Comparative Study of Potassium Halides Parameters with Many Body and van der Waals Three Body Force Shell Model [VTBFSM]

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Research Article

ABSTRACT

In present paper authors have used the theoretical model for calculation of value of different model parameters of potassium halides by using the effect of Many body (Puri and Verma, 1977) (Basic model for calculation and aurthor directley used the all calculated value of many body) and compared by van der Waals three body force shell model. In presence of both the effects, better result came, which gave good agreement between theoratical and experimental result. Inclusion of van der Waals interactions (VWI) and three body interactions in the framework of a polarizable rigid shell model (RSM) gave FOEC (Forth order elastic constants), which is not possible to calculate only by many body effects. By using VTBFS model we can calculate all parameters like second and third order elastic constants (SOEC, TOEC and FOEC), pressure derivatives of first, second order and cauchy relation. So calculated result, compared well with the corresponding experimental results, which provided important theoratical formula to calculate all the property of alkali halides, earth alkaline metal and also for chalcoganides. So inclusion of [VTBFSM] interactions gave complete theoratical investigation for all type crystals.

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1. INTRODUCTION

Many-body forces are short in nature, by the quantum-mechanical analysis Lowdin (1947) and Lundqvist (1935) led idea that they are long-range many–body potential. The effect of long range many body potential on the TOE constants do not study so. In particular, the third–order elastic constants are the cofficient of the cubic terms, Chang (1965) has experimentally determined the TOE constants of alkali halides. Naran'yan (1963) and Ghate (1965) have calculated the TOE constants, using the Born central –force model for which Cauchy relations ($C_{112}=C_{166}$ and $C_{144} =C_{123} =C_{456}$) are satisfied at very low temperature (0 K). In the present paper authors have used van der Waals three body force shell model for calculation of the SOE, TOEC, FOEC and pressure derivative of SOEC, which are giving better result that is closer to experimental values than the other used model. However in present model (VTBFSM) Cauchy discrepancy is smaller for TOE constants than for SOEC. In fact the present model (VTBFSM) has revealed much better description of dynamical properties of Potassium halides. The potential energy of the crystal Φ is given by Tolpygo (1961) and Φ_0 is the crystal potential when the ions are all located at their equlibrium positions.

$$\Phi - \Phi_0 = \frac{1}{2} \sum_{lk\,\alpha} \left[\sum_{l'k'\beta'} \left\{ \Phi^R_{\alpha\beta}\left(lk, l'k'\right) u_\alpha\left(lk\right) u_\beta\left(l'k'\right) + y^{-1}_{(k')} \right. \right.$$

$$\Phi^\tau_{\alpha\beta}\left(lk, l'k'\right) u_\alpha\left(lk\right) \times u_\beta\left(l'k'\right) + y^{-1}_{(k)}\Phi^T_{\alpha\beta}\left(lk, l'k'\right)$$

$$p_\alpha\left(lk\right) p_\beta\left(l'k'\right) + y^{-1}_{(k)} y^{-1}_{(k')} \times \Phi^S_{\alpha\beta}\left(lk, l'k'\right) p_\alpha\left(lk\right)$$

$$\left. p_\beta\left(l'k'\right)\right\} + \alpha^{-1}_{(k)} p^2_\alpha\left(lk\right) - \left\{ p_\alpha\left(lk\right) + Z_{(k)} u_\alpha\left(lk\right)\right\}$$

$$\left. \hat{E}_\alpha\left(lk\right) \vphantom{\sum} \right]$$

1.1 Many-Body Potential

It is well known fact that during lattice vibration ions suffer an appreciable overlap and consequently their electron shells undergo deformation. This mechanism causes a transfer of charge between the overlapping adjacent ions. These transferred charges, in turn, interact via their associated Coulomb field with all other charges of the lattice and give rise to the long-range many-body interactions (MBI) (Lowdin, 1947; Lundqvist, 1952, 1955, 1957, 1961) whose most significant component is the three-body interaction (TBI). The origin of these (TBI) has been well established from the classical as well as quantum mechanical theories.

1.2 Present Model VTBFSM with VWI and TBI Effects

The necessity of including the van der Waals interactions (VWI) and three-body interaction (TBI) effects in the framework of rigid shell model (RSM) (Woods et al., 1960, 1963, 1963) has, to give a detailed account of the essential formalism of the present lattice dynamical model VTBFSM. Thus, the inclusion of VWI and TBI effects in RSM will employ the Hietler-London and the free-electron approximations. The interaction systems of the present model thus consist of the long-range screened Coulomb, VWI and three-body interactions and the short-range overlap repulsion operative up to the second-neighbor ions in potassium halides. Looking into the adequacy of this interaction system, the present models may hopefully be regarded as a successful approach for the dynamical descriptions of the potassium halides. The essential formalism and features of the present models have been discussed below.

2. THEORETICAL FORMALISM OF VTBFSM

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

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

where, the potential energy terms on the right hand side are being expressed as follows:

(i) 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

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

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

$$\Phi^C = \alpha_M \frac{Z^2 e^2}{r_0} \tag{3}$$

where, α_m is the Modelung constant whose value for NaCl-type lattice is −1.7476 and r_0 is

the equilibrium nearest neighbor distance.

(ii) 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 neighboring ions is restricted by the Pauli Exclusion Principle. The repulsive energy is 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

$$\Phi^R\left(r_{ij}\right) = a r_{ij}^{\ n} \qquad \text{(Born Potential)} \qquad (4)$$

$$\Phi^R\left(r_{ij}\right) = b \exp .(-r_{ij}/\rho) \qquad \text{(B-M) Potential)} \qquad (5)$$

where, a(or b) and η(or ρ) are the Born exponents called the strength and hardness parameters, respectively. It is clear from the above expressions that the evaluations of lattice energy require the determination of just two repulsive parameters if the total repulsive energy is contributed by the nearest neighbors only. In order to take explicit account of the B-M repulsion of the second-neighbors in the ionic crystal, a plausible extension of the expression (4) to the second-neighbor yields the repulsive energy (Born and Mayer, 1932; Fumi and Tosi, 1964).

$$\Phi^R = M\beta_{+-}b\exp\left[(r_+ + r_- - r)/\rho\right] + 1/2M'b$$
$$\left[\beta_{++}\exp(2r_+/\rho) + \beta_{--}\exp(2r_-/\rho)\right]\exp\left(-r'/\rho\right) \qquad (6)$$

where M and M' are the number of first and second-neighbors and r' is the distance between the second neighbors β_{ij} .

$$\beta_{ij} = 1 + \left(Z_i/n_i\right) + \left(Z_j/n_j\right) \qquad (7)$$

with Z_i and n_i as the valence and the number of outer electrons of the i-th ion, r_+ and r_- are the ionic radii of the positive and negative ions. The strength parameter (b) and the hardness parameter (ρ) in a family of salts can be determined from the equation of state and the volume derivatives of the lattice energy as indicated earlier. Thus, the expression (6) can be used to represent the repulsive energy up to the second neighbor without increasing the parameter in addition to b and ρ.

(iii) Third term Φ^{TBI} is three-body interactions potential. According to quantum-mechanical theory using Heitler-London approximation (Heitler and London, 1927), 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 (Heitler and London, 1927), 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 (1947) and Lundqvist (1935). This interaction potential is expressed as

$$\Phi^{TBI} = \alpha_m \frac{Z^2 e^2}{r_0}\left[\frac{2n}{Z}f(r)_0\right] \qquad (8)$$

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.

(iv) Fourth term of eqn. (1) ΦVWI and is ver der Waals interactions potential. The nature of this interaction is different and owes its origin to the correlations of the electro motions in different atoms. Using the crystal energy expression (1) the equations of motion of two cores and two shells can be written as

$$\omega^2 \underline{M}\ \underline{U} = (\underline{R} + \underline{Z}_m\ \underline{C'}\ \underline{Z}_m)\ \underline{U} + (\underline{T} + \underline{Z}_m\ \underline{C'}\ \underline{Y}_m)\ \underline{W} \qquad (9)$$
$$O = (\underline{T}^T + \underline{Y}_m\ \underline{C'}\ \underline{Z}_m)\ \underline{U} + (\underline{S} + \underline{K} + \underline{Y}_m\ \underline{C'}\ \underline{Y}_m)\ \underline{W} \qquad (10)$$

following the usual procedure (Woods et al., 1960, 1963, 1963). Here $\underline{U}$ and $\underline{W}$ are vectors describing the ionic displacements and deformations, respectively. $\underline{Z}_m$ and $\underline{Y}_m$ are diagonal matrices of modified ionic charges and shell charges, respectively. The elements of matrix $\underline{Z}_m$ consists of the parameter $\underline{Z}_m$ giving the modified Ionic charge.

$$\qquad (11)$$

$$Z_m = Z\xi = \pm Z\sqrt{1+(12/Z)f_0}$$

The elimination of $\underline{W}$ from eqns. (9) and (10) leads to the secular determinant:

$$\left| \underline{D}\,(\vec{q}\,) - \omega^2\ \underline{M}\ \underline{I} \right| = 0 \qquad (12)$$

for the frequency determination. Here $\underline{D}$ (q) is the (6×6) dynamical matrix given by

$$\underline{D}\,(\vec{q}\,) = \left(\underline{R}' + \underline{Z}_m\ \underline{C}'\underline{Z}_m\right) - \left(\underline{T} + \underline{Z}_m\ \underline{C}'\underline{Y}_m\right)\times$$
$$\left(\underline{S} + \underline{K} + \underline{Y}_m\ \underline{C}'\underline{Y}_m\right)^{-1}\left(\underline{T}^T + \underline{Y}_m\ \underline{C}'\underline{Z}_m\right) \qquad (13)$$

The dynamical matrix, given by eqn. (12), is a matrix (6×6) leading to six Vibrational frequencies (ω_j) corresponding each phonon wave vector $(\vec{q}\,)$. For wave-vector $(\vec{q}\,)$ along the principal symmetry directions $\vec{\Delta}, \vec{\Sigma}\ and\ \vec{\Lambda}, D\,(\vec{q}\,)$ can be reduced to lower order (2×2) matrices which simplify the computational work in solving the characteristic eqn. (12) and also the number of distinct branches of the dispersion relations get reduced because of the degeneracy's.

In view of the above mentioned advantages, let us write the secular eqn. (14) to the reduced order (2×2) determinant:

$$\begin{vmatrix} D\,(11) - m_1\omega^2 & D\,(12) \\[2em] D\,(21) & D\,(22) - m_2\omega^2 \end{vmatrix} = 0 \qquad (14)$$

Here, m_1 and m_2 are the masses of positive and negative ions, respectively. The elements of the dynamical matrix have been derived and obtained as:

$$D(11) = R_1 - \frac{e^2}{f}\left[\frac{d_1^2}{\alpha_1} + \frac{R_3^2}{R_2^2}\frac{d_2^2}{\alpha_2}\right] + \frac{e^2}{vf}\left[C_1(Z_m^2 - \frac{d_1^2\alpha_2}{\alpha_1} - \right.$$

$$\frac{R_3^2}{R_2^2}\frac{d_2^2\alpha_1}{\alpha_2} + 2Z_m d_1) + 2C'_2 d_2 \frac{R_3}{R_2}.(Z_m + d_1) +$$

$$\left.\frac{Z_m\alpha_2}{v}(Z_m + 2d_1)\left(C_1'^2 - C_2'^2\right)\right] \quad (15)$$

$$D(12) = D(21) = R_3 - \frac{e^2}{f}\left(\frac{R_3 d_1^2}{\alpha_1 R_1} + \frac{R_3 d_2^2}{R_2 \alpha_2}\right) + \frac{e^2}{vf}\left[C_1'\left\{\frac{R_3}{R_1}\right.\right.$$

$$\left(\frac{d_1^2\alpha_2}{\alpha_1} - Z_m d_1\right) + \frac{R_3}{R_2}\left(\frac{d_1^2\alpha_1}{\alpha_2} + 2Z_m d_2\right)\right\}$$

$$- C_2'\left\{Z_m^2 - Z_m(d_1 - d_2) - d_1 d_2\left(1 + \frac{R_3^2}{R_1 R_2}\right)\right\}$$

$$+ \frac{Z_m R_3}{v}\left(\frac{d_1\alpha_2}{R_1} - \frac{d_2\alpha_1}{R_2}\right)\left(C_1'^2 - C_2'^2\right)\right] \quad (16)$$

and

$$D(22) = R_2 - \frac{e^2}{f}\left[\frac{d_2^2}{\alpha_2} + \frac{R_3^2}{R_1^2}\frac{d_1^2}{\alpha_1}\right] + \frac{e^2}{vf}\left[C_1'(Z_m^2 - \frac{d_2^2\alpha_1}{\alpha_2} - \right.$$

$$\frac{R_3^2}{R_1^2}\frac{d_1^2\alpha_2}{\alpha_1} - 2Z_m d_2) - 2C'_2 d_1 \frac{R_3}{R_1}.(Z_m - d_2) +$$

$$\left.\frac{Z_m\alpha_1}{v}(Z_m - 2d_2)\left(C_1'^2 - C_2'^2\right)\right] \quad (17)$$

where, R_1, R_2, R_3, represent the elements of the short-range force matrices. Here, C'_1 and C'_2 are the long-range coupling coefficients between like and unlike ions.

The modified expressions for the electrical and mechanical polarizabilities are defined by the following relations:

$$\alpha_i = \frac{(Y_i Z_m)^2 e^2}{R_0 + K_i} \quad , (i = 1,2) \quad (18)$$

and

$$d_i = \frac{R_0(Y_i Z_m)}{R_0 + K_i} = -\frac{\alpha_i R_0}{Ze^2(Y_i Z_m)} \quad , (i = 1,2)$$

The general comparison of the dynamical matrix elements given by the eqn. (15) to (17) shows that besides several modifications introduced in various quantities, there appears a completely new term (underlined) in the expression for D(12). This term gives significant

contribution to the dynamical matrix when shell charge parameters are treated unequal. This inequality represents most realistic situation of the ions in crystals.

The final expressions for SOE , TOE and FOE constants of the NaCl –type crystals derived for elastic constants corresponding to VTBFSM are obtained as:

The expressions

$$\frac{4r_0^4}{e^2}C_{11} = \left[-5.112\,Z_m^2 + A_{12} + \frac{1}{2}(A_{11} + A_{22}) + \frac{1}{2}(B_{11} + B_{22}) + 9.3204\ \xi'^2\right] \tag{19}$$

$$\frac{4r_0^4}{e^2}C_{12} = \left[0.226\,Z_m^2 - B_{12} + \frac{1}{4}(A_{11} + A_{22}) - \frac{5}{4}(B_{11} + B_{22}) + 9.3204\ \xi'^2\right] \tag{20}$$

$$\frac{4r_0^4}{e^2}C_{44} = \left[2.556\,Z_m^2 + B_{12} + \frac{1}{4}(A_{11} + A_{22}) + \frac{3}{4}(B_{11} + B_{22})\right] \tag{21}$$

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

$$B_{11} + B_{22} + B_{12} = -1.165\,Z_m^2 \tag{22}$$

where

$$Z_m^2 = Z^2\left(1 + \frac{12}{Z}f_0\right) \qquad \text{and} \qquad \xi'^2 = Zr_0 f_0' \tag{23}$$

The term f_0 is a function dependent on the overlap integrals of the electron wave functions and the subscript zero indicates the equilibrium value.

$$C_{111} = P\left[37.556\,Z_m^2 + D_1 - 3C_1 + \frac{1}{4}(C_2 - 3A_2 - 9B_2)\right.$$
$$\left. + 13.980\,r_0^2 f_0'' - 89.303\,r_0 f_0'\right] \tag{24}$$

$$C_{112} = P\left[-4.836\,Z_m^2 + \frac{1}{8}(C_2 - 3A_2 - 3B_2)\right.$$
$$\left. + 4.660\,r_0^2 f_0'' - 18.640\,r_0 f_0'\right] \tag{25}$$

$$C_{166} = P\left[-7.166\,Z_m^2 - 2(B_1 + B_2) + \frac{1}{8}(C_2 - 3A_2 + 3B_2)\right.$$
$$\left. + 5.564\,r_0 f_0'\right] \tag{26}$$

$$C_{123} = P\left[2.717\,Z_m^2 + 16.692\,r_0 f_0'\right] \tag{27}$$

$$C_{144} = P\left[2.717\,Z_m^2 + 5.564\,r_0 f_0'\right] \tag{28}$$

$$C_{456} = P\left[\; 2.717 \; Z_m{}^2 \right] \tag{29}$$

and

$$C_{1111} = P\left[\; -305.321\, Z_m{}^2 + D_1 - 6C_1 + 15A_1 + 2R'_2 - 11.25\, B_2 + \right.$$
$$\left. 18.6407\, r_0{}^3 f_0''' - 206.574\, r_0{}^2 f_0'' + 863.498\, r_0 f_0' \right] \tag{30}$$

$$C_{1112} = P\left[\; 17.9034\, Z_m{}^2 + R'_2 + 4.6602\, r_0{}^3 f_0''' + 2.7116\, r_0{}^2 f_0'' + 103.489\, r_0 f_0' \right] \tag{31}$$

$$C_{1166} = P\left[\; 27.2234 \; Z_m{}^2 + 8(B_1 + B_2) + R'_2 + 5.564\, r_0{}^2 f_0'' - 44.2513 \; r_0 f_0' \right] \tag{32}$$

$$C_{1122} = P\left[\; 22.4611\, Z_m{}^2 + R'_2 - 50.2166\, r_0{}^2 f_0'' - 27.158\, r_0 f_0' \right] \tag{33}$$

$$C_{1266} = P\left[\; 27.1211 \; Z_m{}^2 + 4(B_1 + B_2) + R'_2 - 38.6873 \; r_0 f_0' \right] \tag{34}$$

$$C_{4444} = P\left[\; 32.9562 \; Z_m{}^2 + 9(B_1 + B_2) + R'_2 + 10.2242 \; r_0{}^2 f_0'' - 10.2242 \; r_0 f_0' \right] \tag{35}$$

$$C_{1123} = P\left[\; -6.3406 \; Z_m{}^2 + 5.564\, r_0{}^2 f_0'' - 22.5157 \; r_0 f_0' \right] \tag{36}$$

$$C_{1144} = P\left[\; -6.3406 \; Z_m{}^2 + 5.564 \; r_0{}^2 f_0'' + 16.692 \; r_0 f_0' \right] \tag{37}$$

$$C_{1244} = P\left[\; -6.3406 \; Z_m{}^2 - 8.4746 \; r_0 f_0' \right] \tag{38}$$

$$C_{1456} = P\left[\; -6.3406 \; Z_m{}^2 + 10.8678 \; r_0 f_0' \right] \tag{39}$$

$$C_{4466} = P\left[\; -4.0106 \; Z_m{}^2 + 2(B_1 + B_2) + 10.2242 \; r_0{}^2 f_0'' - 10.2229 \; r_0 f_0' \right] \tag{40}$$

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

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

The short-range force parameters (Ai, Bi, Ci and Di; i=1, 2) involved in our expressions is defined as:

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

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

where $G = \frac{2v}{e^2}$ $\textbf{v}$ and $k_1=1.4142$ for NaCl structure. Here $v = 2r_0^3$ is the unit cell volume for NaCl, e is the amount of electronic charge. The Cauchy discrepancies among the SOE and the TOE constants are therefore given by

$$C_{12} - C_{44} = \frac{e^2}{4a^2}[9.320\, r_0 f'] \quad , \quad C_{112} - C_{166} = \frac{e^2}{4a^2}[4.660\, r^2{}_0 f'^2 - 24.204\, r_0 f']$$

$$C_{123} - C_{456} = \frac{e^2}{4a^2}[16.692\, r_0 f'] \quad , C_{144} - C_{456} = \frac{e^2}{4a^2}[5.564\, r_0 f']$$

Cauchy relations break down both for the SOE constants and for the TOE constants in the presence of three-body interactions even at 0 K. If we put the function f and its derivatives equal to zero, the Cauchy relations are satisfied.

2.1 Pressure Derivatives for Rock Salt structure

When a cubic crystal is subjected to hydrostatic pressure, the symmetry of the crystal is preserved. Hence the pressure derivatives of the SOE and TOE constants are given in terms of the parameters A,B,C,f(r_0),r_0f'and f" we get as:

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

$$41.94\, r_0^2 f_0''\Big]$$

(41)

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

$$13.98\, r_0^2 f_0''\Bigg]$$

(42)

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

(43)

$$\frac{dC_{111}'}{dP} = -\frac{1}{3K}\Big[-3C_{11} - 6C_{12} + 3C_{111} + C_{1111} + 2C_{1112}\Big]$$

(44)

We can calculate similarly for other derivative by changing the constant term of C.

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

The theoretical calculation of many body model is reported by Smith (1975) and Haussuhl (1960) in Table 1 and by using our model VTBFSM. The input data are reported in Table 2.

3. RESULTS AND DISCUSSION

The parameters A, B, $f(r_0)$, r_0 f_0' have been evaluated by use of many body model and parameters C can be evaluated by approximating the overlapped repulsive potential. The others calculated values of the pressure derivative, SOE constants can easily be calculated. The input data are given in Table-1. Naran'yan (1963) and Ghate (1965) have deduced the expression for TOE constants from the central Born–Mayer potential, for which the Cauchy relations are satisfied at very low temperature (0 K). The Cauchy relations are failure at a finite temperature T in use of the vibrational energy. In the present study Cauchy relations failure occurred due to many bodies. By VTBFSM calculated values of the FOEC and TOE constants, pressure derivatives of the SOE and TOE constants agree fairly with the experimental values, as compared to theoretical values of Ghate (1965) and Naran'yan (1963) as a matter of fact, the agreement between our values and the experimental ones in case of KCl is excellent. The values of dK'/dP, dC'$_{44}$/dP and dS'/dP are invariable positive, depending on the crystal structure. It is true that agreement between the theoretical and experimental values of dK'/dP and dC'$_{44}$/dP, our calculated values should show some deviations from the room –temperature with experimental results.

Table 1: Input data for KF, KCl, KBr and KI in C_{ij} (in 10^{11} dyn/cm^2), r_o(in 10^{-8} cm), TOEC(in units 10^{12} dyn/ Cm^2) and Pressure derivatives of dS'/dP, SOEC and TOEC (dimensionless)

Property	KF	KCl	KBr	KI
	Present	Present	Present	Present
C_{11}	6.185	3.838	3.263	2.577
C_{12}	1.440	0.683	0.564	0.445
C_{44}	1.250	0.633	0.504	0.370
r_o	2.674	3.146	3.300	3.533
f_0	-0.0169	-0.0189	-0.0212	0.0234
r_0 f_0'	0.0180	0.0009	0.0013	0.0021
A	9.7238	10.386	10.395	10.4348
B	–0.928	–0.9005	–0.8680	–0.8371
C	–101.880	–119.789	–124.499	–130.065
C_{111}	-10.6856	-7.0615	-6.0266	-5.0020
C_{112}	-0.2164	-0.1753	-0.0977	-0.1288
C_{123}	0.2101	0.1325	0.1092	0.0856
C_{144}	0.2328	0.1266	0.1020	0.0767
C_{166}	-0.4459	-0.2171	-0.1716	-0.1242
C_{456}	0.2441	0.1236	0.0984	0.0723
dC'$_{44}$/dP	-0.411	-0.530	-0.565	-0.611
dK'/dP	4.252	5.028	4.854	5.387
dS'/dP	5.25(18)	561(18)	5.68(18)	6.03(18)

Puri & Verma (1977)

By Using VTBFS Model

Table 2: Input data for KF, KCl, KBr and KI C_{ij} (in 10^{11} dyn/cm^2), r_o(in 10^{-8} cm), TOEC and FOEC (in units 10^{12} dyn / Cm^2) and Pressure derivatives of dS′/dP, SOEC and TOEC (dimensionless)

Property	KF	KCl	KBr	KI
	Present	**Present**	**Present**	**Present**
C_{11}	7.570	4.832	4.832	3.380
C_{12}	1.350	0.542[b]	0.560	0.220
C_{44}	1.336	0.663	0.520	0.368
r_o	2.648	3.117	3.278	3.492
f_0	−0.0144	−0.0129	−0.0139	−0.0084
$r_0 f_0′$	−0.0128	−0.0212	−0.0443	−0.0409
A	11.6719	14.1470	13.3905	20.6045
B	−0.7319	−2.6346	−3.0275	−3.7923
C	−1.3303	−0.4289	1.3649	−1.6938
C_{111}	−10.813	−7.596	−6.180	−5.339
C_{112}	−0.249	−0.254	−0.135	−0.336
C_{123}	0.265	0.118	0.074	0.058
C_{144}	0.264	0.132	0.131	0.076
C_{166}	−0.475	−0.237	−0.107	−0.124
C_{456}	0.263	0.140	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
$dC′_{44}/dP$	−0.385	−0.501	−0.519	−0.610
$dK′/dP$	4.205	5.428	4.874	5.087
$dS′/dP$	4.846	5.786	7.222	5.571
$dC′_{111}/dP$	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

4. CONCLUSION

From the above discussion we can fairly conclude that by use of many body models we cannot calculate the value of higher order of pressure derivative and forth order elastic constant and we cannot predict any result for it but by using the present model VTBFSM we can calculate all the values of parameters which is more accurate to experimental values. So by use of present model we can successfully calculate all parameters and complete information for alkali halide crystal. Present model used by different researchers to calculate various property of alkali halide (Srivastava et al., 2004, 2005, 2010, 2011). In the present paper by inclusion of van der Waal model we can calculate third order, forth order elastic constant, pressure derivatives for higher order and Cauchy relation that was possible only through experimentally but by use of this model we can calculate all parameter for alkali halides that give good agreement with experimentally calculated value. So this model plays very important role for theoretical researcher to find out the all calculated value of halides crystal.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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