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Quasi-Harmonic Phonon Dynamics of Potassium Fluoride

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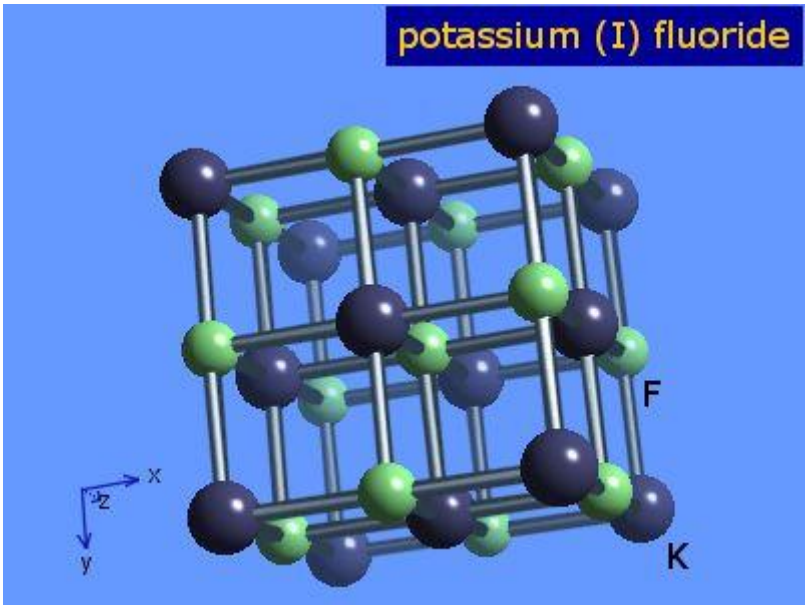
Abstract—The potassium fluoride from an important and interesting class of materials . Crystallizing simply in rock structure. The nature and harmonic properties of these crystals have been extensively studied by several workers with great success but their an harmonic (quasi-harmonic) elastic properties have been reported by experimental and theoretical workers with moderate success. These properties of crystalline solids provide valuable information about their inter atomic forces and thermal properties. The simplest of them are higher order elastic constants. In this paper we are reporting the result of calculated values of the third order elastic constants(TOEC), second order elastic constants(SOEC), pressure derivatives along with Cauchy discrepancies of second and third order elastic constants of potassium fluoride with the help of our own model of lattice dynamics. The calculated results have been compared with observed data available on most of them along with theoretical results of other workers. It is concluded that our approach present better description of quasi harmonic phonon properties of potassium fluoride.



I. INTRODUCTION

The investigation and study of phonon dispersion curves of crystalline solids is true test of phenomenological model in crystal mechanics. For complete stydy of phonon frequencies in Brillouin zone. Debye temperature variation and two phonon Raman scattering and infrared absorption spectra are studied but the study of quasi harmonic properties of the crystals provides us valuable information about their inter atomic forces. The higher order elastic constants provide nature of binding forces between the constituent ions of crystal while the pressure derivatives of second and third order elastic constants give the nature of short range interionic intractions. Several theoretical [1-4] and experimental [5-7] workers have studied the anharmonic properties such as t5hird order elastic constants (TOEC), fourth order elastic constants (FOEC) and pressure derivatives of second order elastic constants (SOEC) and third order elastic constants (TOEC) of potassium halides. Shankar et al.[2] have evaluated the third order elastic constants (TOEC) and pressure derivatives of second order elastic constants (SOEC) of KCl structure alkali halides with the help of model by considering the short range repulsive between first and second neighbours and van der Waals dipole-dipole intractions with moderate success.

The present paper cheiefly aims at the result of comprehensive calculation of quasi-harmonic phonon properties of potassium halides by using a phenomenological model which incorporates the effect of van der Waals intractions (VWI) and three-body intractions (TBI) effect in the frame work of rigid shell model (RSM). The present model has already been employed successfully to investigate the lattice dynamics and anharmonic properties of KF, KCl, KBr and KI [10], uranium sulphide [8].

II. THEORY

The general formalism of ETBFM can be derived from the crystal potential whose relevant expression per unit cell is given by

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

Where, first term Φ^{C} is Coulomb interaction potential and is long range in nature, second term Φ^{R} is short-range overlap repulsion potential, third term Φ^{TBI} is three-body interactions potential and last term Φ^{VWI} is van der Waals interactions potential and its origin to the correlation of the electron motion in different atoms..

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

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

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

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

$$B_{11} + B_{22} + B_{12} = -1.165\ Z_m{}^2 \quad (4)$$

where

$$Z_m^2 = Z^2\left(1 + \frac{12}{Z}f_0\right) \qquad \text{and} \qquad \xi'^2 = Zr_0 f_0' \quad (5)$$

The expressions for these elastic constants and pressure derivatives of second order elastic constants (SOEC) derived by us correspond to three-body lattice energy given by (4.1) and are similar to those derived by **Garg, Puri and Verma [3]** for NaCl structure in the framework of TSM. The short-range force parameters (*Ai, Bi, Ci* and *Di*; *i* = 1, 2) involved in our expressions are defined as :

$$A_{12} = A_1 = G\left[\frac{d^2}{dr^2}\phi_{kk'}^{SR}(r)\right]_{r=r_{kk'}} ; \quad B_{12} = B_1 = -\left[\frac{G}{r}\frac{d}{dr}\phi_{kk'}^{SR}(r)\right]_{r=r_{kk'}}$$

$$A_{11} + A_{22} = A_2 = G\left[\frac{d^2}{dr^2}\phi_{kk}^{SR}(r) + \frac{d^2}{dr^2}\phi_{k'k'}^{SR}(r)\right]_{r=k_1 r_{kk'}}$$

$$B_{11} + B_{22} = B_2 = \left\{-\frac{G}{r}\left[\frac{d}{dr}\phi_{kk}^{SR}(r) + \frac{d}{dr}\phi_{k'k'}^{SR}(r)\right]\right\}_{r=k_1 r_{kk'}}$$

$$C_i = \frac{A_i{}^2}{B_i} \quad \text{and} \quad D_i = \frac{A_i{}^3}{B_i{}^2}$$

where $G = \frac{2\mathrm{v}\ \mathrm{v}}{e^2}$ and $k_1 = 1.4142$ for KCl structure. Here $\mathrm{v} = 2r_0^3$ is the unit cell volume , *e* is the amount of electronic charge.

2.1 Expressions for TOEC and FOEC for Rocksalt Structure :

$$C_{111} = P\Big[37.556Z_m^2 + D_1 - 3C_1 + \frac{1}{4}(C_2 - 3A_2 - 9B_2)$$

$$+ 13.980r_0^2 f_0'' - 89.303r_0 f_0' \Big] \quad (6)$$

$$C_{112} = P\Big[-4.836Z_m{}^2 + \frac{1}{8}(C_2 - 3A_2 - 3B_2)$$

$$+ 4.660r_0^2 f_0^{''} - 18.640r_0 f_0^{'}\Big] \quad (7)$$

$$C_{166} = P\Big[-7.166Z_m^2 - 2(B_1 + B_2) + \frac{1}{8}(C_2 - 3A_2 + 3B_2)$$

$$+ 5.564r_0 f_0^{'}\Big] \quad (8)$$

$$C_{123} = P\big[2.717Z_m^2 + 16.692r_0 f_0^{'}\big] \quad (9)$$

$$C_{144} = P\big[2.717Z_m^2 + 5.564r_0 f_0^{'}\big] \quad (10)$$

$$C_{456} = P\big[2.717Z_m^2\big] \quad (11)$$

where $P = \frac{e^2}{4r_0^4}$, $C_1 = \frac{A_1{}^2}{B_1}$, $D_1 = \frac{A_1{}^3}{B_1{}^2}$, $C_2 = \frac{A_2{}^2}{B_2}$, $D_2 = \frac{A_2{}^3}{B_2{}^2}$

$$R'_2 = \frac{D_2 - 6C_2 + 15A_2 - 15B_2}{16}$$

2.2 Pressure derivatives for Rock Salt structure :

$$\frac{dK'}{dP} = -(3\Omega)^{-1}\Big[13.975Z_m{}^2 + C_1 - 3A_1 + C_2 - 3A_2 - 167.764r_0 f_0^{'}$$

$$+ 41.94r_0^2 f_0^{''}\Big] \quad (12)$$

$$\frac{dS'}{dP} = -(2\Omega)^{-1}\left[23.676Z_m^2 + C_1 + \frac{C_2 + 6A_2 - 6B_2}{4} - 51.07584r_0 f_0^{'}\right.$$

$$\left. + 13.98r_0^2 f_0^{''}\right] \quad (13)$$

$$\frac{dC'_{44}}{dP} = -(\Omega)^{-1}\left[-11.389Z_m{}^2 + A_1 - 3B_1 + \frac{C_2 + 2A_2 - 10B_2}{4} + 44.6524\, r_0^2 f_0''\right] \quad (14)$$

$$\Omega = -2.33Z_m{}^2 + A_1 + A_2 + 27.961r_0 f_0^{'}$$

$$\frac{dC'_{111}}{dP} = -\frac{1}{3K}\big[-3C_{11} - 6C_{12} + 3C_{111} + C_{1111} + 2C_{1112}\big] \quad (15)$$

$$\frac{dC'_{112}}{dP} = -\frac{1}{3K}\big[C_{11} + 2C_{12} + 3C_{112} + C_{1112} + C_{1122} + C_{1123}\big] \quad (16)$$

$$\frac{dC'_{166}}{dP} = -\frac{1}{3K}\big[-C_{11} - 2C_{12} + 3C_{166} + C_{1166} + 2C_{1244}\big] \quad (17)$$

$$\frac{dC'_{123}}{dP} = -\frac{1}{3K}\left[-C_{11} - 2C_{12} + 3C_{123} + 3C_{1123}\right] \quad (18)$$

$$\frac{dC'_{144}}{dP} = -\frac{1}{3K}\left[C_{11} + 2C_{12} + 3C_{144} + C_{1144} + 2C_{1244}\right] \quad (19)$$

$$\frac{dC'_{456}}{dP} = -\frac{1}{3K}\left[-C_{11} - 2C_{12} + 3C_{456} + 3C_{1456}\right] \quad (20)$$

where $K = \frac{C_{11} + 2C_{12}}{3}$.

Table 1 : **Model parameters of potassium fluoride**

Properties	**Values for KF**
Z_m^2	**0.8261**
$r_0 f_0$	**–0.0128**
A_{12}	**11.6719**
B_{12}	**–0.7319**
A_{11}	**–0.5888**
B_{11}	**–0.3640**
A_{22}	**0.2694**
B_{22}	**–1.3303**
d_1	**0.0831**
d_2	**0.0379**
Y_1	**–4.0840**
Y_2	**–5.6541**

Table 2 : **TOEC (in units 10^{12} dyn / cm^2) for potassium fluoride**

Property	**KF**	
	Present	**Exp.***
C_{111}	–11.24552	–10.6856
C_{112}	–0.22896	–0.2164
C_{123}	0.24856	0.2401
C_{144}	0.2445	0.2328
C_{166}	–0.495	–0.4459
C_{456}	0.27352	0.2444

Table 3 : **Pressure derivatives of SOEC and TOEC (dimensionless) of potassium fluoride**

Property	**KF**	
	Present	**Expt.**
dK□ /dP	5.3732	5.260
dS□ /dP	5.03984	5.250
dC□$_{44}$/dP	–0.4004	–0.430
dC□$_{111}$/dP	40.39568	
dC□$_{112}$/dP	1.0088	
dC□$_{166}$/dP	1.27088	
dC□$_{123}$/dP	1.14608	
dC□$_{144}$/dP	–0.93288	
dC□$_{456}$/dP	1.02128	

Table 4 : **The values of Cauchy discrepancy (in 10^{12} dyn /cm^2) for lattice dynamics of potassium fluoride**

Property	**KF**
C_{112}– C_{166}	–0.0002288
C_{123}– C_{456}	0.0026208
C_{144}– C_{456}	0.0008632
C_{123}– C_{144}	0.0017368

Table 5 : **Percentage deviation between experimental data and present study on TOEC and pressure derivatives of potassium chloride**

Property	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}	dK′/dP	dS′/dP	dC′$_{44}$/dP
KCl	5.2	5.7	3.4	5.02	11.02	11.9	4.8	16.2	6.9

III. RESULT AND DISCUSSION

Results on TOEC, FOEC and pressure derivatives of SOEC for potassium fluoride are generally better than those of others. It can also be seen from table 4 that Cauchy discrepancies is smaller for the TOE constants than for SOE constants. A possible explanation for this fact seems to be that many-body and 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 3. A comparative study for percentage deviation between observed data and our theoretical results have been presented in Table 5 for potassium halides. Generally, good agreement with their observed data (wherever available) have been found.

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