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Thermoelastic Behaviour of CsCN

S S Shemim[a] * and N.K. Gaur[b]
[a] *Department of Physics, TKM College of Engineering- 691005, Kerala, India*
[b] *Department of Physics, Barkatullah University - 462026, Bhopal, India*
**Email: shemimsoorajbs@yahoo.co.in*

Abstract

We have investigated the thermal and elastic properties of Cesium Cyanide (CsCN) by means of Extended Three Body Force Shell Model (ETSM). The paper reports the elastic constants up to fourth order and the thermodynamic properties such as molecular force constant (f), Restrahlen frequency (ν), cohesive energy (ϕ), Debye temperature (θD) and Gruneisen parameter (γ) of CsCN crystal for a temperature range of 155K$\leqslant$T$\leqslant$555K with the aid of ETSM.

Keywords: Elastic constants, Cohesive energy, Thermodynamic properties

1. Introduction

The Cesium cyanide possesses cesium chloride structure with a space group pm3m (pseudocubic high temperature phase), in which CN^- elastic dipoles are in disordered orientations. At 193 K, CsCN transforms discontinuously into a triagonal (R3m) structure. The (CN^-) ions are aligned along the three fold 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^o flips. This situation is strongly suggestive for a frozen- in state at the lowest temperature [1,2]. The special interest in CsCN lies in the fact that it exhibits the CsCl structure different from NaCN, KCN and RbCN which are having rock-salt structure. Over the past few years, the cohesive and thermoelastic properties of orientationally disordered alkali metal cyanides (ODMs) have been of interest to the experimental as well as theoretical workers on this field. The lattice mechanics of many ODMs have been reported satisfactorily by means of ETSM. This model which was designed by incorporating Translational-Rotational coupling effect in the framework of Three Body Force Shell Model was found to be excellent in explaining the static, dynamic, dielectric and optic properties of ODMs. Inspired by the great success of ETSM [3] in explaining these properties of ODMs we thought it appropriate to extend the investigation to thermoelastic and cohesive behaviour of CsCN. Also, the requirement of application of ETSM to CsCN evolved from the fact that the Cs+ ions and the CN- ions has larger ionic size difference which makes the three-body interactions (TBI) more effective in this crystal..The formulation of ETSM is given in 2. The results and discussions have been presented in 3.

2. Potential Model and Method of Calculations

The formalism of the Extended Three Body Force Shell Model has been derived from the following interatomic interaction [4-7].

$$\Phi = \frac{e^2}{2}\Sigma Z_k Z_{k'} r_{kk'}^{-1} [1+\Sigma_{kk} f(r_{kk'})]-\Sigma_{kk'} c_{kk} r_{kk'}^{-6}-\Sigma_{kk'} d_{kk'} r_{kk'}^{-8}+b \Sigma_{kk'} \beta_{kk'} \exp(r_k+r_{k'}-r_{kk'}/\rho)+\phi^{TR} \quad (1)$$

Here, the first term is attractive long range (LR) coulomb interactions energy and the second term is the three body interaction potential. The third and fourth term represents the contributions of van derWaals (vdW) attraction for the dipole-dipole interaction and dipole-quadrupole interactions and the fifth term is short range (SR) overlap repulsive energy represented by the Hafemeister–Flygare type (HF) interaction extended up to the second neighbor.$\phi^{TR}$is the contribution due to ranslational rotational coupling. In expression (1), other symbols involved are the same as those defined in our earlier papers [4-7]. b and ρare the hardness and range parameters for the i^{th} cation–anion pair (i = 1, 2) respectively and $\beta_i^{kk'}$ is the Pauling coefficient [8] given by

$$\beta_i^{kk'} = 1 + (Z_k / N_k) + (Z_{k'} / N_{k'}) \quad (2)$$

$Z_k(Z_{k'})$ and $N_k(N_k')$ are the valence and the number of electrons in the outermost orbit of the k (k′) ion respectively. The present model (ETSM)) described above for the CsCl contains three model parameters *(b, ρ* and f*)*, which are used to determine the second- order (SOECs), third order (TOECs) and fourth order (FOECs) elastic constants of CsCN.The expressions for calculating the thermodynamic properties like Debye temperature (θ_D), Reststrahlen frequency (υ), molecular force constant (*f*), and Gruneisen parameter (γ) are taken from our earlier papers [4-7].

Table.1 (a) Input data for CsCN at room temperature.

ro (Ao)	=	*3.68*
c11 (1011 dynes/cm2)	=	*2.11*
c12 (1011 dynes/cm2)	=	*1.18*
c44 (1011 dynes/cm2)	=	*0.40*
α+ (Ao)3	=	*3.34*
ε ∞	=	*2.36*

Table 1.(b) *van der Waals coefficients for CsCN (ckk' and dkk') are in the units of 10-60 ergs. cm6 and 10-76 ergs cm8 respectively*

Compound	C	D	c_{+-}	c_{++}	c_{--}	d_{+-}	d_{++}	d_{+-}
CSCN	2780.21	1235.67	211.09	426.14	105.25	144.63	211.96	615.60

Table 1.(c) *Model parameters for CSCN for temperature range 155 K T 555K*

T(K)	r(A^o)	ρ(A^o)	b(10^{-12} ergs)	f(r)
155	3.415	0.2842	0.6332	-0.04218
175	3.419	0.2844	0.6414	-0.0429
195	3.422	0.2846	0.6493	-0.04250
215	3.426	0.2848	0.6574	-0.04266
235	3.430	0.2850	0.6656	-0.04282
255	3.438	0.28539	0.6733	-0.04318
275	3.442	0.28565	0.6826	-0.04334
295	3.445	0.28585	0.6895	-0.04350
315	3.449	0.28605	0.6975	-0.0436
335	3.453	0.28625	0.67055	-0.0438
355	3.457	0.28645	0.7134	-0.0439
375	3.461	0.28660	0.7213	-0.0441
395	3.465	0.28685	0.7294	-0.0449
415	3.469	0.28715	0.7374	-0.0446
435	3.473	0.28735	0.7452	-0.0448
455	3477	0.28755	0.7532	-0.0449
475	3.481	0.28775	0.7642	-0.04512
495	3.485	0.28795	0.7738	-0.0453
515	3.489	0.28815	0.7846	-0.0455
535	3.493	0.28835	0.7943	-0.0456
555	3.497	0.28855	0.7902	-0.0458

3. Results and Discussions

We have obtained the model parameters (b,ρ and f) as a function of temperature using input data [Table 1(a) and 1(b)]taken from Ref. [10, 13, 14] and are listed [Table 1 (c)]. Using the model parameters [Table 1(c)] we have calculated the second order (SOEC), third order (TOEC) and fourth order (FOEC) elastic constants of CsCN for a temperature range of 155K⩽T⩽555K. The values of SOECs are plotted in Figures 1-3and TOEC s and FOECs are also presented [Table (2)-(3)]. Also, the cohesive and thermal properties are computed for CsCN for the same temperature range with the help of model parameters and are tabulated [Table (4)].

Figure1:C_{11} of CsCN

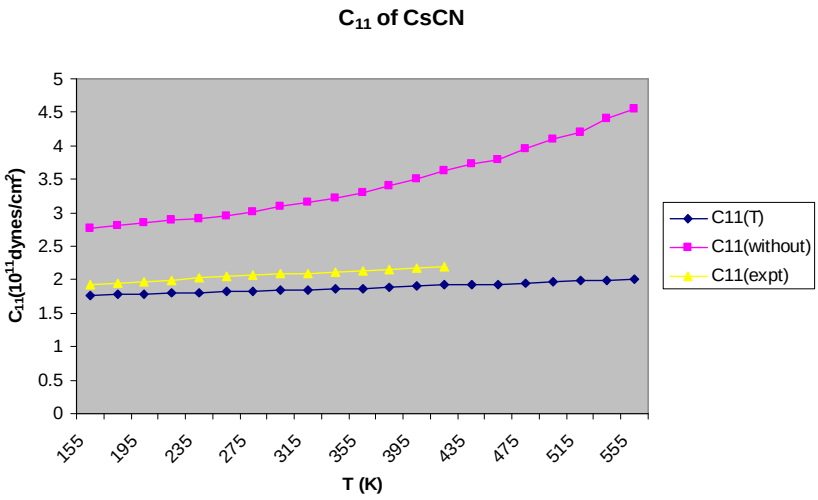

Figure 2:C_{12} of CsCN

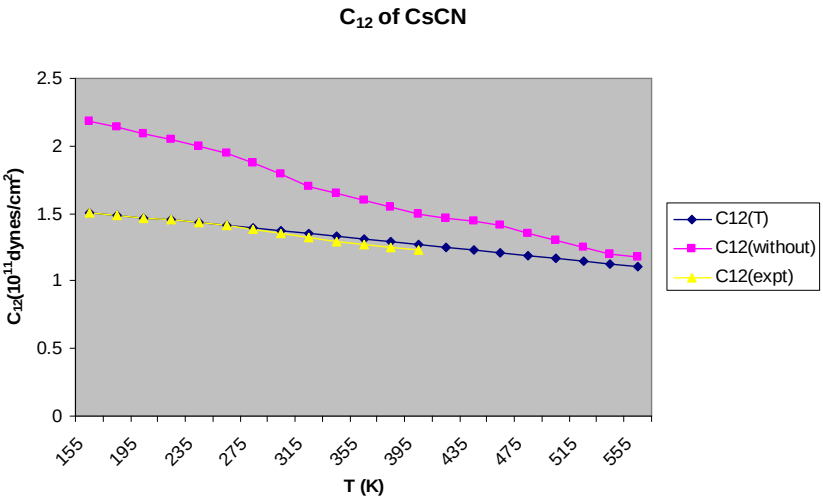

Figure 3: C_{44} CsCN

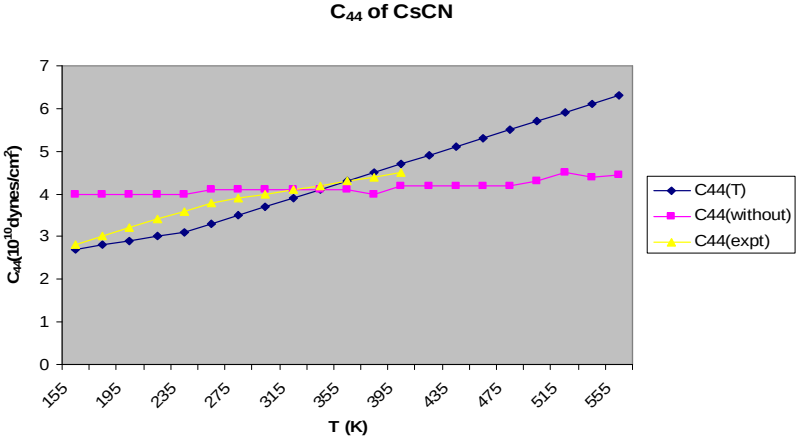

Table 2**.** TOECs of CsCN in the temperature range 155 K ≤ T ≤ 555 (K) in the units of 10^{12} degree / cm^2)

T(K)	c_{111}	c_{112}	c_{166}	c_{123}	c_{144}	c_{456}
155	-5.838	-0.635	-0.455	-0.729	-0.524	-0.428
175	-5.832	-0.635	-0.455	-0.729	-0.524	-0.428
195	-5.826	-0.635	-0.456	-0.729	-0.524	-0.428
215	-5.820	-0.635	-0.456	-0.729	-0.525	-0.428
235	-5.814	-0.635	-0.457	-0.728	-0.525	-0.428
255	-5.806	-0.635	-0.457	-0.728	-0.525	-0.429
275	-5.800	-0.635	-0.458	-0.727	-0.526	-0.429
295	-5.796	-0.635	-0.458	-0.727	-0.526	-0.429
315	-5.590	-0.635	-0.459	-0.727	-0.526	-0.429
335	-5.782	-0.635	-0.460	-0.727	-0.527	-0.429
355	-5.776	-0.635	-0.460	-0.726	-0.527	-0.429
375	-5.770	-0.635	-0.461	-0.726	-0.527	-0.429
395	-5.764	-0.635	-0.461	-0.725	-0.528	-0.430
415	-5.758	-0.635	-0.462	-0.725	-0.528	-0.430
435	-5.752	-0.635	-0.463	-0.725	-0.528	-0.430
455	-5.746	-0.635	-0.463	-0.725	-0.529	-0.430
475	-5.740	-0.635	-0.464	-0.725	-0.529	-0.430
495	-5.734	-0.635	-0.464	-0.725	-0.529	-0.430
515	-5.727	-0.635	-0.465	-0.724	-0.530	-0.431
535	-5.721	-0.635	-0.465	-0.724	-0.530	-0.431
555	-5.715	-0.635	-0.466	-0.723	-0.530	-0.431

Table 3. FOECs of CsCN in the temperature range 155K ≤ T 555K (in units of 10^{12} dynes / cm^2)

T(K)	c_{1111}	c_{1112}	c_{1166}	c_{1122}	c_{1266}	c_{1123}	c_{4444}	c_{1144}	c_{1244}	c_{1456}	c_{4466}
155	142.8	6.228	4.543	6.531	5.699	9.13	4.538	4.687	5.445	3.386	2.873
175	142.7	6.231	4.545	6.534	5.701	9.13	4.539	4.689	5.447	3.387	2.873
195	142.6	6.235	4.547	6.537	5.703	9.13	4.540	4.692	5.449	3.388	2.874
215	142.5	6.238	4.550	6.540	5.704	9.14	4.542	4.694	5.451	3.390	2.875
235	142.4	6.241	4.552	6.543	5.706	9.14	4.543	4.697	5.453	3.391	2.875
255	142.45	6.246	4.554	6.547	5.708	4.544	9.15	4.700	5.455	3.392	2.881
275	142.25	6.249	4.556	6.550	5.710	4.546	9.15	4.702	5.457	3.394	2.877
295	142.15	6.253	4.558	6.553	5.712	4.547	9.16	4.704	5.459	3.395	2.877
315	142.05	6.257	4.560	6.556	5.714	4.548	9.16	4.706	5.461	3.396	2.878
335	141.95	6.261	4.562	6.559	5.716	4.550	9.16	4.706	5.463	3.397	2.879
355	141.85	6.265	4.564	6.562	5.718	4.552	9.17	4.710	5.465	3.398	2.879
375	141.75	6.269	4.566	6.565	5.720	4.554	9.17	4.712	5.467	3.399	2.880
395	141.65	6.273	4.568	6.568	5.722	4.556	9.17	4.714	5.469	3.400	2.881
415	141.55	6.277	4.570	6.571	5.724	4.558	9.18	4.716	5.471	3.401	2.881
435	141.45	6.281	4.572	6.574	5.726	4.560	9.18	4.718	5.473	3.402	2.882
455	141.35	6.285	4.574	6.577	5.728	4.562	9.18	4.720	5.475	3.403	2.883
475	141.25	6.289	4.576	6.580	5.730	4.564	9.19	4.722	5.477	3.405	2.883
495	141.15	6.293	4.578	6.583	5.732	4.566	9.19	4.724	5.479	3.406	2.884
515	141.05	6.297	4.580	6.586	5.734	4.568	9.19	4.726	5.481	3.408	2.885
535	140.95	6.301	4.582	6.589	5.736	4.570	9.20	4.728	5.483	3.410	2.885
555	140.85	6.305	4.584	6.592	5.738	4.572	9.20	4.730	5.485	3.411	2.886

Table 4. Thermophysical properties of CsCN within temperature range 155K ≤ T ≤ 555K.

T (K)	Φ (KJ mol^{-1})	β (10^{-12} dyne^{-1}cm^2)	F (10^4dyne/cm)	υ_0 (THz)	θ_D (K)	α_v/c_v (10^3J)	γ
155	-670.86	4.236	2.987	3.931	202.68	4.950	1.483
175	-670.12	4.257	2.978	3.923	202.23	4.950	1.478
195	-669.45	4.278	2.968	3.915	201.84	4.950	1.472
215	-668.81	4.298	2.957	3.907	201.48	4.950	1.467
235	-668.21	4.317	.947	3.899	201.12	4.950	1.462
255	-667.54	4.338	2.936	3.891	200.86	4.950	1.457
275	-666.78	4.358	2.925	3.883	200.47	4.950	1.451
295	-665.14	4.377	2.915	3.875	200.13	4.951	1.446
315	-664.42	4.399	2.905	3.867	199.84	4.951	1.440
335	-663.96	4.419	2.894	3.859	199.46	4.951	1.435
355	-663.38	4.438	2.878	3.851	199.11	4.951	1.430
375	-662.76	4.457	2.868	3.843	198.98	4.951	1.424
395	-662.10	4.477	2.860	3.835	198.52	4.951	1.418
415	-661.42	4.497	2.850	3.827	198.17	4.952	1.412
435	-660.74	4.518	2.840	3.819	197.81	4.952	1.408
455	-660.02	4.538	2.831	3.811	197.42	4.952	1.401
475	-659.45	4.553	2.820	3.803	197.04	4.953	1.393
495	-659.11	4.572	2.811	3.795	196.62	4.953	1.386
515	-658.75	4.595	2.800	3.788	197.24	4.953	1.379
535	-658.22	4.612	2.791	3.779	196.84	4.953	1.372
555	-657.66	4.635	2.779	3.771	196.44	4.953	1.365
300(expt)	-612	6.71	3.28	3.48			

It is seen that c_{11} and c_{44} increases with increase in temperature, while c_{12} decreases with increase in temperature. The increasing trends of c_{11} and c_{44} indicate the existence of softening over lower range of temperature due to the influence of temperature on them. The results are compared with experimental data and it is found to be in good agreement with Brilliouin scattering measured data [9-12]. The results are interpreted on the basis of Landau theory of the phase transition with a linear coupling between the strain and the order parameter. Here the anomalous behaviour of c_{11} and shear modulus c_{44} of the symmetry adopted elastic constants in the disordered cubic phase c_{44} and $(c_{11} - c_{12})/2$ both become soft in a wide temperature range, whereas bulk modulus ß = $(c_{11} + 2c_{12}) / 2$ is becoming stiffer on reaching the phase transition from the figures [1&3] But temperature dependence of bulk modulus is weak. The main feature is anomalous softening of c_{44} approaching the transition temperature and is found similar to other materials like NaCN, KCN and RbCN.

From the tables (2) and (3) it is evident that all the TOECs are negative ie., less than zero. The values of C_{111} and C_{123} decrease with increase in temperature and the values of all other TOECs increase with increase in temperature. The FOECs are all positive i.e. greater than zero. The FOECs increase with increase in temperature, except that c_{1111}which decrease with increase in temperature. The TOECs and FOECs could not be compared as no experimental data is available. But these values will serve as a guide to the experimental workers in future. The purpose of this study is to incorporate explicitly the effect of temperature on TOECs and FOECs. This may be due to the presence of alkali – halide as one of the counterpart. It is observed from table (4) that the Debye temperature decreases slightly with increase in temperature. The temperature dependence of Debye temperature is useful for understanding the thermodynamic behaviour of solids. In the present system CsCN the cohesive properties like ϕ, f and β are compared

with the experimental values available at 300K and are found to be in good agreement. The Gruneisen parameter decreases with increase in temperature and lies in between 1 and 2 which seems to be correct as reported in available literature [15-23]. Due to non availability of experimental data, our results on other thermal properties could not be compared. Also, theproperties like ϕ, f and U_o shows decreasing trend with temperature, while β, and α_v / c_v increase with increase in temperature.

4. Conclusions

The elastic and thermodynamic properties of the orientationally disordered CsCN mixed crystal are investigated with the help of ETSM. Our calculated results on shear elastic constant c_{44} are in fairly good agreement with the available experimental data. In general, the elastic constants of solids decrease with increase in temperature. But in the mixed crystals of our study, it is found that elastic constants increase with the decrease in temperature. Also, the values of cohesive energy, compressibility and molecular force constant obtained from ETSM are in good agreement with the experimental values of these parameters for pure KCN crystals. Our comments on the other results are restricted until the report of experimental data on them but these results will serve as a guide to the experimental workers in future. A successful description of mechanical properties achieved for such complicated CsCN can be considered remarkable in view of the inherent simplicity of the ETSM and its less parametric nature.

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