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RESEARCH ARTICLE

Lattice Dynamical Properties of CsI (RT)

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Abstract

Lattice dynamical properties of cesium Iodide CsI has been presented by including the effect of van der Waals interactions and three body interactions in the framework rigid shell model. The short-range overlap repulsion is operative to the second neighbor ions. An excellent comparison has been obtained between theoretical and experimental results for their phonon dispersion curves and Debye temperature variations. We also report two-phonon IR/Raman spectra and combined density of states. It is concluded that the VTSM is adequately essential for description of lattice dynamics of Cesium Iodide.

1. INTRODUCTION

Study of crystal dynamics of cesium chloride structure have been the matter of great interest in solid state physics. The detail of this progression for the study of phonon behavior of CsI at room temperature has been traced by some experimental researcher [1-4] and theoretical workers [5-8]. Due to availability of a lot of measured data on elastic constant, dielectric constants, phonon dispersion curves, Debye temperature variations and two phonon IR Raman spectra for all of them with moderate success, has motivated the present author for the need of a lattice dynamical model for the description of various properties. The rigid ion model (RIM) by Kellerman [9] is the first important model for the ionic crystals, which considers the ion of the crystals to be rigid, undeformable and unpolarizable spherical particles. The RIM model was failure as it could not interpret well the dynamical, optical and elastic properties of ionic crystals. It could not give the adequate interpretation of the experimental phonon dispersion curves. The next is the deformation dipole model (DDM) by Karo and Hardy [10] and rigid shell model (RSM) by Dick and Overhauser [11] and Woods et.al. [12]. The DDM allows only the redistribution of charges in deformed electron cloud while the shell models consider the relevant displacement. So both effects (deformation and displacement) are present in ionic crystals. These models have failed to explain successfully the phonon dispersion curves and Cauchy violation $C_{12} \neq C_{44,}$ which is large for CsI as well as ionic crystals. By inclusion of the deformation of electron shell in the framework of RSM we can remove this deficiency. The agreement between model frequencies and those obtained in their experiments is good at low value of q for acoustic branches, but there is discrepancy between the elastic constant derived from model parameters and those obtained from neutron scattering measurements. Later on Singh et al. [7] used extended three body force shell model (ETSM) which are essentially an amalgamation of two most commonly used and realistic phenomenological models namely the RSM and deformation dipole model (DDM). ETSM contains the two-body long-range coulomb interaction and short range repulsion effective up to second-neighbour ions, three body long range interaction, and dipole character of constituent ions. Despite of these successes ETSM has revealed some features which do not have much physical significance. A formal description of VWI and TBI in the framework of RSM has been described in next section. The present model VTSM as mentioned above has been applied to describe the complete lattice dynamics of cesium halides (CsCl, CsBr, CsI).

The motivation for present solids lies in the fact that they have high energy gap, some discrepancies in PDCs and Cauchy violations. The present study has been carried out by determining a set of 12- parameter. Also we have tasted the adequacy of VTSM model by calculating the two phonon Raman spectra, Debye temperature and combined density of states.

THEORY

The general formulation of VTSM can be derived from the crystal potential whose relevant expression per unit cell is given by

$$\Phi = \Phi_{COL} + \Phi_{TBI} + \Phi_{SR} + \Phi_{vWI} \quad (1)$$

where the first two terms represent, respectively, long range Coulomb and three body interactions (TBI) energies. The next term is the Hafemeister and Flygare [19] form of SR overlap repulsive energy extended to the next nearest neighbor ions. The last term is the short range vWI interaction due to dipole-dipole and dipole-quaderpole interactions. The introduction of vWI and TBI in the frame work of RSM [10, 14] yields secular determinant

$$|D(q) - \acute{\omega}^2 MI| \quad (2)$$

where D (q) is written as

$$D(q) = (R + Zm\, C'\, Zm) - (T + Zm\, C'Ym)\,(S + Ym\, C'\, Ym)^{-1}\,(T^{T} + Ym\, C'Zm) \quad (3)$$

The expression for the elastic constants derived from the dynamical matrix corresponding to our model is

$$C_{11} = e^2/4a^4 \{0.7010\, Z^2m + (A_{12}+2B_{12})/6 + (A_{11}+A_{22})/4 + 5.4283\, Z\, r_0f'_0\} \quad (4)$$

$$C_{12} = e^2/4a^4 \{-0.6898\, Z^2m + (A_{12}+4B_{12})/6 + (B_{11}+B_{22})/4 + 5.283\, Zrof'_0\} \quad (5)$$

$$C_{44} = e^2/4a^4 \{-0.3505\, Z^2m + (A_{12}+2B_{12})/6 + (B_{11}+B_{22})/4\} \quad (6)$$

And $r0 = (a\sqrt{3})$ is interionic separation .In view of well known equilibrium condition

$$B_{11} + 2B_{12} + B_{22} = -0.6786\, Z^2m \quad (7)$$

These elastic constants lead to the Cauchy violation

$$C_{12} - C_{44} = e^2/4a^4\,(5.4283\ \ Zr_0f'_0) \quad (8)$$

The expression for zone centre optical vibration frequencies are given by

$$\mu\acute{\omega}^2_{LO}{}^{(\Gamma)} = R'o + 8\pi\,(Z'e)^{2/}3\,Vf_L\,(1 + 12\,Z^{-2}m\,Zr_0f'_0) + Wo \quad (9)$$

$$\mu\acute{\omega}^2_{TO}{}^{(\Gamma)} = R'_o - 4\pi\,(Z'e)^{2}/3\,Vf_T + Wo \quad (10)$$

where the parameters are as $Zm = \pm Z\{1 + 16\, f(r_0)\}^{1/2}$, $R'_0 = R_0 - e^2\,(d_1^2/\alpha_1 + d_2^2/\alpha_2)$

$Z' = Zm + d_1 - d_2$, $f_L = 1 + (8\pi\alpha/3V)\,(1 + 12\,Z^{-2}m\,Zr_0\,f'_0)$, $f_T = 1 - (4\pi\alpha/3V)$ and Wo is the van der Waals interactions term.

4. RESULTS:

The input data and calculated 12 model parameter for CsI crystal at room temperature are listed in Table-1.The model parameters have been calculated by using experimental values of inter ionic distance (r_0), elastic constants ($C_{11,}\, C_{12,}\, C_{44}$) and vibrations frequencies ($\nu_{TO}^{(\Gamma)}$, $\nu_{LO}^{(R)}$, $\nu_{LA}^{(R)}$, $\nu_{TO}^{(X)}$, $\nu_{TA}^{(X)}$). The phonon dispersion relation have been computed by solving the secular equation for the six vibration frequencies corresponding to allowed 56-nonequivallent wave vectors in first Brillion Zone along principal symmetry directions [q,o,o], [q,q,o], [q,q,q]. Phonon dispersion curves have been obtained for CsI have been plotted in Figure–1 along with their observed data. From Figure-1 it is clear that inclusion of van der Waals interactions and short range repulsion effective up to the second neighbor have influence both LO and TO branches in almost all the symmetry directions rather than the LA and TA modes. There is a good agreement between the theoretical and experimental results [1-8]. The phonon dispersion curves of this crystal calculated from present model agree reasonably well with the measured data. It is evident that the "optical behavior" is explained better than the "acoustical behavior". A good agreement is also for longitudinal acoustic (LA) branch along [q,q,q] direction. Also the result obtained from the present model almost

identical along [q,q,q] direction. This may be particularly because the zone centre vibration frequencies have been used as input data in calculation of model parameter of this model.

Table -1: Input data and model parameter for CsI
[C_{ij} (in 10^{12} dyne/cm^2), ω (in 10^{13} Hz), r_0 (in 10^{-8} cm), α_i (in 10^{-24} cm^3), a (in 10^{-8} cm)]

Input Data			Model Parameter	Values
Physical Properties	Values	Ref.		
C_{11}	2.434	2	Z^2m	0.8062
C_{12}	0.636	2	$r_0f'0$	-0.0026
C_{44}	0.666	2	A_{11}	-0.9536
$\nu_{TO}^{(\Gamma)}$	1.918	4	B_{11}	0.0682
$\nu_{LO}^{(R)}$	1.815	4	A_{12}	7.1051
$\nu_{LA}^{(R)}$	1.719	4	B_{12}	-0.4030
$\nu_{TO}^{(X)}$	1.214	4	A_{22}	2.969
$\nu_{TA}^{(X)}$	1.266	4	B_{22}	-1.680
α_1	3.131	7	d_1	0.3094
α_2	6.191	7	d_2	0.5053
ε_0	5.65	2	Y_1	-1.784
ε_∞	3.020	7	Y_2	-2.1601
2a (10^{-8} cm)	4.567	7		

Table -2
Assignment of Two Phonon Raman and Infra-red peaks for CsI (RT)

CDS Peaks (cm^{-1})	Raman Active			Infra-red Active	
	Observed[21,22] Peaks (cm^{-1})	Present Study		Present Study	
		Assignment	Values (cm^{-1})	Assignment	Values (cm^{-1})
17	20 22				
30	28	LO-TO(X) LA-TA(X)	29 29		
52	44 52				
61	61				
67	67				
94	94	TO+LA(M)	88	TO+LA(M)	88

		LA+TA(M) 2LA(M)	88 90	LA+TA(M) 2LA(M)	88 90
107	107	LA+TA(X)	109		
113	113	LO+TA(X) TO+LA(X)	112 112		
128	122 128	2LO(R) 2TO(R) LO+TO(R) LO+LA(M) 2TO( )	120 120 120 120 128	LO+LA(M)	120
133	135	2LA(X)	138		
160	160	2LO(M)	150	2LO(M)	150
167	167	2LO( )	174		
184	180 184				
200	200				

[21, 22]

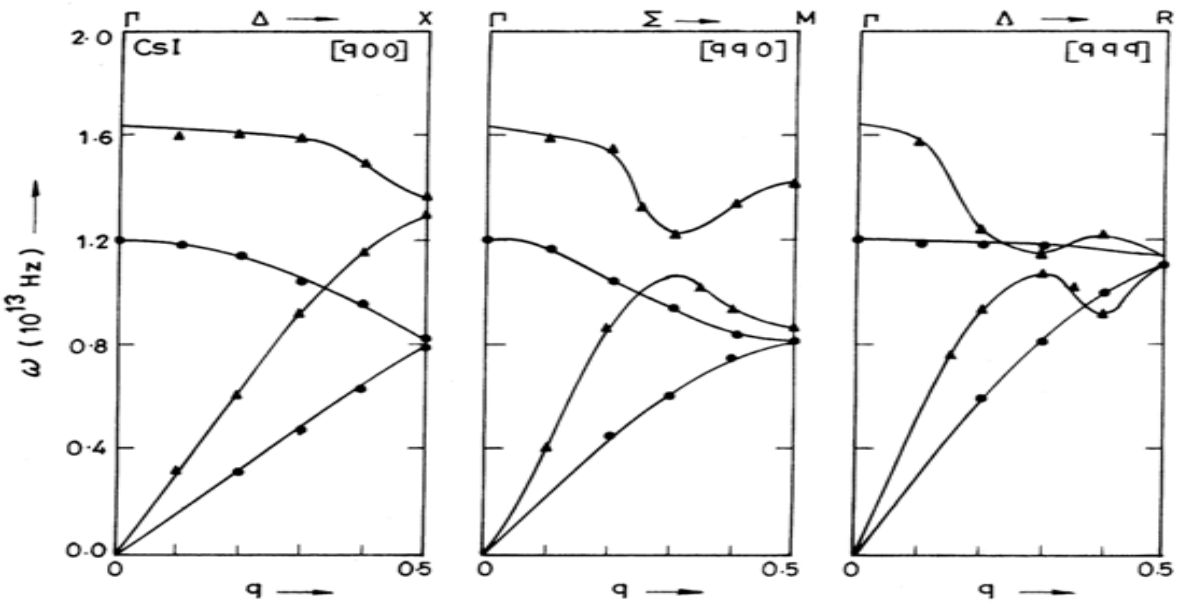

Fig. 1: Phonon dispersion curves of CsI
▲ Longitudinal
• Transverse
} Experimental points, —— Present study

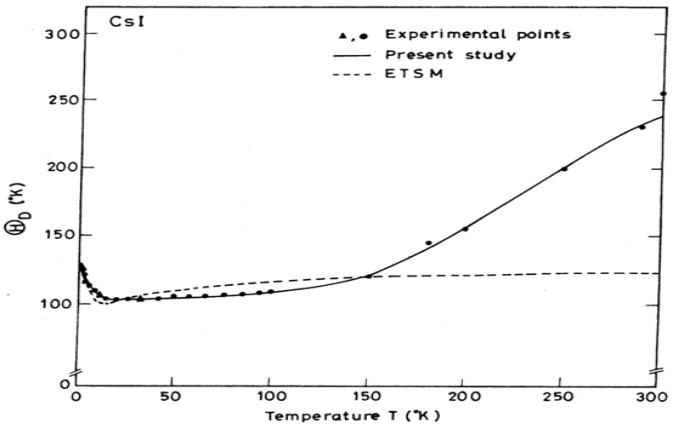

Fig. 2: Debye temperatures variation for CsI

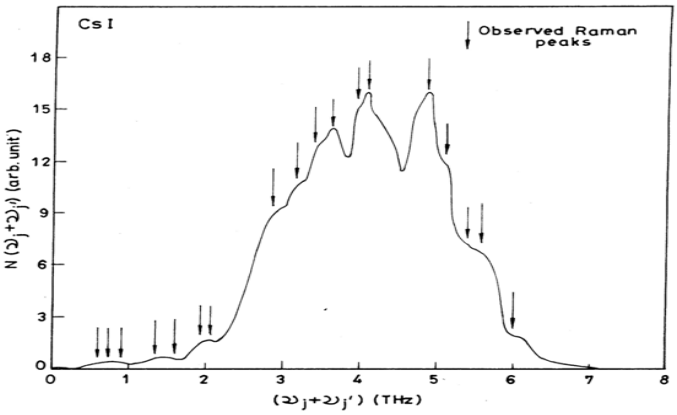

Fig. 3 Combined density of states curves for CsI

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