0)$
50	3.688	0.3240	0.6744	-0.0467
60	3.690	0.3241	0.6782	-0.0468

70	3.691	0.3242	0.6819	-0.0468
80	3.693	0.3243	0.6858	-0.0469
90	3.695	0.3244	0.6896	-0.0470
100	3.696	0.3245	0.6935	-0.0471
110	3.698	0.3246	0.6973	-0.0471
120	3.700	0.3247	0.7012	-0.0472
130	3.701	0.3248	0.7052	-0.0473
140	3.703	0.3249	0.7091	-0.0474
150	3.705	0.3250	0.7131	-0.0475
160	3.706	0.3251	0.7170	-0.0475
170	3.708	0.3252	0.7211	-0.0476
180	3.709	0.3253	0.7251	-0.0477
190	3.711	0.3254	0.7291	-0.0478
200	3.713	0.3255	0.7332	-0.0478
210	3.714	0.3256	0.7373	-0.0479
220	3.716	0.3257	0.7414	-0.0480
230	3.718	0.3258	0.7455	-0.0481
240	3.719	0.3259	0.7497	-0.0482
250	3.721	0.3260	0.7538	-0.0482
260	3.723	0.3261	0.7580	-0.0483
270	3.724	0.3262	0.7623	-0.0484
280	3.726	0.3263	0.7665	-0.0485
290	3.727	0.3264	0.7708	-0.0486
300	3.729	0.3265	0.7751	-0.0486

Result and discussion

Elastic constants are used to describe the response of a crystal to a small stress applied uniformly over the crystal. They are defined as the ratio of stress to the strain, where the strain is a measure of the crystal distortions. Elastic constants in orientationally disordered crystals are reduced (or softened) by the indirect coupling of rotator function $v^+M^{-1}v$ at the zone centre resulting from translation-rotation matrix v, coupling rotator functions to long wavelength acoustic displacements. These constants are softened if free energy of the crystal is lowered by a change in the orientational probability function when the strain is applied. The TR results in a phase transition to a more ordered state. The softening of the corresponding elastic constant is strongly and anomalously temperature dependent[26]. The acoustic modes of long wavelength ($q\rightarrow0$) propagate as in a continuous medium and their frequencies as well as polarization properties are related to the elastic constants of the crystal[27]. We have applied TR coupling in studying the second order elastic constants (SOECs) with the help of which higher

order elastic constants i.e. Third Order Elastic Constants, Fourth Order Elastic Constants have been calculated for CsCN.

Table 4.4 Pressure Derivatives of TOECs (in the units 10^{12}dynes/cm^2) for CsCN at 50K ≤ T ≤ 300K

dc_{111}/dp	dc_{112}/dp	dc_{166}/dp	dc_{123}/dp	dc_{144}/dp	dc_{456}/dp
-176.69	-25.88	-16.79	-30.07	-18.52	-9.735
-177.03	-25.90	-16.81	-30.09	-18.53	-9.735
-177.08	-25.92	-16.82	-30.12	-18.55	-9.753
-177.14	-25.94	-16.84	-30.14	-18.56	-9.762
-177.20	-25.96	-16.85	-30.17	-18.58	-9.771
-177.26	-25.98	-16.85	-30.20	-18.59	-9.780
-177.31	-26.00	-16.87	-30.20	-18.61	-9.789
-177.37	-26.02	-16.88	-30.24	-18.62	-9.798
-177.43	-26.04	-16.88	-30.25	-18.63	-9.807
-177.48	-26.07	-16.89	-30.27	-18.65	-9.816
-177.54	-26.09	-16.90	-30.30	-18.66	-9.825
-177.60	-26.11	-16.91	-30.33	-18.68	-9.834
-177.65	-26.13	-16.93	-30.35	-18.69	-9.843
-177.71	-26.15	-16.94	-30.38	-18.71	-9.852
-177.77	-26.17	-16.96	-30.40	-18.72	-9.861
-177.82	-26.19	-16.97	-30.43	-18.74	-9.870
-177.88	-26.21	-16.99	-30.45	-18.75	-9.878
-177.94	-26.23	-17.00	-30.48	-18.76	-9.887
-178.99	-26.25	-17.02	-30.50	-18.78	-9.896
-178.05	-26.27	-17.03	-30.53	-18.79	-9.905
-178.10	-26.29	-17.05	-30.56	-18.81	-9.914
-178.16	-26.32	-17.06	-30.58	-18.82	-9.923
-178.21	-26.34	-17.12	-30.63	-18.84	-9.932
-178.27	-26.36	-17.13	-30.66	-18.85	-9.940
-178.32	-26.38	-17.15	-30.68	-18.86	-9.949
-178.38	-26.40	-17.16	-30.71	-18.88	-9.958

The difference between the cyanides and halides are surprisingly small in view of the different transition temperature, but exist distinct differences between the regular alkali halide which might be interpreted as mainly originating from interactions similar to those dominating in fluids. Among the pressure derivatives of TOECs, dc_{111}/dp, dc_{112}/dp, dc_{166}/dp, dc_{111}/dp dc_{123}/dp and dc_{456}/dp show increasing trend with increasing temperature as shown in figure 4.4.

References

1. *J.F. Berret, A.F. Farkadi, M. Boissner, J. Pelous, Phys. Rev. B., 39, (1989), 13451.*
2. *R.M. Lynden –Bell, K.H. Michel, Rev. Mod. Phys., 66, (1994), 721.*
3. *P. Zielenski, K.H. Michel, Phys. Rev., B., 46, (1992), 4806.*
4. *J.Z. Kwiecien, R.C. Leung, C.W. Garland, Phys. Rev. B., 23, (1981), 4419.*
5. *S.C. Kim, T.H. Kwon, J. Phys. Chem. Solids., 53, (1992), 539.*
6. *K.H. Michel, J. Naudts, Phys. Rev. Lett., 39, (1977), 212.*
7. *J.O. Fossum, C.W. Garland, Phys. Rev. Lett., 60, (1988), 592.*

8. J.M. Rowe, J.J. Rush, D.G.Hinks, S.Susman, Phys. Rev. Lett., 43, (1979), 1158.
9. A. Loidl, R. Feile, K. Knorr, R. Renker, J. Daubert, D. Durand, J.B. Suck, Z. Phys. B., 38, (1980), 253.
10. K.H. Michel, J.M. Rowe, Phys. Rev. B., 22, (1980), 1417.
11. V.Yu. Topolov, Z. Phys., B100, (1996), 27.
12. R.K. Singh, N.K. Gaur, Physica B., 150, (1988), 385.
13. R.K. Singh, N.K. Gaur, Z. Phys., 75, (1989), 127.
14. D.W. Hafemeister, W.H. Flygare, J. Chem. Phys., 43, (1965), 795.
15. Preeti Singh, N.K. Gaur, R.K. Singh, Phys. Stat. Sol.(b)., 244, (2007), 3099; Phys. Lett. A., 371, (2007), 349.
16. Nupinderjeet Kaur, Rajneesh Mohan, N.K.Gaur, R.K. Singh, Physica C., 451, (2007), 24.
17. P. Singh, N.K. Gaur, JOAM 3 (5), (2009) 501
18. P. Singh, N. K. Gaur, SOP Transactions on Theoretical Physics 1, (2014) 68
19. P. S. Bahadur, JCTN 15 (4), 1(2018) 1415
20. AlpanaTiwari, N K Gaur and P SinghJOP: Conference Series, 215 (2009)
21. Dr. Preeti Singh1,2 , Dr Subhadra Rajpoot, IJSR, 3 (2014)
22. N.K. Gaur, N. Kaur, J.Galgale, M. Manke, R.K. Singh, Mod. Phys. Lett. B., 17, (2003), 1391.
23. J. Galgale, N. Kaur, P. Singh, M. Manke, N.K. Gaur, R.K. Singh, Pramana., 63, (2004), 413.
24. N.K. Gaur, P. Singh, E.G. Rini, J. Galgale, R.K. Singh, Pramana., 63, (2004), 419.
25. D. Sahu, S.D. Mahanti, Phys. Rev. B., 26, (1982), 2981.
26. L. Vegard, Z. Phys. 5, (1921), 17.
27. W. N. Mei, L. L. Boyer, M. J. Mehl, M. M. Ossowski and H. T. Stokes, Phys. Rev. B 48, (2000), 11425.