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Harmonic dynamical studies of potassium halides (KCl, KBr, KI and KF)

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ABSTRACT

A unified description of a series of Phonon properties of potassium halides (KCl, KBr, KI and KF) by means of van der Waals three-body force shell model (VTBFSM) is presented in this paper. This model includes van der Waals interactions (VWI) and three-body interactions (TBI) in the framework of both ion polarizable rigid shell model (RSM). In fact the present model (VTBFSM) has revealed much better descriptions of IR/Raman spectra and anhormonic properties and other dynamical properties of potassium halides .Behavior of potassium halides has been investigated theoretically by using van der Waals three-body force shell model (VTBFSM). A comparative study of the dynamical behavior of all these halides has also been done between the halides in present models. Good agreement has been observed between the theoretical and experimental results, which give confidence that it is an appropriate model for the complete description of ionic crystals with NaCl structure.

Key words: Phonons; van der Waal's model; Debye temperature; combined density curve; phonon dispersion curve and IR/Raman spectra

INTRODUCTION

From last two decades, a considerable interest has been shown by theoretical and experimental workers in the investigation of lattice dynamical behavior of potassium halides. The subject has so for been extensively investigated by several theoretical models, which have developed through simple phenomenological approaches to sophisticated microscopic approaches. The knowledge of phonon dispersion curves (PDC), Debye temperature variation, two phonons IR/Raman spectra, third order elastic constants (TOEC), fourth order elastic constants (FOEC), the pressure derivatives of second order elastic constants (SOEC) and Cauchy discrepancy (C_{12} - C_{44}) have been of fundamental importance. Due to availability of experimental data on elastic [1], dielectric [2], vibrational [3-7] and optical properties [8] of these solid, it is quite interesting

U C Srivastava

and encouraging for theoretical workers to predict its lattice dynamical properties. In the recent past some researchers have studied the lattice dynamics of MC_{60} compounds in FCC (Face centered cubic) phase by using Rigid Shell Model (RSM) [9-11]. The TOEC, FOEC and the pressure derivatives of SOEC and their experimental values reported independently by Roberts [8] and Chang [12]. In the present paper we have study the lattice dynamics of an alkali halide, namely potassium halide. This new model [VTBFSM] considers all possible interactions for explaining the harmonic as well as an-harmonic properties of potassium halides.

2. Theory

The essential formalism of (VTBFSM) is the inclusion of VWI and TBI in the framework of RSM. The interactions system of present model thus consists of long-range screened Coulomb, VWI, three-body interactions and short-range overlap repulsion operative up to the second - neighbor's ions in potassium halides. Looking into the adequacy of the interaction system, the present model successfull for the dynamical descriptions of potassium halides. The general form of VTBFSM can be derived from the crystal potential energy per unit cell, given by

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

Where, First term Φ^{C} is Coulomb interaction potential which is long-range in nature. An ionic crystal 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

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

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. If we consider infinite lattice, the Coulomb potential energy for the whole

crystal is given as
$$\boldsymbol{\Phi}^{C} = \boldsymbol{\alpha}_{M} \ \frac{Z^{2} e^{2}}{r_{0}}$$

Where, α_m is the Modelung constant and r_0 is the equilibrium nearest neighbors distance.

Second term Φ^{R} is short-range overlap repulsion potential. In order to prevent the lattice from collapsing under the Coulomb attraction, there must be the overlap repulsion between the ions. These forces have quantum mechanical origin and arise when further overlap between neighbouring ions is restricted by the Pauli Exclusion Principle. The repulsive energy in not so well understood as the Coulomb attraction. The most commonly used analytical expressions for the repulsive energy are given by the inverse and exponential power laws such that

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

Where, a (or b) and $\eta(or\rho)$ are the Born exponents called the strength and hardness parameters, respectively.

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10

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. This does not mean that the electron-charge density is sum of charge densities for a system of free-ions. The reason for this lies in the fact that when the ions are put in a lattice their electron wave function overlaps and get deformed. These effects lead to the non-orthogonality of the one electron wave function. This non-orthogonality causes the charge distribution to differ from the sum of the densities for free ions, the differences being more pronounced in the regions where the overlap between the atomic wave-functions in large. As a natural consequence of the anti-symmetry requirement on the wave function [13], 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 [15] and Lundqvist [16]. This interaction potential is 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 a function dependent on the overlap integrals of the electron wave-functions and the subscript zero on the bracket indicates the equilibrium value of the quantities inside. Φ^{TBI} is also long-range in nature hence it is added to the Φ^{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) and introducing the effect of VWI and TBI, the secular determinant is given as

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

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

$$\underline{D}(\vec{q}) = (\underline{R'} + \underline{Z}_m \underline{C'Z}_m) - (\underline{T} + \underline{Z}_m \underline{C'Y}_m) \times \\
(\underline{S} + \underline{K} + \underline{Y}_m \underline{C'Y}_m)^{-1} (\underline{T}^T + \underline{Y}_m \underline{C'Z}_m)$$
(3)

In order to reduce the number of parameters they have been treated equal (R = T = S) by allowing short range forces act only through the shells.

Where R, T and S are short ranges forces appear in the form of matrices defined by [16].

$$\underline{\mathbf{C}}' = \underline{\mathbf{C}} + (\mathbf{Z}_{\mathrm{m}}^{-2} \, \mathbf{Z} \, \mathbf{r}_0 f_0') \, \underline{\mathbf{V}} \tag{4}$$

Where C and V are the Coulomb and three–body interaction matrices, $f_0^{'}$ is the first –order space derivative and Z_m modified ionic polarizability

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

$$\Phi_{dd}^{VWI}(r) = -S_V \left| \frac{C_{++} + C_{--}}{6r^6} \right| = \Phi^V(r)$$
(5)

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11

(9)

Where, S_{ν} is lattice sum and the constants $C_{\scriptscriptstyle ++}$ and $C_{\scriptscriptstyle --}$ are the van der Waals coefficients corresponding to the positive-positive and negative-negative ion pairs, respectively.

By solving the secular equation (2) the expressions derived for elastic constants (C11, C12, C44) corresponding to (VTBFSM) are follows as:

$$\frac{4r_0^4}{e^2}C_{11} = \left[-5.112Z_m^2 + A_{12} + \frac{1}{2}(A_{11} + A_{22}) + \frac{1}{2}(B_{11} + B_{22}) + 9.3204\,\boldsymbol{\xi}'^2\right]$$
(6)

$$\frac{4r_0^4}{e^2}C_{12} = \left[0.226Z_m^2 - B_{12} + \frac{1}{4}(A_{11} + A_{22}) - \frac{5}{4}(B_{11} + B_{22}) + 9.3204\,\boldsymbol{\xi}^{\prime 2}\right]$$
(7)

$$\frac{4r_0^4}{e^2}C_{44} = \left[2.556Z_m^2 + B_{12} + \frac{1}{4}(A_{11} + A_{22}) + \frac{3}{4}(B_{11} + B_{22})\right]$$
(8)

In view of the equilibrium condition $[(d\Phi/dr)_0=0]$ we obtain $B_{11}+B_{22}+B_{12}=-1.165 Z_m^2$

Where
$$Z_m^2 = Z^2 \left(1 + \frac{12}{Z} f_0 \right)$$
 and $\xi'^2 = Zr_0 f_0'$ (10)

The term fo is function dependent on overlap integrals of electron wave functions. Similarly, expressions for long wave optical vibration frequencies ($_{\omega L}$ and $_{\omega T}$) can be written as:

$$\left(\mu\omega_{L}^{2}\right)_{q=0} = R_{0}' + \frac{(Z'e)^{2}}{Vf_{L}} \cdot \frac{8\pi}{3} \left(Z_{m}^{2} + 6\xi'^{2}\right)$$
(11)

$$\left(\mu\omega_{T}^{2}\right)_{q=0} = R_{0}^{\prime} - \frac{(Z^{\prime}e)^{2}}{Vf_{T}} \frac{4\pi}{3} Z_{m}^{2}$$
(12)

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

$$R'_{0} = R_{0} - e^{2} \left(\frac{d_{1}^{2}}{\alpha_{1}} + \frac{d_{2}^{2}}{\alpha_{2}} \right); Z' = Z_{m} + d_{I} - d_{2}$$

$$R_{0} = \frac{Z^{2} e^{2}}{V} \left(A_{12} + 2B_{12} \right) , f_{L} = 1 + \left(\frac{\alpha_{1} + \alpha_{2}}{V} \right) \frac{8\pi}{3} \left(Z_{m}^{2} + 6\xi'^{2} \right)$$
and
$$f_{T} = 1 - \left(\frac{\alpha_{1} + \alpha_{2}}{V} \right) \frac{4\pi}{3} \left(Z_{m}^{2} \right)$$

а

where α_1, α_2 electrical polarizabilities and Y_1, Y_2 are shell charges of positive and negative ion.

$$d_1 = \frac{-\alpha_1 R_0}{e^2 Y_1}$$
, $d_2 = \frac{-\alpha_2 R_0}{e^2 Y_2}$ and $V = 2r_0^3$ (Unit cell volume for NaCl type lattice)

by solving the dynamical matrix along [.5, .5, .5] directions at L-Point modified expressions for $\omega_{LO}(L), \omega_{TO}(L), \omega_{LA}(L), and \omega_{TA}(L)$ are as follows:

$m_2\omega_{LO}^2(L) = R_0 + [(e^2/V) (2A_{22} + B_{22})] + [(e^2/V) Z_m^2C_{1L}]$	(13)
$m_1\omega_{LA}^2(L) = R_0 + [(e^2/V) (2A_{11} + B_{11})] + [(e^2/V) Z_m^2C_{1L}]$	(14)
$m_2\omega_{TO}^2(L) = R_0 + [(e^2/2V) (A_{22} + 5B_{22})] + [(e^2/V) Z_m^2C_{1T}]$	(15)
$m_1\omega_{TA}^2(L) = R_0 + [(e^2/2V) (A_{11}+5B_{11}] + [(e^2/V) Z_m^2C_{1T}]$	(16)
r 1	

$$C'_{1L} = \left[C\underline{C} + Zr_0 f'_0 Z_m^{-2} \underline{V} + Z^2 Z_m^{-2} \underline{D}\right]_{XX}$$

$$C'_{1L} = \left[C\underline{C} + Zr_0 f'_0 Z_m^{-2} \underline{V} + Z^2 Z_m^{-2} \underline{D}\right]_{YY}$$
(17)

Where

<u>C</u> and <u>V</u> is Coulomb and three body force matrices evaluated at L-Point and <u>D</u> is van der Waals contribution. We have used the further expressions for the TOEC, FOEC and pressure derivatives of SOEC and TOEC derived by Roberts et al [8].

3 Computations:-

The model parameters have been determined from the knowledge of experimental values of the equilibrium interatomic separation (r_0), the elastic constants (C_{11} , C_{12} and C_{44}), polarizabilities (α_1,α_2) and frequencies $\nu_{LO}(\Gamma),\nu_{TO}(\Gamma),\nu_{LO}(L)$, $\nu_{TO}(L)$, $\nu_{LA}(L)$ and $\nu_{TA}(L)$. These model parameters are used to compute the phonon spectra for the allowed 48 non-equivalent wave vectors in the first Brillouin zone. The frequencies along the symmetry directions have been plotted against the wave vector to obtain the phonon dispersion curves (PDC). These curves have been compared with those measured by means of the coherent inelastic neutron scattering technique. Since the neutron scattering experiments provide us the data for the symmetry directions only, we have studied the Debye temperatures variation and two-phonon combined density of states (CDS) for the complete description of the frequencies for the Brillouin zone. For this purpose, the specific heat C_v has been computed at different temperatures using Blackmann's [52], sampling technique. The corresponding values of Θ_D have been plotted against the absolute temperature (T) in figure-5. They have also been compared with the available experimental data.

The phonon spectra have been used to calculate the combined density of states (CDS), N ($v_j + v_j'$) corresponding to the sum modes ($v_j + v_j'$), following the procedure of Smart et al. [53]. A histogram between N($v_j + v_j'$) and ($v_j + v_j'$) is plotted and smoothed out to obtain the CDS curves. These curves show well defined peaks which correspond to two-phonon infra-red absorption and Raman scattering peaks. These CDS peaks have been compared with the available observed peaks. Since the division of the Brillouin zone in the present case is somewhat coarse, therefore, the fine structure of the infra-red and Raman shifts may not be reproduced completely. In order to interpret them, the critical point analysis has been used following the method prescribed by Burstein et al. [60]. Besides above properties, the third order elastic constants (TOEC) and fourth order elastic constants (FOEC) and their pressure derivatives have also been calculated in table-7 and 8. The input data along with their relevant references and calculated model parameters for KF, KCl, KBr and KI are given in tables -1 and 2, respectively. The phonon dispersion curves for these halides have been presented in figs-1, 2, 3 and 4. The experimental values [3, 4, 12-14] for these curves have also been shown on the same figure for visual comparison. Variation of Debye temperature Θ_D with temperature T for

KF, KCl, KBr and KI have been plotted in the same fig.-5. (Θ_D - T) curves for KF, KCl, KBr and KI have also been compared with the available experimental data [16].

Properties	Values for	Values for	Values for KBr	Values for
	KF	KCl		KI
C ₁₁	7.570^{a}	4.832 ^b	3.980 [°]	3.380 ^d
C ₁₂	1.350 ^a	0.542 ^b	0.560 [°]	0.220 ^d
C ₄₄	1.336 ^a	0.663 ^b	0.520 °	0.368 ^d
$v_{LO}(\Gamma)$	9.540 ^e	6.390 ^f	5.000 ^g	4.260 ^h
ν _{TO} (Γ)	5.660 ^e	4.450^{f}	3.600 ^g	3.210 ^h
$v_{LO}(L)$	8.060 ^e	4.750 ^f	4.330 ^g	3.940 ^h
v _{to} (L)	5.520 ^e	4.620 ^f	2.960 ^g	2.930 ^h
$v_{LA}(L)$	5.670 ^e	3.500 ^f	2.670 ^g	2.060 ^h
v _{ta} (L)	3.730 ^e	3.180 ^f	2.220 ^g	1.650 ^h
r _o	2.648 ⁱ	3.117 ⁱ	3.278 ^j	3.492 ^k
α ₁	1.201 ¹	0.830 ^m	1.030 ^m	1.370 ^m
α_2	0.759^{1}	3.340 ^m	4.500 ^m	5.310 ^m
C++	64.90 ⁿ	64.90 ⁿ	64.90 ⁿ	64.90 ⁿ
C	29.20 ⁿ	271 ⁿ	503 ⁿ	1090 ⁿ

 $\begin{array}{c} \mbox{Table-1 Input data for KF, KCl, KBr and KI C_{ij} (in 10^{11} dyn/cm^2), v (in 10^{12} Hz), r_o (in 10^{-8} cm), α_i (in 10^{-24} cm^3) and C_{++}, C_{--} (in 10^{-60} erg cm^6) $ \end{tabular}$

a-Calculated from compressibility value Ref. 1, b-Ref.2, c-Ref. 7, d-Ref. 21, e-Ref. 3, f-Ref. 4, g-Ref. 16, h-Ref. 13, i-Ref. 17, j-Ref. 16, k-Ref. 22, l-Ref. [194], m-Ref. 18, n-Ref. 19

Table -2	Model	parameters	of	potassium	halides
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Properties	Values for	Values for	Values for	Values for
-	KF	KCl	KBr	KI
\mathbf{f}_0	-0.0144	-0.0129	-0.0139	-0.0084
r ₀ f ₀ '	-0.0128	-0.0212	-0.0443	-0.0409
Z_m^2	0.8261	0.8444	0.8325	0.8985
A ₁₂	11.6719	14.1470	13.3905	20.6045
B ₁₂	-0.7319	-2.6346	-3.0275	-3.7923
A ₁₁	-0.5888	-3.8638	-4.8688	-1.8612
B ₁₁	-0.3640	1.2219	-2.6324	-2.0391
A ₂₂	0.2694	1.2339	9.3775	3.8319
B ₂₂	-1.3303	-0.4289	1.3649	-1.6938
d ₁	0.0831	0.0362	0.1346	0.0452
d ₂	0.0379	0.1035	0.2086	0.1855
Y ₁	-4.0840	-4.6946	-1.2215	-4.7047
Y ₂	-5.6541	-6.6206	-3.4430	-4.4489
Y	-12.2627	-12.7256	-11.9229	-7.4029

The Combined density of states for KF, KCl, KBr and KI have been presented in figures- 6,7,8 and 9 respectively. CDS peaks, observed data on two phonon IR/Raman spectra and their assignments from present study have been shown in tables 3 to 6.The third order and Fourth order elastic constants, pressure derivatives of second order elastic constants and Cauchy Discrepancy of potassium halides have been presented in tables (7–9).Experimental results [18,19] on these elastic constants and their pressure derivatives have also been shown in the same tables for visual comparison.

	Rama	n Active	Infra-red Active		
CDS Peaks (cm ⁻¹)	Presen	nt Study	Present Study		
	Assignments	Values (cm ⁻¹)	Assignments	Values(cm ⁻¹)	
87	LA-TA(X)	86			
123	LO–TA(X)	123			
154					
190	2TA(Δ) 2TA(X)	186 193			
280	$\begin{array}{c} LA+TA(\Delta) \\ LA+TA(X) \end{array}$	280 280			
297	$\begin{array}{c} \text{TO+TA}(X) \\ \text{TO+TA}(\Delta) \end{array}$	293 293	$TO+TA(\Delta)$	293	
320	$LO+TA(\Delta)$	320	$LO+TA(\Delta)$	320	
365	2LA(X)	366	$2LA(\Delta)$	373	
413	$LO+LA(\Delta)$	413	$LO+LA(\Delta)$	413	
426	$LO+TO(\Delta)$	426	$LO+TO(\Delta)$	426	

Table -3 Assignment of two phonon Raman and Infra-red peaks for KF

Table -4 Assignment of two	phonon Raman and	Infra-red	peaks for KCl
Daman Astina			Traffing and A stin

			Raman Active	Infra-red Active				
CDS Peaks	Obse	rved*	Presen	at Study	Observed*	Present Stu	ıdy	
(cm)	Peaks	Peaks (cm ⁻		Assignments	Values (cm ⁻¹)	Peaks (cm ⁻¹)	Assignments	Values (cm ⁻¹)
50		50 ^b	LO-LA(X)	50			_	
120	122 ^a	118 ^b	2TA(X)	123				
166		166 ^b	LA+TA(X)	170				
200			$TO+TA(\Delta)$	201	196 ^a			
213	212 ^a				207 ^a	$LO+TO(\Delta)$	205	
236	237 ^a		2LA(L)	233	243 ^a			
288		290 ^b	2TO(Γ)	293	285 ^a	$LO+LA(\Delta)$	285	
330	331 ^a							
350	349 ^a							

a-Ref. 5, b-Ref. 7

Table -5 Assignment of two phonon Raman and Infra-red peaks for KBr

	Rama	an Active		Infra-red Active		
CDS Peaks	Obser	rved*	Present Study	7	Present Study	7
(cm ⁻⁺)	Peaks	s (cm ⁻¹)	Assignments	Values (cm ⁻¹)	Assignments	Values (cm ⁻¹)
32			LA-TA(X)	31		
50	46 ^a	50 ^b	$TO-LA(\Delta)$	51		
84	84 ^a	86 ^b	TO-TA(X)	83		
110	105 ^a	112 ^b				
125	126 ^a		$LA+TA(\Delta)$	123	$LA+TA(\Delta)$	123
146	146 ^a	142 ^b	2LA(X)	146		
			2TA(L)	146		
170	170 ^a		$LO+TA(\Delta)$	162	TO+TA(L)	172
186	186 ^a				TO+LA(L)	188
216	216 ^a	217 ^b	LO+LA(X)	207	LO+TA(L)	217
230	230 ^a					
253	242 ^a		2TO(Γ)	240	$2LO(\Delta)$	250
			$2TO(\Delta)$	243		

a – Ref. 5, b– Ref. 7

CDS Basks (am ⁻¹)		Ra	man Active		Infra-red Active	
CDS Peaks (cm)	Obser Peaks	rved* (cm ⁻¹)	Present St	tudy	Present Study	
			Assignments	Values (cm ⁻¹)	Assignments	Values (cm ⁻¹)
32			LO-TO(L)	33		
64	64 ^a	65 ^b	2TA(X)	63		
84	85 ^a		LA+TA(X)	83		
			$LO-TA(\Delta)$	86	$LA+TA(\Delta)$	93
92	96 ^a	91 ^b				
		92 ^b	$LA+TA(\Delta)$	93		
101	101 ^a	101 ^b	2LA(X)	104		
163		163 ^b	TO+LA(X)	140	$TO+LA(\Delta)$	165
170	170 ^a		$LO+LA(\Delta)$	180		
200	200 ^a					
220		219 ^b	$2TO(\Delta)$	220	$2TO(\Delta)$	220
226		228 ^b	$2LO(\Delta)$	227	$2LO(\Delta)$	227
254	250 ^a	256 ^b	2LO(L)	260		
270		271 ^b				
284		284 ⁶	$2LO(\Gamma)$	284		

Table -6 Assignment of two phonon Raman and Infra-red peaks for KI

a – Ref. 5, b– Ref. 7

Table -7 TOEC and FOEC (in units $10^{12}\ dyn\,/\,Cm^2)$ for potassium halides

Duononty	KF	K	Cl	KBr	KI
roperty	Present	Present	Expt.	Present	Present
C ₁₁₁	-10.813	-7.596	-7.010^{a}	-6.180	-5.339
C ₁₁₂	-0.249	-0.254	-0.244^{a}	-0.135	-0.336
C ₁₂₃	0.265	0.118	0.133 ^a	0.074	0.058
C ₁₄₄	0.264	0.132	0.127 ^a	0.131	0.076
C ₁₆₆	-0.475	-0.237	-0.245 ^a	-0.107	-0.124
C ₄₅₆	0.263	0.140	0.118 ^a	0.113	0.085
C ₁₁₁₁	2.191	1.590		1.929	1.884
C ₁₁₁₂	-0.425	-0.338		0.495	2.534
C ₁₁₆₆	-0.448	0.102		0.629	0.984
C ₁₁₂₂	0.003	1.074		0.961	-1.046
C ₁₂₆₆	0.005	0.007		1.010	0.482
C ₄₄₄₄	0.470	1.389		0.942	1.503
C ₁₁₂₃	-0.617	-0.179		-0.213	0.350
C ₁₁₄₄	-0.611	-0.230		-0.303	0.288
C ₁₂₄₄	0.615	-0.316		-0.244	-0.185
C ₁₄₅₆	-0.612	-0.341		-0.288	-0.215
C ₄₄₆₆	-0.616	-0.096		-0.243	0.760
		a – R	ef.8		

Property	K	F	K	Cl	KBr		KI	
	Present	Expt.	Present	Expt.	Present	Expt.	Present	Expt.
dK'/dP	4.205	5.260 ^a	5.428	5.340 ^a	4.874	5.380 ^a	5.087	5.470 ^a
dS'/dP	4.846	5.250 ^a	5.786	5.610 ^a	7.222	5.680 ^a	5.571	6.030 ^a
dC'_{44}/dP	-0.385	-0.430 ^a	-0.501	–0.390 ^a	-0.519	-0.328^{a}	-0.610	-0.244^{a}
dC'_{111}/dP	38.842		-37.761		-88.070		30.765	
dC'_{112}/dP	0.970		-1.223		-1.164		0.075	
dC'_{166}/dP	1.222		0.956		0.984		1.055	
dC'_{123}/dP	1.102		1.031		1.081		0.678	
dC'_{144}/dP	-0.897		-0.921		23.216		-1.038	
dC'_{456}/dP	0.982		0.986		0.990		0.989	
-			а	– Ref 8				

Table -8 Pressure derivatives of SOEC and TOEC (dimensionless) of potassium halides

Table -9 The values of Cauchy discrepancy (in 10¹² dyn /cm²) for lattice dynamics of potassium halides

Property	KF	KCl	KBr	KI
$C_{112} - C_{166}$	-0.00022	0.13045	0.05412	0.46835
$C_{123} - C_{456}$	0.00250	-0.02166	-0.03815	-0.02650
$C_{144} - C_{456}$	0.00083	0.00722	0.01272	-0.00883
$C_{123} - C_{144}$	0.00167	0.01444	-0.02544	-0.01767
$C_{1112} - C_{1166}$	0.02222	1.02244	-0.33636	-1.58388
$C_{1122} - C_{1266}$	0.00239	-1.15051	-0.01309	-4.61456
$C_{1122} - C_{4444}$	-0.00174	-1.16221	0.05469	-5.54924
$C_{1123} - C_{1144}$	-0.00588	-0.28320	0.08966	0.06225
C_{1123} - C_{1456}	0.00508	0.35938	0.07487	0.56633
$C_{1123} - C_{1244}$	-0.00218	-0.01682	0.03064	0.53561
$C_{1123} - C_{4466}$	-0.01784	-0.01024	0.02934	-0.41042

RESULTS AND DISCUSSIONS

In this paper a systematic theoretical investigation of lattice dynamic of potassium halides is presented. The model proposed for this purpose has been developed by incorporating the effects of van der Waals interactions (VWI) and three-body interactions (TBI) effects in the frame work of rigid shell model (RSM) originated by Cochran and his collaborators [16,18,32]. The link between theoretical and experimental results established, it evident that the present model is reasonably realistic for describing the phonon dispersion curves, Debye temperatures variation and two phonon infra-red and Raman spectra of ionic potassium halides.

The knowledge of the model parameters have 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 1000 wave vectors [33]. From the symmetry, these 1000 points are reduced to 48 non-equivalent points at which the vibration frequencies have been obtained by solving the secular determinant. These frequencies represent the complete vibration (or phonon) spectra. The phonon dispersion relations have been computed by solving the secular equation for the six vibration.

frequencies corresponding to each phonon wave vector (\vec{q}) along the principal symmetry directions [q,o,o], [q,o,o] and [q,q,q]. The phonon dispersion curves have been obtained by plotting these vibration frequencies (ω) against the wave vector (\vec{q}) and displayed in figures -1, 2, 3 and 4 for KF, KCl, KBr and KI, respectively. The phonon dispersion curves (PDC) for these halides are almost similar but their certain features specially mention.

(i)Three body interactions have influenced to both LO and TO branches much more than the acoustic branches (LA and TA) in these halides.

(ii) Another striking feature of the present model in noteworthy from the excellent reproduction of almost all the acoustic branches. The agreement achieved from the present model is also excellent for the longitudinal acoustic (LA) branch along [qqq] direction.

(iii) Also the result obtained from present model is almost identical along [qqq] direction. This may be particularly because the zone centre vibration frequencies have been used as input data in the calculation of model parameters.

(iv) A quantitative interpretation of the general features of PDC is also obvious from the present model when it predicts the gap between the acoustical and optical branches similar to forbidden gap between the valence and the conduction band.

In view of the overall success, it may be concluded that VTBFSM provides a good agreement of PDC which is certainly better than those yielded by experimental [3,4,12-14] and theoretical workers [11,14,34-51]. Although quantitatively the agreement achieved from present model is comparatively better in the sense that some of the fitted parameters given by other workers [3,4,12-14,34-51], have attained unrealistic values. Moreover, we have tested the adequacy of the present model by calculating the Debye temperatures variation, two phonon Raman and infra-red spectra and anharmonic elastic properties.

The variations of Debye temperature (Θ_D) with the temperature (T) are shown in figure -5 for all halides. The calculated (Θ_D -T) curves for KF, KCl, KBr and KI are in excellent agreement with the experimental results [18] but there is 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. This success of present model in exploring the specific heats indicates its adequacies to describe the lower range of frequency spectra. This is not surprising because the present model is quite capable to explain the elastic constants and hence the acoustic frequencies in terms of three-body interactions.

As the two-phonon Raman and infra-red (IR) spectra are sensitive to the higher frequency side of the phonon spectra and the specific heats are sensitive to its lower side. It seems, therefore, essential to investigate the extent to which the present model is capable to interpret the Raman and IR spectra. This will provide a complete test for the validity of the present model for entire range of the spectra. The result of these investigations from CDS approach depicted in figures -6, 7,8 and 9 show that the agreement between experimental [19,20] and our theoretical peaks is generally good for both Raman and IR spectra in almost all the potassium halides except for KF where measured peaks are not available. Since our CDS curves are derived from somewhat

U C Srivastava

course mesh division of the Brillouin zone, therefore we have used a critical points analysis [54] to present complex interpretation of the observed Raman spectra. The assignment made by the present study listed in tables-3, 4,5 and 6 which shows reasonably good agreement with the observed peaks corresponding to Raman and IR spectra for KF, KCl, KBr, and KI. Our extensive study of two-phonon Raman and IR spectra is basically aimed to correlate the theoretical and optical experimental results. The interpretation of Raman and IR spectra achieved from both CDS approach and critical points analysis may be considered satisfactory in all cases. These predictions can be improved further using a sophisticated programme [55], for generating the combined density of states. A successful interpretation of these spectra has provided the next best test of any model for higher range of frequency spectra.

It is interesting to note that our results on TOEC, FOEC and pressure derivatives of SOEC are generally better than those of others as is evident from the table (7–9). However, the results are closer to their experimental values [21,22]. It can also be seen from table 2 and 9 that the Cauchy discrepancy is smaller for the TOE constants than for SOE constants. A possible explanation for this fact seems to be that many-body and/or thermal effects are more pronounced for SOEC than for TOEC. The pressure derivatives of the effective SOE constants calculated by us have been given in table -8 and found to be generally in good agreement with their observed data. As such this model has been more successfully applied to other alkali halides [22-31].

In view of overall achievements described above and the recent works reported elsewhere [56-62], it may be concluded that the modifications introduced by VWI and TBI in the frame work of RSM is important in potassium halides. In fact the present model VTBFSM has revealed much better descriptions of dynamical properties of these halides.







Fig-4. Phonon dispersion curves of KF. *Experimental points*: • Longitudinal



Fig-5. Debye temperature variations for KF, KCl, KBr and KI



Fig-7 Combined density of states curve for KCl



CONCLUSION

In addition of Cauchy discrepancy, and shell model in contrast of this, our model VTBFSM is based on more realistic account of the long range interactions by including the contribution of

the three-body forces, whose existence in ionic crystals is well founded There is, however, an important difference between shell model and our model that in shell model the value of Z less than 1 but in my model value of Z greater than 1.Our model successfully explained the phonon anomalies in the longitudinal optical branch along the (qoo) and (qqo) directions. The present model VTBFSM has also predicted zero splitting of optical branches at X-point. However our predictions using present model VTBFSM are better than those by using other models [20, 23]. The assignment made by the critical point analysis, the present study has been listed in Table 3-6. The interpretation of Raman / IR spectra achieved from both CDS approach and critical point analysis is quite satisfactory.

The calculated phonon dispersion curves are shown in figures-1-4, after inclusion of van der waals interaction have improved the agreement between experimental data[3] and our calculated results. It is evident from figure-5 our results for Debye temperature curve is good with measured experimental data [6] and generally better than of breathing shell model (BSM). The CDS curve for potassium halides has plotted in figure-6-9; the basic aim of the study of two phonon IR/Raman scattering spectra is to correlate the neutron and optical experimental data of potassium halides. We have also investigated the anhormonic properties by using VTBFSM this includes the predictions of TOE and FOE constants for these halides. we have systematically reported phonon dispersion curves, Debye temperature ,combined density of states and anhormanic property of these halides . To sum up, we can say that the contributions of VWI and TBI are essential for the description of the lattice dynamics of potassium halides. In future, it is suggested that further improvements may be obtained by considering the effect of anharmonicity of vibrational energy.

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