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Lattice dynamical investigation of RbI

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ABSTRACT

Rubidium Iodide crystals are bcc in structure. Study about RbI crystal in present of two body body interaction has been observed some shortcomings especially with respect to the Cauchy violation, high dielectric constants, high electronic polarizabilities and phonon dispersion relation because of lack of many body terms. So overcome to these difficulties a new model proposed, van der Waals three body force shell model (VTBFSM) come in existence .Which incorporates the effects of the van der Waals interaction with long-range Coulomb interactions, three-body interactions and short-range second neighbour interactions in the framework of rigid shell model (RSM).The theoretical predictions achieved for Phonon dispersion, Debye temperature variations, two phonon Raman and infra red–absorption spectra for RbI. The obtained theoretical results are very close agreement with experimental result.

Keywords: *Phonon; Debye temperature; combined density of state; Raman & van der Waals interaction.*

INTRODUCTION

The purpose of this paper is to report due to an availability of measured data on phonon dispersion curves [1,2], Debye temperature variations [3,4] along with their theoretical values [5], two-phonon IR and Raman spectra [6,7], elastic constants [1,8] and dielectric constants [9,10] of (RbI) the nature and the physical properties of the Rubidium Iodide have been attracted and their interpretations by means of theoretical models [11-14] with successfully describe their interesting properties. The rigid ion model (RIM) of Kellermann [15] could not interpret well the dynamical, optical and elastic properties. Then the deformation dipole model (DDM) of Karo and Hardy [16] and rigid shell model (RSM) of Dick and Overhauser [17] & Woods et al [18] by two different groups of workers has given for study of lattice property. The most prominent amongst them are breathing shell model (BSM) of Schroder [19], the deformable shell model (DSM) of Basu and Sengupta [20] and three-body force shell model (TSM) of Verma & Singh [21-22].

In consideration of the van der Waals interaction effect recently, Upadhyaya et al [23] have obtained good results between theory and experiment for ionic semiconductors using van der Waals interaction. This has motivated the author to incorporate the effects of van der Waals interactions and three-body interactions in the framework of ion polarizable RSM with short-range interactions effective up to the second neighbour. Therefore, it may be inferred that the most realistic model for complete harmonic dynamical behavior of the crystals under consideration can be developed by introducing the effect of van der Waals interactions (VWI) and three-body interactions (TBI) in the framework of RSM. The present model is known as van der Waals three-body force shell model.

MATERIALS AND METHODS

2. THEORY

The van der Waals interaction (VWI) potential owes its origin to the correlations of the electron motions in different atoms. The electrons of each atom shift with respect to the nucleus in the presence of other atoms and consequently an atom becomes an electric dipole. The instantaneous dipole moment of a closed shell atom induces as the van der Waals interaction potential. The necessity of including the (VWI) and (TBI) effects in the framework of (RSM) [18] has already been discussed above. Thus, the inclusion of VWI and TBI effects in RSM will employ the Hietler London and the free-electron approximations. The interaction systems of the present model thus consist of the long-range screened Coulomb, VWI,TBI and the short-range overlap repulsion operative up to the second-neighbour ions in Rubidium Iodide . The general formalism of VTBFSM can be derived from the crystal potential whose relevant expression per unit cell is given by

$$\Phi^{C}+\Phi^{R}+\Phi^{TBI}+\Phi^{VWI} \tag{1}$$

where, First term Φ^{C} is Coulomb interaction potential. This interaction potential is long-range in nature. An ionic crystal can be regarded as made up of positive and negative ions separated by a distance $|\vec{r}_{ij}|$, where $\vec{r}_{ij}$ is a vector joining the ions i and j. According to electrostatic theory, the Coulomb energy of interaction of i-th ion with j-th ion is written as $\Phi^{C}(\vec{r}_{ij})$. Thus, total Coulomb energy for the crystal is

$$\Phi^{C}(r) = \sum_j{}' \Phi^{C}(r_{ij}) = \sum_j{}' \varepsilon_{ij} \frac{e^2}{|\vec{r}_{ij}|}$$

where, the prime means summation over all ions except i=j, ε_{ij} will be +1, if i and j are like ions and –1, if they are unlike Second term Φ^{R} is short-range overlap repulsion potential. The most commonly used analytical expressions for the repulsive energy are given by the inverse and exponential power laws such that

$$\Phi^{R}(r_{ij}) = a r_{ij}^{\ n} \quad \text{(Born Potential)} \quad , \quad \Phi^{R}(r_{ij}) = b \exp.(-r_{ij}/\rho) \quad \text{(B-M) Potential)}$$

Where, a (or b) and η(orρ) are the Born exponents called the strength and hardness parameters, respectively.

Third term Φ^{TBI} is three-body interactions potential. According to quantum-mechanical theory using Heitler-London approximation, the atomic wave-functions are treated rigidly connected with their nuclei and supposed not to change in a deformation of the lattices. As a natural consequence of the anti-symmetry requirement on the wave function [16], this alteration in the electronic charge density causes a charge depletion which depends on the inter nuclear separation and interacts with all other charges via Coulomb force law and gives rise to long-range TBI introduced by Lowdin [17] and Lundqvist [18]. This interaction potential is expressed as

$$\Phi^{TBI} = \alpha_m \frac{Z^2 e^2}{r_0}\left[\frac{2n}{Z} f(r)_0\right]$$

Where, the term $f(r)_0$ is a function dependent on the overlap integrals of the electron wave-functions . Φ^{TBI} is also long-range in nature hence it is added to the $\Phi^{C.}$ and last term Φ^{VWI} is Van der Waals interaction potential and owes its origin to the correlations of the electron motions in different atoms.

Using the potential energy expression (1), the equations of motion of two cores and two shells can be given as.

$$\omega^2 MU = (R + Z_m C' Z_m)U + (T + Z_m C' Y_m)W \tag{2}$$

$$0 = (T^T + Y_m C' Z_m)U + (S + K + Y_m C' Y_m)W \tag{3}$$

Here, *U* and *W* are vectors describing the ionic displacements and deformations respectively, *Zm* and *Ym* are the diagonal matrices of modified ionic charges and shell charges, respectively, *M* is the mass of the core, *T* and *R* are the repulsive Coulombian matrix respectively; *C'* and *Ym* are the long-range interaction matrices which includes Coulombian and three-body interaction respectively; *S* and *K* are core-shell and shell-shell repulsive interaction matrices respectively T^T is the transpose of the matrix *T*. All these variables are as described in [18].The secular in form of determinant given as:

$$\left|\underline{D}(\vec{q}) - \omega^2 \underline{M}\,\underline{I}\right| = 0 \tag{4}$$

Here $\underline{D}$ $(\vec{q})$ is the (6 x 6) dynamical matrix for Rigid Shell model expressed as :

$$\underline{D}(\vec{q}) = (\underline{R}' + \underline{Z}_m \underline{C}'\underline{Z}_m) - (\underline{T} + \underline{Z}_m \underline{C}'\underline{Y}_m)\times (\underline{S} + \underline{K} + \underline{Y}_m \underline{C}'\underline{Y}_m)^{-1}(\underline{T}^T + \underline{Y}_m \underline{C}'\underline{Z}_m) \tag{5}$$

The numbers of adjustable parameters have been largely reduced by considering all the short-range interactions to act only through the shells. This assumptions leads to $\underline{R} = \underline{T} = \underline{S}$ $\underline{C}'$ is modified long-range interaction matrix given by .Where R, T and S are short ranges forces appear in the form of matrices defined by [13].

$$\underline{C}' = \underline{C} + (Z_m^{-2} Z\, r_0 f_0')\,\underline{V} \tag{6}$$

Where f_0' is the first –order space derivative and Z_m modified ionic polarizability

If we consider only the second neighbour dipole-dipole van der Waals interaction energy, then it is expressed as:

$$\Phi_{dd}^{VWI}(r) = -S_V \left|\frac{C_{++} + C_{--}}{6r^6}\right| = \Phi^V(r) \tag{7}$$

Where, S_v is lattice sum and the constants C_{++} and C_{-} are the Van der Waals coefficients corresponding to the positive-positive and negative-negative ion pairs, respectively. By solving the secular equation (4) the expressions derived for elastic constants ($C_{11,}$ C_{12}, C_{44}) corresponding to VTBFSM are follows as:

$$C_{11} = \frac{e^2}{4r_0^4}\left[-5.112 Z_m^2 + A_{12} + \frac{1}{2}(A_{11} + A_{22}) + \frac{1}{2}(B_{11} + B_{22}) + 9.3204\,\xi'^2\right] \tag{8}$$

$$C_{12} = \frac{e^2}{4r_0^4}\left[0.226 Z_m^2 - B_{12} + \frac{1}{4}(A_{11} + A_{22}) - \frac{5}{4}(B_{11} + B_{22}) + 9.3204\ \xi'^2\right] \tag{9}$$

$$C_{44} = \frac{e^2}{4r_0^4}\left[2.556\, Z_m^2 + B_{12} + \frac{1}{4}(A_{11} + A_{22}) + \frac{3}{4}(B_{11} + B_{22})\right] \tag{10}$$

In view of the equilibrium condition [$(d\Phi/dr)_0=0$] we obtain

$$B_{11}+B_{22}+2B_{12}= -0.6786\, Z_m^2 \tag{11}$$

Where $Z_m^2 = Z^2\left(1 + \frac{16}{Z} f_0\right)$ and $\xi'^2 = Z r_0 f_0'$ (12)

The term fo is function dependent on overlap integrals of electron wave functions. Similarly, expressions for two distinct optical vibration frequencies (ω_L and ω_T) are obtained as:

$$\left(\mu\omega^2{}_L\right)_{q=0} = R' + \frac{(Z'e)^2}{Vf_L}\frac{8\pi}{3V_f}\left(Z_m{}^2 + 6\zeta'^2\right) \tag{13}$$

$$\left(\mu\omega_T{}^2\right)_{q=0} = R'_0 - \frac{(Z'e)^2}{Vf_T}\frac{4\pi}{3V_f}Z_m{}^2 \tag{14}$$

where the abbreviations reported by R.K.Singh [11]stand for

$$R'_0 = R_0 - e^2\left(\frac{d_1{}^2}{\alpha_1} + \frac{d_2{}^2}{\alpha_2}\right); \; Z' = Z_m + d_1 - d_2, \qquad R_0 = \frac{Z^2e^2}{V}(A_{12} + 2B_{12})$$

$$f_L = 1 + \left(\frac{\alpha_1 + \alpha_2}{\mathrm{v}}\right).\frac{8\pi}{3V}\left(Z_m{}^2 + 6\xi'^2\right)$$

$$f_T = 1 - \left(\frac{\alpha_1 + \alpha_2}{\mathrm{v}}\right).\frac{4\pi}{3V}\left(Z_m{}^2\right)$$

where α_1, α_2 electrical polarizabilites andY_1,Y_2 are shell charge parameters of positive and negative ions.

Debye's model define the frequency distribution function which is given by

$$\Theta_D = h\nu_m/K \tag{15}$$

To determine the phonon density of states for each polarization is given by

$$g(\omega) = dN/d\omega = N\int_{BZ}\sum_j \delta\left[\omega - \omega_j(q)\right]dq = (VK^2/2\pi^2).dK/d\omega \tag{16}$$

N = $(L/2\pi)^3$ $(4\pi K^3/3)$, K is wave vector and L^3=V. where N as a normalization constant such that $\int g(\omega)d\omega = 1$ and g$(\omega)d\omega$ is the ratio of the number of eigen states in the frequency interval ($\omega, \omega + d\omega$) to the total number of eigen states $\omega_j(q)$ is phonon frequency of the jth normal mode of the phonon wave vector q.

3. COMPUTATIONS

Model parameters for Rubidium Iodide (RbI) have been computed for [VTBFSM] from the known experimental values of the elastic constants (C_{11}, C_{12} and C_{44}), polarizabilities (α_1, α_2), frequencies $\nu_{LO}(\Gamma)$,$\nu_{TO}(\Gamma)$, $\nu_{LO}(L)$, $\nu_{TO}(L)$, $\nu_{LA}(L)$ and $\nu_{TA}(L)$ and inter atomic separation (r_0). These model parameters are used to calculate the phonon spectra in the first Brillouin zone for the 48- allowed non-equivalent wave vectors.

RESULTS AND DISCUSSION

By use of VTBFSM model parameters and input data have calculated given in Table-1. These model parameters have used to calculate the phonon frequencies in the first Brillouin zone, to compute the variations of Debye temperatures with specific heats in Fig-1. The observed Raman spectra has been interpreted with the help of phonon density of state (PDS) approach and critical point analysis, using the above spectrum shown in Fig-2. The two-phonon Raman spectra are sensitive to the higher frequency side and the specific heats to its lower side of the phonon spectra. Debye temperature variations and combined density of state (CDS) curves for (RbI) through use of VTBFSM have been computed at different temperatures by Blackman's [24].By use of sampling technique the corresponding values of Θ_D have compared with the available experimental data [3,4] and curve for Θ_D against the absolute temperature (T) plotted ,are shown in Fig.-1 for RbI. The calculated (Θ_D–T) curve for RbI has given excellent agreement with the experimental value [25].Though the agreement is almost better with our model, VTBFSM, there is a slight discrepancy between theoretical and experimental results at higher temperatures which can be due to the exclusion of the effect of anharmonicity in the present model. The third order and forth order elastic constant and their pressure derivatives for RbI reported in Table-3 and Table-4 which gives strength to author for complete structural descriptions and dynamical study of RbI crystal. The two-phonon Raman spectra are sensitive to the higher frequency side of the phonon spectra and the specific heats are sensitive to its lower frequency side the calculated results for Raman spectra shown in table-2. This will provide a complete test for the validity of the present model for the all range of the spectra.

Table.1 Input data and model parameters for RbI C_{ij} (in 10^{11} dyn/cm^2), ν (in 10^{12} Hz), ρ (10^{-8} cm), r_o(in 10^{-8} cm), α_i (in 10^{-24} cm^3) and C_{++}, C_{--} (in 10^{-60} erg cm^6)

Input data for RbI		Model parameters for RbI	
Properties	**Values for RbI**	**Properties**	**Values for RbI**
C_{11}	3.210^a	r_0	3.634
C_{12}	0.360^a	$r_0 f_0'$	0.0219
C_{44}	0.292^a	ρ	3.604
$\nu_{LO}(\Gamma)$	3.151^b	Z_m^2	0.74
$\nu_{TO}(\Gamma)$	2.435^b	A_{12}	13.44
$\nu_{LO}(L)$	2.673^b	B_{12}	-0.94
$\nu_{TO}(L)$	1.925^b	A_{11}	–6.01
$\nu_{LA}(L)$	1.948^b	B_{11}	2.79
$\nu_{TA}(L)$	1.671^b	A_{22}	4.92
r_o	3.627^c	B_{22}	–2.67
α_1	1.679^d	d_1	0.14
α_2	6.116^d	d_2	0.124
C_{++}	133^e	Y_1	–3.442
C_{--}	1090^e	Y_2	–6.427

Ref-a-[15],b-[17], c-[18],d-[16]and e-[16]

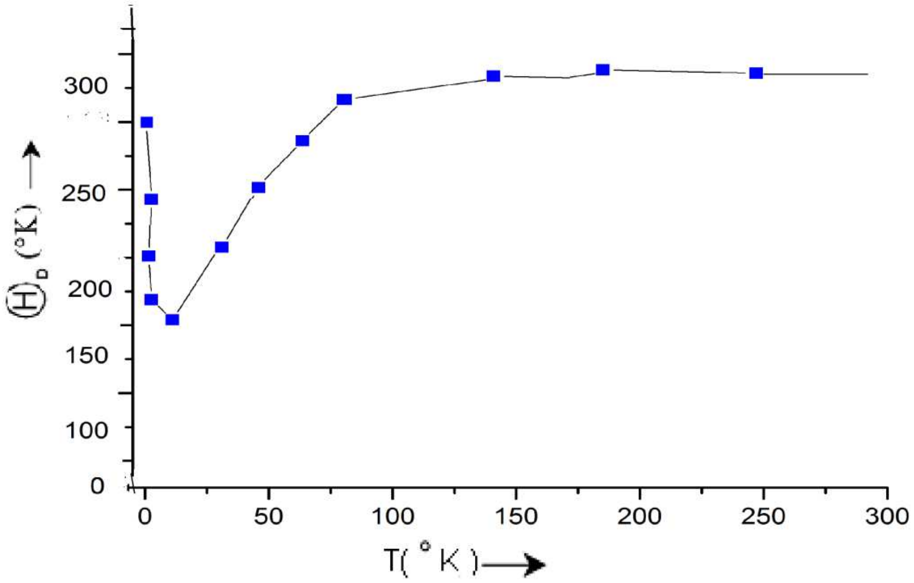

Fig.1. Debye temperature variations for RbI

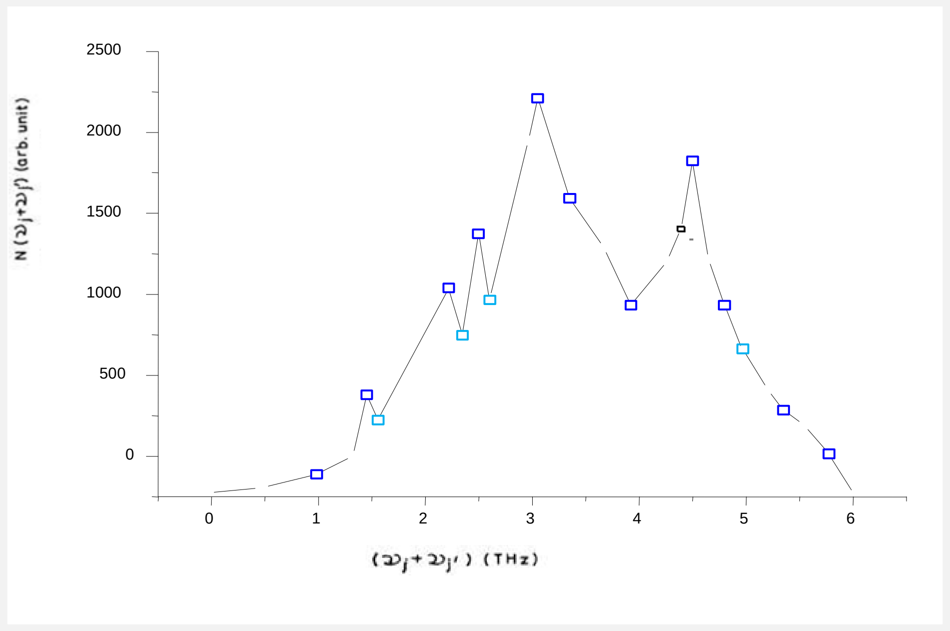

Fig. 2 Combined density state curve for RbI

Table. 2 two phonon raman peaks for RbI

CDS peaks (cm^{-1})[35]	**Raman active**		**CDS peaks (cm^{-1})[35]**	**Raman active**	
	Present study			**Present study**	
	Assignments	**Values (cm^{-1}) by [VTBFSM]**		**Assignments**	**Values (cm^{-1}) by [VTBFSM]**
51	2TA(X)	50	127	2TO(L)	130
55	TO(X)–TA(X)	57	145	LO(L)+TA(L)	149
60	LO(X)–TA(X)	56	150	LO(L)+TO(L)	153
69	LA(X)+TA(X)	69	162	2TO(Δ)	162
80	2LA(X)	88	163	2TO(X)	164
108	TO(X)+TA(X)	107	165	2LO(X)	168
115	2TA(L)	111		LO+TA(Δ)	161
118	TO(L)+TA(L)	119		LA-TA(Δ)	31

CONCLUSION

The theoretical investigation of Debye temperature and Raman/IR Raman spectra explain correctly by use of calculated results of model parameter. The agreement between experimental [6,7] and our theoretical peak is very good for Raman spectra of RbI. The interpretation of Raman spectra achieved from PDS approach and critical point analysis may be considered satisfactory in all cases. Our extensive study of two-phonon Raman spectra is basically aimed to correlate the theoretical and optical experimental results. A successful interpretation of these spectra has provided the next best test of any model for higher range of frequency spectra. The calculation of TOEC & FOEC with pressure derivative reported in Table .3 & 4 successfully .The theoretical results have been compared with the available experimental data and reveal better agreement [10-14].

Therefore, it may be inferred that the inclusion of van der Waals interaction is very essential for the complete description of the phonon dynamical behaviour of Rubidium crystals.The basic idea about the RbI crystal has taken by [26] and author highly thank him. Some researchers also have been successfully reported theoretical result for other alkali halides [27-34].

Table. 3 TOEC and FOEC (in units 10^{12} dyn / Cm^2) for RbI

Property	**C_{111}**	**C_{112}**	**C_{123}**	**C_{144}**	**C_{166}**	**C_{456}**	**C_{1111}**	**C_{1112}**	**C_{1166}**	**C_{1122}**	**C_{1266}**	**C_{4444}**	**C_{1123}**	**C_{1144}**	**C_{1244}**
RbI (Present)	89.21	0.17	0.80	0.73	0.32	0.06	130.43	0.39	0.29	0.51	0.38	0.50	-0.23	-0.13	-0.22

Table- 4 Pressure derivatives of SOEC and TOEC (dimensionless) of RbI

Property	**dK'/dP**	**dS'/dP**	**dC'_{44}/dP**	**dC'_{111}/dP**	**dC'_{112}/dP**	**dC'_{166}/dP**	**dC'_{123}/dP**	**dC'_{144}/dP**	**dC'_{456}/dP**
RbI (Prsent)	5.95	6.98	-0.57	-779.81	-1.97	1.53	1.65	-0.13	1.71

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