Van der Waals three-body force shell model (VTSM) for the Lattice dynamical studies of Potassium fluoride

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The vander Waals three–body force shell model (VTSM) has been developed by modifying the three –body force shell model (TSM) for the Lattice dynamic of ionic crystals with (NaCl) structure. This model includes van der Waals interactions (VWI) and three-body interactions (TBI) in the framework of rigid shell model (RSM). In fact the present model (VTSM) has revealed much better descriptions of dynamical properties of KF behaviour of potassium floride has been investigated theoretically by using van der Waals three-body force shell model (VTSM).A comparative study of the dynamical behaviour of KF has also been done between the present model (VTSM). 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.

1. Introduction

During the last two decades, a considerable interest has been shown by theoretical and experimental workers in the investigation of lattice dynamical behavior of potassium floride (KF). This solid is an important member of potassium halides and forms a simple class of ionic solids. 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 [1], dielectric [2], vibrational [3-7] and optical properties [8] of this solid, it is quite interesting 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 [12] and Chang [13]. In the present paper we have developed a new model to study the lattice dynamics of alkali halides which we take here (KF). The new model developed by us 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 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 KF. 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 floride. The general form of VTBFSM can be derived from the crystal potential energy per unit cell, given by

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

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 $\left|\vec{r}_{ij}\right|$, 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

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

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

$$\Phi^C = \alpha_M \frac{Z^2 e^2}{r_0}$$

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

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

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. 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 [17], this alteration in the electronic charge density causes a charge depletion which depends on the internuclear separation and interacts with all other charges via Coulomb force law and gives rise to long-range TBI introduced by Lowdin [18] and Lundqvist [19]. 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 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 $\Phi^{C.}$ 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) and introducing the effect of VWI and TBI, the secular determinant is given as

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

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

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

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

$$\underline{C}' = \underline{C} + (Z_m^{-2}\, Z\, r_0 f_0')\, V \qquad (4)$$

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

$$\Phi_{dd}^{vwI}(r) = -\,\mathbf{S_v}\left|\frac{C_{++} + C_{--}}{6r^6}\right| = \Phi^v(r) \qquad (5)$$

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) the expressions derived for elastic constants (C_{11}, C_{12}, C_{44}) corresponding to VTBFSM are follows as:

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

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

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

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

$$B_{11} + B_{22} + B_{12} = -1.165\,Z_m^{\ 2} \qquad (9)$$

Where

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

The term f_0 is function dependent on overlap integrals of electron wave functions. By using the secular equation (2) along [q o o]direction and subjecting the short and long-range coupling coefficients to the long wavelength limit $\vec{q} \to 0$ expressions for two distinct optical vibration frequencies (ωL and ωT) are obtained as:

$$\left(\mu\omega_L{}^2\right)_{q=0} = R'_0 + \frac{(Z'e)^2}{Vf_L} \frac{8\pi}{3}\left(Z_m{}^2 + 6\xi'^2\right)$$

$$\left(\mu\omega_T{}^2\right)_{q=0} = R'_0 - \frac{(Z'e)^2}{Vf_T} \frac{4\pi}{3} Z_m{}^2 \qquad (12)$$

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

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

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

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

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

$$d_1 = \frac{-\alpha_2 R_0}{e^2 Y_1}, \quad d_2 = \frac{-\alpha_2 R_0}{e^2 Y_1} \text{ and } V = 2r_o{}^3 \text{ (Unit}$$

cell volume for NaCl lattice)

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

$$m_2\omega^2{}_{LO}(L) = R_0 + [(e^2/V) (2A_{22} + B_{22})] + [(e^2/V) Z^2{}_m C'{}_{1L}]$$

$$m_1\omega^2{}_{LA}(L) = R_0 + [(e^2/V) (2A_{11} + B_{11})] + [(e^2/V) Z^2{}_m C'{}_{1L}]$$

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

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

Where

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

$$(11)$$

$$C'_{1T} = \left[\ \underline{C} + Zr_o f'_0 Z^{-2}{}_m \underline{V} + Z^2 Z^{-2}{}_m \underline{D}\ \right]_{YY}$$

$\underline{C}$ and $\underline{V}$ is Coulomb and three body 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 [8].

3. Results and discussion

The input data and calculated model parameters for KF are listed in Table 1. We have computed phonon dispersion frequencies for the allowed 48 non - equivalent wave vectors in the first Brillouin zone by using our model parameters. We present the phonon dispersion curves [PDC] only along the three principal symmetry directions Fig. 1. Our phonon dispersion curves for KF agree well with the measured data reported by W. Buhrer [3]. It is evident from that our predictions using present model VTBFSM are better than those by using other models [13-14]. 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 [6] in Fig. 2. Though, the agreement is better with our model, still, there is slight discrepancy between theoretical and experimental results at higher temperatures.

Table 1. Input data and model parameters for KF.

Input data		Model Parameters	
Parameters	Value	Parameters	Value
C_{11} (10^{11} dyn/cm^2)	7.570 [1]	A_{12}	11.6719
C_{12} (10^{11} dyn/cm^2)	1.350 [1]	B_{12}	-0.7319
C_{44} (10^{11} dyn/cm^2)	1.336 [1]	A_{11}	-0.5888
v_L (TH$_Z$)	5.660 [3]	B_{11}	-0.3640
v_T (TH$_Z$)	3.730 [3]	A_{22}	0.2694
r_0 (10^{-8}cm)	2.648 [10]	B_{22}	-1.3303
α_1 (10^{-24} cm^3)	1.201 [10]	d_1	0.0831
α_2 (10^{-24} cm^3)	0.759 [10]	d_2	-4.0840
C^{++} (10^{-60} erg cm^6)	64.90 [12]	Y_1	-4.0840
C^{--} (10^{-60} erg cm^6)	29.20 [12]	Y_2	-5.6541
		$r_o f_o'$	-0.0128
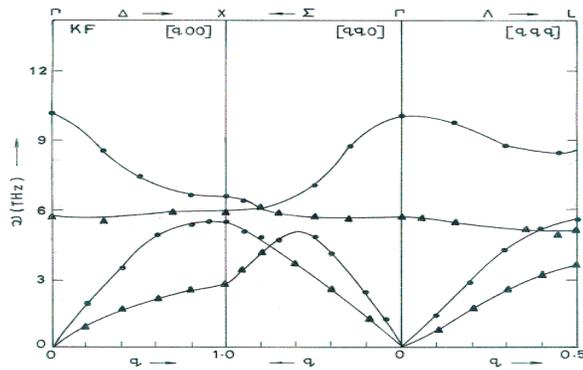
Fig. 1. Phonon dispersion curve for KF. Experimental points
• Longitudinal; ∇ Transeverse; — Present study

Fig. 3. Combined density curve.

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

Fig. 2. Shows the Debye temperature variation of KF.

CDS Peaks Cm^{-1}	Raman active Present Study		Infra-red Active 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	LA+TA(Δ) LA+TA(X)	280 280		
297	TO+TA(X) TO+TA(Δ)	293 293		293
320	LO+TA(Δ)	320	LO+TA (Δ)	320
365	2LA(X)	366	2LA(Δ)	373
413	LO+LA(Δ)	413	LO+LA(Δ)	413
426	LO+TO(Δ)	426	LO+TO(Δ)	426

The present model is also capable to predict the two phonon Raman/IR spectra. The results of these investigations from combined density states (CDS) approach have been shown in Fig. 3 which shows that the agreement between experimental data [4-5] and our theoretical peaks is generally good for both two phonon Raman/IR spectra for KF. 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 [7-8] as evident from Table 3. However, our results are closer to their experimental values reported independently by Roberts [12] and Chang [13]. It can also see that Cauchy discrepancy is smaller for TOEC than for SOEC. The pressure derivatives of effective SOEC given in Table 3 are found to be generally in good agreement with their observed data [7-8]. To sum up, we can say that the inclusion of VWI and TBI are essential for the description of lattice dynamics of potassium halides [15]. As such this model has been more successfully applied to other alkali halides [16-23].

Table 3. TOEC and FOEC (10^{12} dyn/cm^2), pressure derivatives of SOEC and TOEC (dimensionless) and Cauchy discrepancy (in 10^{12} dyn/cm^2) for KF.

Property	KF	Property	KF		Property	KF
	Present		Present	Expt.		Present
C_{111}	-10.813	dk^1/dp	40205	5.260[a]	$C_{112}- C_{166}$	-0.00022
C_{112}	-0.249	ds^1/dp	4.846	5.250[a]	$C_{123}- C_{456}$	0.00250
C_{123}	0.265	dc^1_{44}/dp	-0.385	-0.430[a]	$C_{144}- C_{456}$	0.00083
C_{144}	0.264	dc^1_{111}/dp	38.842		$C_{123} - C_{144}$	0.00167
C_{166}	- 0.475	dc^1_{112}/dp	0.970		$C_{1112} - C_{1166}$	0.02222
C_{456}	0.263	dc^1_{166}/dp	1.222		$C_{1122} - C_{4444}$	-0.00174
C_{1111}	2.191	dc^1_{123}/dp	1.102		$C_{1123} - C_{1144}$	-0.00588
C_{1112}	- 0.425	dc^1_{144}/dp	-0.897		$C_{1123} - C_{1244}$	-0.00218
C_{1166}	- 0.425	dc^1_{456}/dp	0.982		$C_{1123} - C_{1456}$	0.00508
C_{1122}	-0.003				$C_{1123} - C_{4466}$	- 0.01784
C_{1266}	0.005				$C_{1122} - C_{1266}$	0.00239
C_{4444}	0.470					
C_{1123}	-0.617					
C_{1144}	- 0.611					
C_{1244}	-0.615					
C_{1456}	-0.612					
C_{4466}	-0.616					

[a] - Ref. [8,9]

4. Conclusions

The computed phonon dispersion curves in Fig. 1 that inclusion of Van der Waals interaction have improved the agreement between experimental data [3] and our results. The inclusion of Van der Waals interaction (VWI) with (TBI) have influence both longitudinal and transverse optic modes much more than acoustic branches. The agreement between theory and experimental data at x point is also excellent. Another striking feature of present model is noteworthy from the excellent reproduction of almost all branches hence the prediction of phonon dispersion curves (PDC) for KF using (VTSM) may be considered more satisfactory than from other models [11] we have plotted Debye temperature curve at temperature (T). It is evident from Fig. 2 our results is good with measured experimental data [6] and generally better than of breathing shell model (BSM). The combined density of states (CDS) for KF has plotted in Fig. 3 the basic aim of the study of two phonon IR/Raman scattering spectra is to correlate the neutron and optical experimental data of KF. We have also investigated the anhormonic properties of KF by using VTBFSM this includes the predictions of third and forth order elastic constants. Since no

experimental values on these SOE and TOE constants.. Since some on point only experimental values [8, 9] on these properties have been reported so for, we are unable to comment as such on the reliability of our results

In this paper we have systematically reported phonon dispersion curves, Debye temperature, combined density of states and anhormanic property of KF on the basis of overall fair agreement, it may be concluded that the present model van der waals three body force shell model (VTBFSM) is adequately capable to describe the crystal dynamic of KF.

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