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Lattice dynamic study of potassium bromide using theoretical approach

U. C. Srivastava^{1*}, R. S. Pandey¹ and K. S. Upadayaya²

¹Department of Physics, Amity Institute of Applied Sciences, Sector-125, Noida -201301, U. P., India.

²K. N. Government P. G. College, Gyanpur, Bhadohi, U. P., India.

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A unified description of a series of Phonon properties of potassium bromide by means of Van der Waals three-body force shell model [VTBFSM]. 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 anharmonic properties and other dynamical properties of KBr. Excellent agreement is found between calculated values and measured data for phonon dispersion curve. It is simple crystal but its various properties give better future prospective.

Key words: Lattice vibrational properties, Phonon dispersion curve and Raman/IR spectra.

INTRODUCTION

The shell model of ionic crystals proposed by Dick and Overhauser (1958) presents a simple description of the electronic polarization in these solids. The basic ideas of this model were developed by Woods et al. (1960) into a theory of lattice dynamics which, with its various modifications so that it can be accepted as a convenient representation of a relatively exact theory of lattice dynamics. The shell model begins by assuming that every ion is divided into a rigid spherical shell of a portion of the nucleus and the rest of the electron cloud. The two are coupled together by an isotropic spring and have a common center in the equilibrium configuration. This departure from the rigid-ion-picture produces a different response to the long-wave optical (electromagnetic) waves, but does not make any impression on the long-wave acoustical (mechanical) vibrations, with the result that while the model permits a better description of the dielectric polarization in ionic crystals, it does not go beyond the rigid-ion model with respect to the elastic behavior of these solids. In particular, the shell models employing only central interactions lead to the Cauchy relation $C_{12} = C_{44}$. However, the low temperature

measurements of elastic constants, now available for large number of solids, do not support this result. Phenomenological, the Cauchy discrepancy can be accounted for by including various kinds of non central interactions amongst the ion pairs in fact, some of the later modifications of the shell model include non central short-range interactions and give a better description of the vibrational properties of the solids under consideration. In general these modifications are not based on the existing knowledge about the nature of the interaction responsible for the Cauchy discrepancies in ionic solids. Thus these modified models effectively replace a part of the operative forces by others of an entirely different nature. This replacement of one force by another could modify the parameters of the rest of the interactions also, particularly when the model is constrained to give agreement with experiments.

This has motivated us to frame a new model of lattice dynamics. This is known as Van der Waals Three-Body Force Shell Model [VTBFSM]. This model considers all possible interactions for explaining the harmonic as well as anharmonic properties of potassium halides. During the recent past, a considerable interest has been shown by theoretical and experimental workers in the investigation of lattice dynamical behavior of potassium Bromide (KBr). This solid is an important member of potassium halides and forms a simple class of ionic solids.

*Corresponding author. E-mail: ucsrivastava@amity.edu. Tel: No. 91-9313160879. Fax: 01202432780.

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) and 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 (Lewis et al., 1967), dielectric (Kittel, 1966), vibrational (Buhrer, 1970; Raunio, 1969; Krishnan, 1969; Berg and Marrison, 1957; Potts and Walker, 1973) and optical properties (Roberts and Smith, 1970) of this solid, it is quite interesting and encouraging for theoretical workers to predict its lattice dynamical properties.

THEORY

The essential formalism of VTBFMS 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 KBr. Looking into the adequacy of the interaction system, the present model may hopefully be regarded as a successful approach for the dynamical descriptions of potassium Bromide. The general form of VTBFMS can be derived from the crystal potential energy per unit cell, given by.

$$\Phi = \Phi^C + \Phi^R + \Phi^{TBI} + \Phi^{VWI} \quad (1)$$

where, the first term Φ^C is Coulomb interaction potential and is long range in nature, second term Φ^R is short overlap repulsion potential, third term Φ^{TBI} is three-body interactions potential 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.

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

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

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

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 Woods et al. (1963)

$$\underline{C}' = \underline{C} + (\underline{Z}_m^{-2} \underline{Z} r_0 f_0') \underline{V} \quad (4)$$

Where f_0' is the first -order space derivative and \underline{Z}_m modified ionic polarizability

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

$$\phi_{dd}^{vwi}(r) = -S_v |C_{++} + C_{--}| \div |6r^6| = \Phi^v(r) \quad (5)$$

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 (2) along (q o o) subjecting the short and long-range coupling coefficients to the long wavelength limit, the expressions derived for elastic constants (C_{11} , C_{12} , C_{44}) are follows as:

$$\frac{4r_0^4}{e^2} C_{11} = \left[-5.11 \underline{Z}_m^2 + A_{12} + \frac{1}{2}(A_{11} + A_{22}) + \frac{1}{2}(B_{11} + B_{22}) + 9.3204 \xi'^2 \right] \quad (6)$$

$$\frac{4r_0^4}{e^2} C_{12} = \left[0.226 \underline{Z}_m^2 - B_{12} + \frac{1}{4}(A_{11} + A_{22}) - \frac{5}{4}(B_{11} + B_{22}) + 9.3204 \xi'^2 \right] \quad (7)$$

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

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

$$B_{11} + B_{22} + B_{12} = -1.165 \underline{Z}_m^2 \quad (9)$$

Where

$$\underline{Z}_m^2 = \underline{Z}^2 \left(1 + \frac{12}{\underline{Z}} f_0 \right) \quad \text{and} \quad \xi'^2 = \underline{Z} r_0 f_0' \quad (10)$$

f_0 is function dependent on overlap integrals of electron wave function. Similarly, expressions for two distinct optical vibration frequencies (ω_L and ω_T) are obtained as:

$$(\mu \omega_L^2)_{q=0} = R'_0 + \frac{(Z'e)^2}{\underline{V} f_L} \cdot \frac{8\pi}{\underline{V} f_L} (\underline{Z}^2 + 6\xi'^2) \quad (11)$$

$$(\mu \omega_T^2)_{q=0} = R'_0 - \frac{(Z'e)^2}{\underline{V} f_T} \cdot \frac{4\pi}{\underline{V} f_T} \underline{Z}^2 \quad (12)$$

Where the abbreviations stand for

$$R'_0 = R_0 - e^2 \left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right); \quad \underline{Z}' = \underline{Z}_m + d_1 - d_2$$

$$R_0 = \frac{\underline{Z}^2 e^2}{\underline{V}} (A_{12} + 2B_{12})$$

$$f_L = 1 + \left(\frac{\alpha_1 + \alpha_2}{\underline{V}} \right) \cdot \frac{8\pi}{3} (\underline{Z}_m^2 + 6\xi'^2)$$

$$f_T = 1 - \left(\frac{\alpha_1 + \alpha_2}{\underline{V}} \right) \cdot \frac{4\pi}{3} (\underline{Z}_m^2)$$

Where α_1, α_2 electrical polarizabilities and Y_1, Y_2 are shell charge parameters of positive and negative ions.

$$d_1 = \frac{-\alpha_1 R_0}{e^2 Y_1}$$

$$d_2 = \frac{-\alpha_2 R_0}{e^2 Y_2}$$

and

$$V = 2r_0^3 \text{ (Unit cell volume for NaCl lattice)}$$

by solving the dynamical matrix along [.5, .5, .5] directions at L-Point modified expressions for

$\omega_{LO}(L), \omega_{TO}(L), \omega_{LA}(L), \text{ and } \omega_{TA}(L)$ are as follows:

$$m_2 \omega_{LO}^2(L) = R_0 + [(e^2/V)(2A_{22} + B_{22})] + [(e^2/V) Z_m^2 C'_{1L}] \quad (13)$$

$$m_1 \omega_{LA}^2(L) = R_0 + [(e^2/V)(2A_{11} + B_{11})] + [(e^2/V) Z_m^2 C'_{1L}] \quad (14)$$

$$m_2 \omega_{TO}^2(L) = R_0 + [(e^2/2V)(A_{22} + 5B_{22})] + [(e^2/V) Z_m^2 C'_{1T}] \quad (15)$$

$$m_1 \omega_{TA}^2(L) = R_0 + [(e^2/2V)(A_{11} + 5B_{11})] + [(e^2/V) Z_m^2 C'_{1T}] \quad (16)$$

where

$$\left. \begin{aligned} C'_{1L} &= \left[\begin{array}{c} \underline{C} + Zr_0 f_0 Z_m^2 \underline{V} + Z^2 Z_m^2 \underline{D} \\ \underline{C} + Zr_0 f_0 Z_m^2 \underline{V} + Z^2 Z_m^2 \underline{D} \end{array} \right] \begin{array}{l} \text{xx} \\ \text{yy} \end{array} \end{aligned} \right\} \quad (17)$$

Where \underline{C} and \underline{V} are Coulomb and three bodies force matrices evaluated at L-Point and \underline{D} 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. (1970). Debye's model define the frequency distribution function which is given by

$$\Theta_D = hv_m/K \quad (18)$$

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

$$D(\omega) = dN/d\omega = (VK^2/2\pi^2) \cdot dK/d\omega \quad (19)$$

Where $N = (L/2\pi)^3 (4\pi k^3/3)$, K is wave vector and $L^3 = V$.

RESULTS

The experimental values of input data and model parameters for KBr are listed in Table 1 given by many workers (Sharma, 1979; Garg et al., 1977; Kushwala and Kushwaha, 1980; Mohan and Sudha, 1993). We have computed phonon dispersion frequencies for the allowed 48 non-equivalent wave vectors in the first Brillouin zone

by using our model parameters (Srivastava, 2004). The calculated phonon dispersion curves of KBr are shown in Figure 1. The agreement between our computed phonon spectra and experimental data is excellent for KBr and well with the measured data reported by Buhner (1970). In the present study the variation of Debye temperatures (Θ_D) at different temperatures T have also been calculated and curve has been plotted along with available experimental data (Berg and Marrison, 1957) in Figure 2. Though, the agreement is better with our model, still, there is slight discrepancy between theoretical and experimental results at higher temperatures. At high temperatures lattice instability develops in which above a certain critical temperature the vibrational and static pressures cannot balance each other at any volume. It is argued that this instability plays a role in causing solids to melt. Anharmonic corrections tend to rise at critical temperatures by about 20%. Debye's theory agrees very well with experiment, especially at low temperatures, because at low temperature and at high temperature it is almost exact. Lattice imperfections are not an important factor for temperatures up to about 90% of the melting temperature.

A brief inspection of Figure 3 shows that the peaks of the CDS curves compare favorably with the corresponding peaks observed in the two-phonon Raman and infrared spectra. Which shows that the agreement between experimental data (Raunio, 1969; Krishnan, 1969) and our theoretical peaks for KBr. The assignment made by the critical point analysis, the present study has been listed in Table 2. The interpretation of Raman / IR spectra achieved from both CDS approach and critical point analysis is quite satisfactory.

It is interesting to note our results on TOEC, FOEC and the pressure derivatives of SOEC are generally better than those of others [9, 10] as evident from Table 3. However, our results are closer to their experimental values reported independently by Roberts (Roberts and Smith, 1970) Chang (Sharma, 1979). It can also see that Cauchy discrepancy is smaller for TOEC than for SOEC (Garg et al., 1977). The pressure derivatives of effective SOEC given in Table 3 are found to be generally in good agreement with their observed data (Potts and Walker, 1973; Roberts and Smith, 1970).

DISCUSSION

Addition of Cauchy discrepancy and shell model in contrast of this, our model VTSM 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 $Z < 1$ but in my model value of $Z > 1$.

Our model successfully explained the phonon anomalies

Table 1. Input data and model parameters for KBr.

Input data		Model parameters	
Parameter	Value	Parameter	Value
C_{11}	3.980 ^c	f_0	-0.0139
C_{12}	0.560 ^c	$r_0 f_0'$	-0.0443
C_{44}	0.520 ^c	Z_m^2	0.8325
$\nu_{LO}(\Gamma)$	5.000 ^g	A_{12}	13.3905
$\nu_{TO}(\Gamma)$	3.600 ^g	B_{12}	-3.0275
$\nu_{LO}(L)$	4.330 ^g	A_{11}	-4.8688
$\nu_{TO}(L)$	2.960 ^g	B_{11}	-2.6324
$\nu_{LA}(L)$	2.670 ^g	A_{22}	
$\nu_{TA}(L)$	2.220 ^g	B_{22}	1.3649
r_0	3.278 ^j	d_1	0.1346
α_1	1.030 ^m	d_2	0.2086
α_2	4.500 ^m	Y_1	-1.2215
C_{++}	64.90 ⁿ	Y_2	-3.4430
C_{--}	503 ⁿ	Y	-11.9229

c - Mohan and Sudha (1993), g - Claytor and Marshall (1960), j - Cowley (1963), m - Kushwala and Kushwaha (1980), n - Potts and Walker (1973).

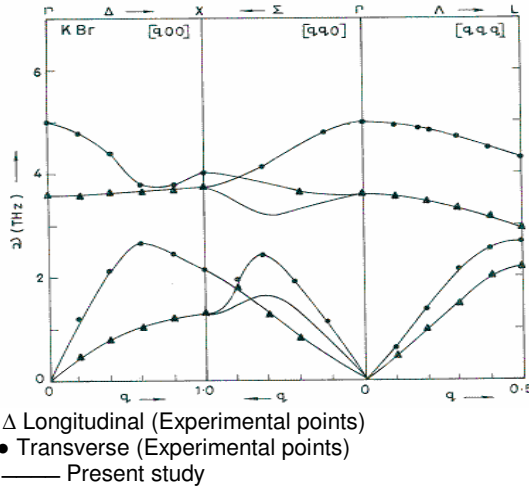


Figure 1. Phonon dispersion curves for KBr.

even along (q00) and (qq0) directions. The present model VTSM has also predicted zero splitting of optical branches at X-point. However our predictions using present model VTBFM are better than those by using other models (Garg et al., 1977; Kushwala and Kushwaha, 1980). The assignment made by the critical point analysis, the present study has been listed in Table 2. The interpretation of Raman / IR spectra achieved from both CDS approach and critical point analysis is quite satisfactory.

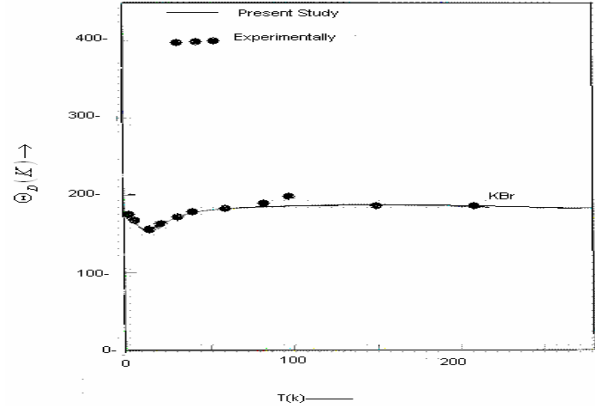


Figure 2. Debye temperature variation of KBr.

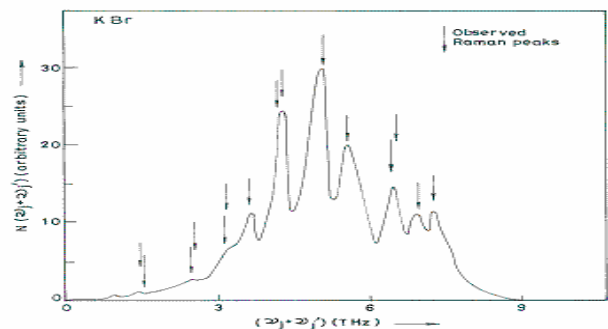


Figure 3. Combined density of states curve for KBr.

Table 2. Assignments of two-phonon Raman and infra-red peaks for KBr.

CDS peaks (cm ⁻¹)	Raman active				Infra-red active	
	Observed*	Peaks (cm ⁻¹)	Present study		Present study	
			Assignments	Values (cm ⁻¹)	Assignments	Values (cm ⁻¹)
32			LA-TA(X)	31		
50	46 ^a	50 ^b	TO-LA(Δ)	51		
84	84 ^a	86 ^b	TO-TA(X)	83		
110	105 ^a	112 ^b				
125	126 ^a		LA+TA(Δ)	123	LA+TA(Δ)	123
146	146 ^a	142 ^b	2LA(X)	146		
			2TA(L)	146		
170	170 ^a		LO+TA(Δ)	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	LO(Δ)	250
			2TO(Δ)	243		

a – Buhrer (1970), b – Krishnan (1969).

Table 3. TOEC and FOEC (10¹² dyn/cm²), pressure derivatives of SOEC and TOEC (dimensionless) and Cauchy discrepancy (in 10¹² dyn/cm²) for KBr.

Property	KBr		Property	KBr		Property	KBr	
	Present			Present	Expt.		Present	
C ₁₁₁	-6.180	dk ¹ /dp	4.874	5.380 ^a	C ₁₁₂ - C ₁₆₆	0.05412		
C ₁₁₂	-0.135	ds ¹ /dp	7.222	5.680 ^a	C ₁₂₃ - C ₄₅₆	-0.03815		
C ₁₂₃	0.074	dc ¹ ₄₄ /dp	-0.519	-0.328 ^a	C ₁₄₄ - C ₄₅₆	0.01272		
C ₁₄₄	0.131	dc ¹ ₁₁₁ /dp	-88.070		C ₁₂₃ - C ₁₄₄	-0.02544		
C ₁₆₆	-0.107	dc ¹ ₁₁₂ /dp	-1.164		C ₁₁₁₂ - C ₁₁₆₆	-0.33636		
C ₄₅₆	0.113	dc ¹ ₁₆₆ /dp	0.984		C ₁₁₂₂ - C ₁₂₆₆	-0.01309		
C ₁₁₁₁	1.929	dc ¹ ₁₂₃ /dp	1.081		C ₁₁₂₂ - C ₄₄₄₄	0.05469		
C ₁₁₁₂	0.495	dc ¹ ₁₄₄ /dp	23.216		C ₁₁₂₃ - C ₁₁₄₄	0.08966		
C ₁₁₆₆	0.629	dc ¹ ₄₅₆ /dp	0.990		C ₁₁₂₃ - C ₁₄₅₆	0.07487		
C ₁₁₂₂	0.961				C ₁₁₂₃ - C ₁₂₄₄	0.03064		
C ₁₂₆₆	1.010				C ₁₁₂₃ - C ₄₄₆₆	0.02934		
C ₄₄₄₄	0.942							
C ₁₁₂₃	-0.213							
C ₁₁₄₄	-0.303							
C ₁₂₄₄	-0.244							
C ₁₄₅₆	-0.288							
C ₄₄₆₆	-0.243							

a - Berg (1957).

CONCLUSION

To sum up, we can say that the inclusion of VWI and TBI are essential for the description of lattice dynamics of potassium halides (Mohan and Sudha, 1993; Claytor and Marshall, 1960; Cowley et al., 1963; Woods et al., 1963; Lynch, 1967). We have also investigated the anharmonic properties of KBr by using VTSM. Some researchers successfully calculated theoretical values by using the model for other alkali halides (Upadhyaya et al., 2002; Pandey et al., 2006).

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