ORIGINAL PAPER

LATTICE DYNAMICAL STUDY OF RBF BY USE OF (VTBFS) MODEL POTENTIAL

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Abstract. *In present paper, combined density of states, Debye temperature and elastic property of RbF have been theoretically studied using the lattice dynamics with the help of existing experimental data. The present model is incorporated in a framework of van der Waals three-body force shell model (VTBFSM) for RbF, based on the many-body interactions from the charge transfer mechanisms & electron-shell deformation. VTBFSM includes (TBI) three-body interactions and (VWI) van der Waals interactions in the framework of both (IPRSM) ion polarizable rigid shell model including next-nearest neighbour interaction approach with both polarizable ions. The merit of this model has been verified by an in-depth comparison of theoretical and experimental results.*

Keywords: *lattice vibrational properties, Debye temperature, combined density of states curve, Raman spectroscopy.*

1. INTRODUCTION

The pioneer work of Kellerman [1] for ionic interactions in the alkali halides has devoted a considerable attention theoretically as well as experimentally. Lowdin's [2] and Lundqvist's [3] theory for ionic solids leads to the first important term as many body force in which the three body component included. Couchy discrepancy has been explained by this term in an approximate way for alkali halides. Science it considers the crystal lattice as static and thus completely ignores the displacements of the electron clouds relative to the corresponding nuclei. The electronic polarization is produced due to vibration of lattice and shells move relatively to their cores and due to shifting of electrons of each atom in the presence of other atoms with respect to the nucleus the atom become an electric dipole. As the resulting atom induces the van der Waals interaction potential due to the instantaneous dipole moment of a closed shell. The Hietler London and the free-electron approximations will employ, the inclusion of VWI and TBI effects in RSM [4]. The effects of VWI and TBI in the framework of IPRSM effective up to the second neighbour with short-range interactions. Therefore, the most realistic model for the complete harmonic dynamical behavior of the crystals under consideration can be developed by introducing the effect of VW and TB interaction. The experimental investigation for phonon dispersion curve of RbF has been done with coherent inelastic neutron scattering, Debye temperature variations & two-phonon Raman spectra [5]. The elastic constants and dielectric constants [6], the physical and natural properties of the (RbF) have been attracted and their interpretations by means of different theoretical models [7-11], which has also successfully describe their interesting properties.

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The Kellermann [1] RIM model had failed to explain the different properties like dynamic, optical and elastic of alkali halides. Then the Karo and Hardy [12] deformation dipole model, Woods et al ,Overhauser & Dick [13] rigid shell mode1 by two different groups of workers has reported lattice property of alkali halides. The other most prominent model was also proposed by some researcher amongst them are Schroder [14] breathing shell mode1 of, Basu and Sengupta [15] deformable shell model of and three-body force shel1 mode1 of Verma & Singh [16-17] for such halides. In consideration of the effect of VWI, reported by Upadhyaya et al [18] have been obtained excellent results between experiment & theory for ionic halides and semiconductors. This has to motivate the author to incorporate this model in the present study.

The VWI potential owes its origin to the correlations of the motions of an electron in various atoms, due to which shifting in electrons of each atom has occurred with respect to the nucleus in the presence of other atoms and consequently an atom becomes an electric dipole. The present mode1 thus consists of the long-range screened Coulomb, VWI, TBI and the short-range overlap repulsion operative up to the second-neighbor ions in RbF. The relevant expression for the crystal potential per unit cell can be derived with VTBFSM, is given as

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

where Φ^{C} is long-range Coulomb interaction potentia1. Thus, total Coulomb interaction energy of i-th ion with j-th ion are as $\Phi^{C}(\vec{r}_{ij})$for the crystal is given by

$$\boldsymbol{\Phi}^{C}(r)=\sum_{j}{}'\boldsymbol{\Phi}^{C}\left(r_{ij}\right)=\sum_{j}{}'\boldsymbol{\varepsilon}_{ij}\,\frac{e^{2}}{\left|\vec{r}_{ij}\right|}$$

For infinite lattice in crystal the Coulomb potential energy is given as

$$\boldsymbol{\Phi}^{C}=\boldsymbol{\alpha}_{M}\,\frac{Z^{2}e^{2}}{r_{\mathrm{o}}}$$

where, α_m and r_0 are Madelung constant and equilibrium nearest neighbors distance.

The analytical expressions by the inverse and exponential power laws for the repulsive energy are given as

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

where, a (or b) and η(orρ) are the Born exponents called the strength and hardness parameters, respectively. Φ^{R} is a short-range overlap repulsion potential.Third term Φ^{TBI} long-range TBI interaction potential expressed as

$$\boldsymbol{\Phi}^{TBI}=\boldsymbol{\alpha}_{m}\,\frac{Z^{2}e^{2}}{r_{0}}\left[\frac{2n}{Z}\,f(r)_{0}\right]$$

where, the term $f(r)_0$ is the equilibrium electron wave-functions. Since we consider only one ion to be polarizable and deformable, the basic equations of Singh and verma's [16] model are modified. The secular determinant equation is given by

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

Here $\underline{\vec{D}}$ (*q)* is the (6 x 6) dynamical matrix for Rigid Shell model expressed as:
The dipole-dipole (VWI) energy up to second neighbour is expressed as:

$$\Phi_{dd}^{VWI}(r) = -S_V \left| \frac{C_{++} + C_{--}}{6r^6} \right| = \Phi^V(r) \tag{3}$$

where S_v is lattice sum and the constants C_{++} and C_{--} are the positive-positive and negative-negative ion pairs, respectively. By use of the secular equation (2) the expressions for elastic constants can derive and given as:

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

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

$$C_{44} = \frac{e^2}{4r_0^4}\left[2.556Z_m^{\ 2} + B_{12} + \frac{1}{4}(A_{11}+A_{22}) + \frac{3}{4}(B_{11}+B_{22})\right] \tag{6}$$

at equilibrium condition [$(d\Phi/dr)_0=0$] we obtain

$$B_{11}+B_{22}+2B_{12} = -0.6786\ Z_m^{\ 2} \tag{7}$$

where

$$Z_m^2 = Z^2\left(1+\frac{16}{Z}f_0\right) \qquad \text{and} \qquad \xi'^2 = Zr_0 f_0^{'} \tag{8}$$

the frequency distribution function by use of Debye's model is given by

$$\Theta_D = h\nu_m/K \tag{9}$$

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

$$g(\omega) = dN/d\omega = N\int_{BZ}\sum_j \delta[\omega-\omega_j(q)]dq = (VK^2/2\pi^2).dK/d\omega \tag{10}$$

and

$$N = (L/2\pi)^3\,(4\pi K^3/3)$$

where N as a normalization, K is wave vector and $L^3=V$. The value of $g(\omega)d\omega$ 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 such that $\int g(\omega)d\omega = 1$.

2. NUMERICAL COMPUTATIONS

In the present paper eight parameters including elastic constants (C_{11}, C_{12} and C_{44}),six short range force constants a parameters r_0 f_0'arising from the deformation forces, the ionic charge z, the shell charge Y, polarizabilities (α_1, α_2), and mechanical polarizability 'd' developed by [16] have theoretically calculated for RbF and given in Table 1. By solving Eq.1-2 we can obtain the phonon spectra in the first Brillouin zone for the non-equivalent 48-allowed wave vectors. The theoretical results obtained by three-body force shell model. We have used the computed vibration spectra to study the dynamical properties like specific heat and IR/Raman spectra in the present paper. The specific heat and Debye temperature Θ_D has been calculated as function of temperature T from the lattice frequency spectra is shown in Fig. 1. The (CDSc) have been obtained by computing the density of states N ($\nu_j + \nu'_j$) of the combined frequencies ($\nu_j + \nu'_j$) from the knowledge of lattice vibration frequency spectra. The frequencies values corresponding to theoretical and experimental peaks and to Cauchy-Discrepancy for lattice dynamics of RbF have been reported in Tables 2-3.

Table.1 Input data and model parameters for RbF
C_{ij} (in 10^{11} dyn/cm^2), 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 RbF		**Model parameters for RbF**		**MODEL PARAMETERS Expt. 1st model result [22]**	
PROPERTIES	VALUES FOR RBF	PROPERTIES	VALUES FOR RBF	PROPERTIES	
C_{11}	6.55[A]	$R_0 F_0'$	0.0445	A_{12}	12.32 ± 0.31
C_{12}	1.35[A]	Z_M^2	0.8410	B_{12}	----------
C_{44}	0.965[A]	A_{12}	11.4112	A_{11}	-0.17 ± 0.13
R_O	2.80[A]	B_{12}	-0.8646	B_{11}	0.050 ± 0.036
α_1	0.037[B]	A_{11}	-0.9534	A_{22}	----------
α_2	0.032[B]	B_{11}	5.5646	B_{22}	----------
C_{++}	133[A]	A_{22}	0.6945	α_1	1.54 ± 0.18
C_{--}	29.2[A]	B_{22}	-5.4234	α_2	1.15 ± 0.18
		D_1	0.06441	D_1	-0.007 ± 0.018
		D_2	0.02454	D_2	0.1 ± 0.013
		Y_1	-7.4213	R_O	2.805
		Y_2	-8.404	Z	1.01 ± 0.02

Ref-a-[5],b-[23]

Table 2. Two phonon Raman peaks, TOEC and FOEC (in units 10^{12} dyn / Cm^2), Pressure derivatives of SOEC and TOEC (dimensionless) for RbF.

Raman Active - (Present study)			**TOEC and FOEC (in units 10^{12} dyn / Cm^2)**		**Pressure derivatives of SOEC and TOEC (dimensionless)**	
Frequency In (THz)	Branch	Values (cm^{-1}) by [VTBFSM]	Property	RbF (Present)	Property	RbF (Present)
3.54	2TA(X)	109	**C_{111}**	165.5469	dK′/dP	4.9152
3.08	TO(X)–TA(X)	121	C_{112}	-0.5540	dS′/dP	4.7543
3.215	LO(X)–TA(X)	119	C_{123}	0.34093	dC'_{44}/dP	-1.5671
4.735	LA(X)+TA(X)	158	C_{144}	0.2341	dC'_{111}/dP	-771.4254
5.93	2LA(X)	208	C_{166}	-0.2955	dC'_{112}/dP	-3.4465
6.625	TO(X)+TA(X)	230	C_{456}	0.1921	dC'_{166}/dP	1.9814
3.73	2TA(L)	139	C_{1111}	187.5244	dC'_{123}/dP	1.9402
6.31	TO(L)+TA(L)	230	C_{1112}	2.4796	dC'_{144}/dP	-0.09751
8.89	2TO(L)	322	C_{1166}	1.5436	dC'_{456}/dP	0.93550
4.40	2LO(L)	150	C_{1122}	2.4240		
6.645	LO(L)+TO(L)	236	C_{1266}	1.4445		
9.53	2TO(Δ)	319	C_{4444}	1.4491		
9.71	2TO(X)	351	C_{1123}	-1.4234		
9.97	2LO(X)	347	C_{1144}	-0.5414		
7.57	LO+TA(Δ)	249	C_{1244}	-0.4964		
130	LA-TA(Δ)	47	C_{1456}	-0.4356		

Table 3. Cauchy-Discrepancy (in units 10^{12} dyne/cm^2) for lattice dynamics of RbF.

Property	**C_{112}– C_{166}**	**C_{123}– C_{456}**	**C_{144}– C_{456}**	**C_{123}– C_{144}**	**C_{1112}– C_{1166}**	**C_{1122}– C_{1266}**	**C_{1122}– C_{4444}**	**C_{1123}– C_{1144}**	**C_{1123}– C_{1456}**	**C_{1123}– C_{1244}**
Values for RbF	-0.2585	0.14883	0.0420	0.10683	0.9360	0.9795	0.9749	-0.882	-0.9878	-0.927

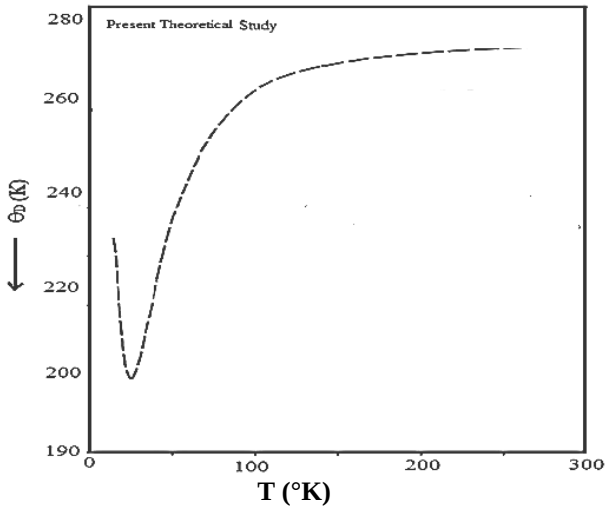

Figure 1. Debye temperature variations for RbF.

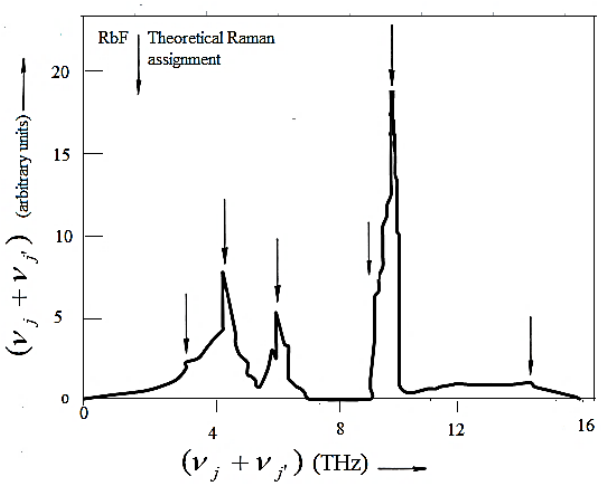

Figure 2. Combined density of States Curve for RbF.

3. DISCUSSION

At a glance, the various investigated properties in the present study clearly show the success of the used model which has been providing complete description about RbF. The mode1 parameters are determined in Table-l.The knowledge of the model parameters has been used to solve the secular equation for specified values of wave vectors in the first Brillouin zone, which is divided in an evenly spaced sample of l000 wave vectors (Kellermann) [1]. From the symmetry, these l000 points are reduced to 48 non- equivalent points at which the vibration frequencies have been obtained by solving the secular determinant. Debye temperature variations at different temperatures by Blackman's [19] and (CDC) curves for (RbF) crystals have been computed by using VTBFSM model.By using the sampling technique and the corresponding values of Θ_D has been compared with the available experimental data [20-22] and curve for Θ_D Vs absolute temperature (T) plotted, are shown in Fig. l for RbF. In this temperature range one should take into account the temperature dependence of the frequency spectrum, this requires, however, knowledge of the phonon frequencies at more than one temperature. The variations of Θ_D with specific heats have used to compute with phonon frequencies in the first Brillouin zone, shown in Fig 1. In the present model due to the exclusion of the effect of anharmonicity, there is a slight discrepancy between theoretical and experimental results at higher temperatures can be seen.Though the agreement is almost better with VTBFSM. The calculated (Θ_D–T) curve for RbF has given excellent agreement with the experimental value [5]. The observed Raman spectra and critical point analysis have been interpreted with the help of PDS approach, using the above spectrum given in Fig. 2. The two-phonon Raman spectra are sensitive to the high-frequency side of the phonon spectra and the specific heats are sensitive to its lower side which is stated the validity of the present model for an entire wavelength range. The third order and fourth order elastic constant and their pressure derivatives for RbF (Tables 2-3) are probably the first reports and in the absence of experimental data, their reliability test is not possible. However, it is interesting that they show a close resemblance in sign with those obtained for NaCl structure, crystal reported in Table 3, which gives strength to the author for complete structural descriptions and dynamical study of RbF crystal.

4. CONCLUSIONS

The investigation of model parameter, Debye temperature and Raman spectra have been reported using the van der Waals three-body force shell model **(**VTBFSM**)** for RbF. The agreement between experimental [5] and our theoretical peak is very good for Raman spectra of RbF. For correlating the theoretical and optical experimental results we have extensive study about the two-phonon Raman spectra. A successful interpretation of these spectra has been providing the next best test of any model for a higher range of frequency spectra. The small deviations have been obtained at the higher temperature side due to harmonic approximation in the Debye curve. The calculation of TOEC & FOEC with pressure derivative reported in Table-3 successfully.The better agreement has been compared and reveals with the available experimental data [11-15] and theoretical results. The motivation of this work is the availability of the theoretical [23-24] and experimental [22] work on Rubidium.Therefore, it may be inferred that the inclusion of VW interaction is very essential for the complete description of the phonon dynamical behavior of Rubidium crystals. Some researchers also have been successfully reported theoretical result for other alkali halides [25-34]. In view of its adequacies, the present model may be understood to provide a powerful and simple approach for a comprehensive study of the harmonic as well as anharmonic elastic properties of the crystals under- consideration. The only limitation of the model is the requirement of knowledge of certain experimental information to be used as input data.

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