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## RESEARCH ARTICLE

### CRYSTAL DYNAMIC AND STRUCTURAL STUDY OF THORIUM SELENIDE (ThSe): ELASTIC BEHAVIOUR AND PRESSURE EFFECT

<sup>1</sup>Dwiwedi, B.P., <sup>2</sup>Mishra, K.K and <sup>1,2</sup>Upadhyaya, K.S

<sup>1</sup>Dept. of Physics, K.N.Govt. P.G. College, Gyanpur, S.R.N. Bhadohi (U.P.) India

<sup>2</sup>Dept. of Physics, Nehru Gram Bharati University Kotwa-Jamunipur, Allahabad, (U.P.) India

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#### ABSTRACT

The present paper is a result of the Endeavour's dedicated to put in practice a systematic theoretical examination of the phonon dispersion curves, variation of specific heat, two phonon density of states, anharmonic properties and high pressure phase transition study of ThSe by the suppletion of TRSM (three-body force shell model) and TRIM (three-body force rigid ion model). It is concluded that our theoretical results predicted by TRSM on phonon dynamics and derivable properties will be very much close to their measured data whenever reported in future. These are probably the first reports of its kind and they will certainly help the experimental workers to analyze their data in future

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#### INTRODUCTION

The electronic structure of thorium chalcogenides (ThS, ThSe, ThTe) which crystallize in rock-salt structure except for ThTe (which crystallizes in CsCl structure) has been extensively studied in recent decade. The detailed informations have been searched out experimentally and theoretically both on uranium chalcogenides in recent past. Since uranium ion has 5f electrons and thorium ion has essentially no 5f electrons, therefore, comparison of elastic and phonon properties of the uranium and thorium compounds should give some information on the influence of the 5f electrons and the type of bonding in these compounds. The nature of these compounds can be well understood by high energy gap, high dielectric constants and large negative ion polarizability. Due to their unique physical properties in optical vibration frequencies at zone centre ( $\Gamma$ -point), they have been a remarkable compound for those workers who are working experimentally and theoretically both. The details of the progression have been traced in review articles by (Bilz and Kress, 1979); (Singh, 1982) and research papers (Mahendra et. al, 2002; mahendra et. al, 2005; Pandey et.al, 2002; Sanyal and singh, 2003; Upadhyay et. al. 2001, 2002, 2004, 2005; pandey et.al. 2006; Upadhyay, 2006, Singh et.al. 2006; Srivastawa et. al., 2006; Ojha et.al., 2007). This fact is self evident from the development of numerous phenomenological models for predicting a few available experimental data on phonon dispersion, specific heats, harmonic and anharmonic elastic constants, optic constants and phase transition.

Theoretical models for dia-atomic crystals have progressed from classical model of (Kellermann, 1940) to more elaborate models, like, rigid shell model (RSM) and deformation dipole

model (DDM) developed, respectively, by (Cochran, 1959) and (Hardy, 1959, 1960, 1961, 1962). The restrictions imposed by the assumption of undeformable and unpolarizable ions in Kellermann's rigid ion model (RIM) prevents it from predicting the Cauchy violation, the phonon dispersion the polarization, the sziget effective charge and the long wave optical modes of vibrations. On contrary, the other two models (RSM and DDM) are although quite successful in predicting many crystal properties, but they suffer from some common drawbacks (Kellermann, 1940) due to which they are unable to explain the Cauchy violation (or elastic properties) and the longitudinal optical (LO) phonon modes along  $[qqq]$  direction of the first Brillouin zone.

The rigid ion model (RIM) fit used by (Jackmann et al., 1986) for uranium compounds exhibit common lack of agreement in the neighbourhood of X-point in the Brillouin zone. In case of ThTe the model places the LA mode at X above the TA mode, whereas in fact, the LA mode falls below the TA mode. The maxima in PDC are not matched by the model and neither is the upward curvature in the  $\Sigma_1$  acoustic mode. This suggests a need for further Fourier terms and hence forces that are long ranged than the nearest and next nearest neighbour forces are considered. The RIM and RSM models fail to explain the Cauchy violation ( $C_{12} \neq C_{44}$ ) in the elastic constants. In addition, these compounds exhibited strong optical phonon anomalies throughout the Brillouin zone and peculiar acoustic phonon propagation along  $[qqq]$  directions. These facts suggest that some types of many-body interactions are responsible for the elastic and phonon anomalies in these compounds.

It is emergent from the descriptions that the most realistic models for the lattice dynamics and statics of these solids can

\* Corresponding author: +91-5922-258206

E-mail address: krrish1225@gmail.com

be developed by introducing the effect of three-body interactions (TBI) in the framework of RIM and RSM. These two models TRIM and TRSM have different approaches as far as the interactions between ions are concerned. We have plotted the PDCs for these compounds using TRIM and TRSM. But according to lattice dynamical studies of Thorium chalcogenides it is clear that the TRSM explain PDC better than those of TRIM. For further studies of specific heats CDS peaks, two phonon IR Raman, anharmonic properties and study of phase transition of these chalcogenides, we have used TRSM only. The present study will be helpful in making qualitative understanding of these properties.

### Theoretical framework of the present model

In view of the remarkable success achieved from rigid ion model (RIM) and rigid shell model (RSM) to describe the lattice dynamics of alkali halides it seems worthwhile to explore the adequacies of RIM and RSM in doing so far these compounds. For betterment, we have presented two diversifications of the models, i.e., TRIM and TRSM, which arise by the inclusion of the effect of the long-range three-body interactions and short range overlap repulsive interactions (only upto the nearest neighbours) in the framework of RIM (Kellerman, 1940) and RSM (Woods et.al., 1960).

### Present Models TRIM and TRSM

The necessity of including the effect of short range overlap repulsive interactions in the framework of RIM (Kellerman, 1940) and RSM (Woods et.al., 1960) have already been emphasized in earlier descriptions. The aim of this section is, therefore, to give a detailed account of the essential formalism of the present lattice dynamical models (i) three-body force rigid ion model (TRIM) and (ii) three-body force rigid shell model (TRSM). The interaction systems of the present models thus consist of the long-range Coulomb and three-body interactions and the short range overlap repulsion operative upto the nearest neighbour ions in thorium chalcogenides (ThSe, ThTe and ThTe). Looking into the adequacy of these interaction systems, the present models may hopefully be regarded as a successful approach for the dynamical descriptions of these compounds. The essential formalism and features of the present models have been discussed below.

### Theoretical Formalism of TRSM for NaCl Structure

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

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

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

(i). First term  $\Phi^C$  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  $|\vec{r}_{ij}|$ , 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

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

where, the prime means summation over all ions except  $i=j$ ,  $\epsilon_{ij}$  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

$$\Phi^C = \alpha_M \frac{Z^2 e^2}{r_0} \quad (3)$$

where,  $\alpha_M$  is the Madelung constant whose value for NaCl-type lattice is -1.7476 and  $r_0$  is the equilibrium nearest neighbour distance.

(ii). Second term  $\Phi^R$  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 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

$$\Phi^R = M\beta_{++}b \exp[(r_+ + r_- - r)/\rho] + 1/2M'b [\beta_{++} \exp(2r_+/\rho) + \beta_{--} \exp(2r_-/\rho)] \exp(-r'/\rho) \quad (4)$$

where  $M$  and  $M'$  are the number of first and second-neighbours and  $r'$  is the distance between the second neighbours  $\beta_{ij}$  are the Pauling coefficients (Pauling, 1928 and Huggins and Mayer, 1933) defined as

$$\beta_{ij} = 1 + (Z_i/n_i) + (Z_j/n_j) \quad (5)$$

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 ( $\rho$ ) 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 (4) can be used to represent the repulsive energy upto the second-neighbour without increasing the parameter in addition to  $b$  and  $\rho$ .

(iii). Third term  $\Phi^{TBI}$  is three-body interactions potential expressed as

$$\Phi^{TBI} = \alpha_m \frac{Z^2 e^2}{r_0} \left[ \frac{2n}{Z} f(r)_0 \right] \quad (6)$$

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.  $\Phi^{TBI}$  is also long-range in nature hence it is added to the  $\Phi^C$ .

The equations of motion of two cores and two shells can be written as:

$$\omega^2 \underline{M} \underline{U} = (\underline{R} + \underline{Z}_m \underline{C}' \underline{Z}_m) \underline{U} + (\underline{T} + \underline{Z}_m \underline{C}' \underline{Y}_m) \underline{W} \quad (7)$$

$$O = (\underline{T}' + \underline{Y}_m \underline{C}' \underline{Z}_m) \underline{U} + (\underline{S} + \underline{K} + \underline{Y}_m \underline{C}' \underline{Y}_m) \underline{W} \quad (8)$$

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  $Z_m$  consists of the parameter  $Z_m$  giving the modified ionic charge.

$$Z_m = \xi = \pm Z \sqrt{1 + (12/Z)f_0} \quad (9)$$

This means that the ionic charge parameter ( $Z$ ) of RSM gets modified by a factor  $\{1 + (12/Z)f_0\}$  in TRSM. However, the core and shell charge parameters ( $X$ ,  $Y$ ) of RSM will be modified to  $(X\xi, Y\xi)$ . This modification leads to the following relation:

$$Z_m = \xi = X_m + Y_m \quad (10)$$

$\underline{R}$ ,  $\underline{T}$  and  $\underline{S}$  are matrices describing various short-range interactions in the crystal.  $\underline{C}'$  is the modified long-range interaction matrix given by

$$\underline{C}' = \underline{C} + (Z_m^{-2} Z r_0 f_0') \underline{V} \quad (11)$$

where the first term is due to Coulomb interactions and the second term is due to the three body interaction.

The elimination of  $\underline{W}$  from eqns. (7) and (8) leads to the secular determinant:

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

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

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

The number of adjustable parameters has been largely reduced by considering all the short-range interactions to act only through the shells. This assumption leads to  $\underline{R} = \underline{T} = \underline{S}$ . The element of short-range matrix  $\underline{R}$ , including nearest neighbour interactions have been represented by

$$R_{\alpha\beta}(kk') = [\Phi_{\alpha\alpha}(kk)]_0 + \sum \frac{e^2}{2v} \left\{ \frac{X_\alpha X_\beta}{r^2} \cdot (A - B) - \delta_{\alpha\beta} B \right\} \quad (14)$$

where first term in it shows a "self-interaction",  $v$  is the volume of unit cell,  $\delta_{\alpha\beta}$  is the Kronecker delta and  $(A, B)$  are the short-range parameters for the nearest neighbours. These are defined by

$$B = \frac{4r_0^2}{e^2} \left[ \frac{d}{dr} \Phi_1^{(R)}(r) \right]_{r=r_0}, \quad A = \frac{4r_0^3}{e^2} \left[ \frac{d^2}{dr^2} \Phi_1^{(R)}(r) \right]_{r=r_0} \quad (15)$$

where,  $\Phi_1^{(R)}(r)$  is the overlap potentials between the nearest neighbours.

### Elastic Properties for NaCl Structure

The expressions derived for elastic constants corresponding to TRSM (for nearest neighbours) are obtained as

$$\frac{4r_0^4}{e^2} C_{11} = [-5.112Z_m^2 + A_{12} + 9.3204 \xi'^2] \quad (16)$$

$$\frac{4r_0^4}{e^2} C_{12} = [0.226Z_m^2 - B_{12} + 9.3204 \xi'^2] \quad (17)$$

$$\frac{4r_0^4}{e^2} C_{44} = [2.556Z_m^2 + B_{12}] \quad (18)$$

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

$$B_{12} = -1.165 Z_m^2 \quad (19)$$

$$\text{where } Z_m^2 = Z^2 \left( 1 + \frac{12}{Z} f_0 \right) \quad \text{and} \quad \xi'^2 = Z r_0 f_0' \quad (20)$$

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.

### Vibrational Properties for NaCl Structure:

By solving the secular eqn. (12) along  $[q \ 0 \ 0]$  direction and subjecting the short and long-range coupling coefficients to the long-wavelength limit  $\vec{q} \rightarrow 0$ , two distinct optical vibration frequencies are obtained as

$$(\mu\omega_L^2)_{q=0} = R'_0 + \frac{(Z'e)^2}{v f_L} \cdot \frac{8\pi}{3} (Z_m^2 + 6\xi'^2) \quad (21)$$

$$(\mu\omega_T^2)_{q=0} = R'_0 - \frac{(Z'e)^2}{v f_T} \cdot \frac{4\pi}{3} Z_m^2 \quad (22)$$

where the abbreviations stand for

$$R'_0 = R_0 - e^2 \left( \frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right); \quad Z' = Z_m + d_1 - d_2 \quad (23)$$

$$f_L = 1 + \left( \frac{\alpha_1 + \alpha_2}{v} \right) \cdot \frac{8\pi}{3} (Z_m^2 + 6\xi'^2) \quad (24)$$

$$f_T = 1 - \left( \frac{\alpha_1 + \alpha_2}{v} \right) \cdot \frac{4\pi}{3} Z_m^2 \quad (25)$$

$$\text{and} \quad \alpha = \alpha_1 + \alpha_2 \quad (26)$$

### 2.3 Theoretical Formalism of TRIM for NaCl Structure

In an attempt to solve expressions for TRIM, all the equations of TRSM (from 1 to 26) remain the same, only the difference is in the expressions from (21) and (22). On solving the dynamical matrix along  $(q, 0, 0)$  and subjecting it to the long wavelength limit ( $q \rightarrow 0$ ) expressions for  $\omega_L(\Gamma)$  and  $\omega_T(\Gamma)$  are obtained as :

$$(\mu\omega_L^2)_{q=0} = R_0 + \frac{8\pi}{3} (Z_m^2 + 6\xi'^2) \quad (27)$$

$$(\mu\omega_T^2)_{q=0} = R_0 - \frac{4\pi}{3} (Z_m^2) \quad (28)$$

where  $R_0$  has been defined as

$$R_0 = [R_{\alpha\alpha}(kk)]_{q \rightarrow 0} = -[R_{\alpha\alpha}(kk')]_{q \rightarrow 0} \\ = \frac{Z^2 e^2}{v} (A + 2B)$$

### Anharmonic properties for NaCl Structure

We have studied the anharmonic elastic properties by calculating third and fourth order elastic constants as they provide physical insight into the nature of binding forces between the constituents of a crystal. 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 (1) and are similar to those derived by (Garg, Puri and Verma, 1977) for NaCl structure in the framework of TSM. The short-range force parameters ( $A_i$ ,

$B_i$ ,  $C_i$  and  $D_i$ ;  $i=1, 2$ ) involved in our expressions are defined as:

$$A = A_1 = G \left[ \frac{d^2}{dr^2} \phi_{kk'}^{SR}(r) \right]_{r=r_{kk'}}; B = B_1 = - \left[ \frac{G}{r} \frac{d}{dr} \phi_{kk'}^{SR}(r) \right]_{r=r_{kk'}} \quad (29)$$

$$C_i = \frac{A_i^2}{B_i} \quad \text{and} \quad D_i = \frac{A_i^3}{B_i^2} \quad (30)$$

where  $G = \frac{2v}{e^2}$ . Here  $v = 2r_0^3$  is the unit cell volume for NaCl,  $e$  is the amount of electronic charge.

### Expressions for TOEC and FOEC for NaCl structure

$$C_{111} = P \left[ 37.556 Z_m^2 + D_1 - 3C_1 + \frac{1}{4} (C_2 - 3A_2 - 9B_2) \right] \quad (31)$$

$$C_{112} = P \left[ -4.836 Z_m^2 + \frac{1}{8} (C_2 - 3A_2 - 3B_2) \right] \quad (32)$$

$$C_{166} = P \left[ -7.166 Z_m^2 - 2(B_1 + B_2) + \frac{1}{8} (C_2 - 3A_2 + 3B_2) \right] \quad (33)$$

$$C_{123} = P \left[ 2.717 Z_m^2 + 16.692 r_0 f_0' \right] \quad (34)$$

$$C_{144} = P \left[ 2.717 Z_m^2 + 5.564 r_0 f_0' \right] \quad (35)$$

$$C_{456} = P \left[ 2.717 Z_m^2 \right] \quad (36)$$

and

$$C_{1111} = P \left[ -305.321 Z_m^2 + D_1 - 6C_1 + 15A_1 + 2R_2' \right] \quad (37)$$

$$C_{1112} = P \left[ 17.9034 Z_m^2 + R_2' + 4.6602 r_0^3 f_0''' + 2.7116 r_0^2 f_0'' \right] \quad (38)$$

$$C_{1166} = P \left[ 27.2234 Z_m^2 + 8(B_1 + B_2) + R_2' + 5.564 r_0^2 f_0'' \right] \quad (39)$$

$$C_{1122} = P \left[ 22.4611 Z_m^2 + R_2' - 50.2166 r_0^2 f_0'' \right] \quad (40)$$

$$C_{1266} = P \left[ 27.1211 Z_m^2 + 4(B_1 + B_2) + R_2' \right] \quad (41)$$

$$C_{4444} = P \left[ 32.9562 Z_m^2 + 9(B_1 + B_2) + R_2' + 10.2242 r_0^2 f_0'' \right] \quad (42)$$

$$C_{1123} = P \left[ -6.3406 Z_m^2 + 5.564 r_0^2 f_0'' - 22.5157 r_0 f_0' \right] \quad (43)$$

$$C_{1144} = P \left[ -6.3406 Z_m^2 + 5.564 r_0^2 f_0'' + 16.692 r_0 f_0' \right] \quad (44)$$

$$C_{1244} = P \left[ -6.3406 Z_m^2 - 8.4746 r_0 f_0' \right] \quad (45)$$

$$C_{1456} = P \left[ -6.3406 Z_m^2 + 10.8678 r_0 f_0' \right] \quad (46)$$

$$C_{4466} = P \left[ -4.0106 Z_m^2 + 2(B_1 + B_2) + 10.2242 r_0^2 f_0'' \right] \quad (47)$$

$$\frac{dK'}{dP} = -(3\Omega)^{-1} \left[ 13.975 Z_m^2 + C_1 - 3A_1 + C_2 - 3A_2 \right] \quad (48)$$

$$\frac{dS'}{dP} = -(2\Omega)^{-1} \left[ 23.676 Z_m^2 + C_1 + \frac{C_2 + 6A_2 - 6B_2}{4} - 51.07584 r_0 f_0' \right] \quad (49)$$

$$\frac{dC'_{44}}{dP} = -(\Omega)^{-1} \left[ -11.389 Z_m^2 + A_1 - 3B_1 + \frac{C_2 + 2A_2 - 10B_2}{4} \right] \quad (50)$$

$$\Omega = -2.33 Z_m^2 + A_1 + A_2 + 27.961 r_0 f_0' \quad (51)$$

$$\frac{dC'_{111}}{dP} = -\frac{1}{3K} [-3C_{11} - 6C_{12} + 3C_{111} + C_{1111} + 2C_{1112}] \quad (52)$$

$$\frac{dC'_{112}}{dP} = -\frac{1}{3K} [C_{11} + 2C_{12} + 3C_{112} + C_{1112} + C_{1122} + C_{1123}] \quad (53)$$

$$\frac{dC'_{166}}{dP} = -\frac{1}{3K} [-C_{11} - 2C_{12} + 3C_{166} + C_{1166} + 2C_{1244}] \quad (54)$$

$$\frac{dC'_{123}}{dP} = -\frac{1}{3K} [-C_{11} - 2C_{12} + 3C_{123} + 3C_{1123}] \quad (55)$$

$$\frac{dC'_{144}}{dP} = -\frac{1}{3K} [C_{11} + 2C_{12} + 3C_{144} + C_{1144} + 2C_{1244}] \quad (56)$$

$$\frac{dC'_{456}}{dP} = -\frac{1}{3K} [-C_{11} - 2C_{12} + 3C_{456} + 3C_{1456}] \quad (57)$$

$$\text{where } P = \frac{e^2}{4a^4}; K = \frac{C_{11} + 2C_{12}}{3}; S' = \frac{C'_{11} - C'_{12}}{2}$$

$$\Omega = -0.3392 Z_m^2 + \frac{A_1 + A_2}{2} + 9.4008 r_0 f_0'$$

### 2.6. Theory of phase transition study

The inter-atomic potential of the present system in the framework of three body interaction approach is expressed as:

$$\phi(r) = u(r) = \sum_{ij} z_i z_j e^2 / r_{ij} + \sum_{ijk} z_i z_j e^2 f(r_{ik}) / r_{ij} \quad (58)$$

$$+ \sum_{ij} b \beta_{ij} \exp[r_i + r_j - r_{ij}] / P_{ij}$$

This potential includes long range Coulomb (first term), three body interaction term (second term) and Hartee-Fock form of short range repulsive energy (third term) where  $\beta_{ij}(i, j=1, 2)$

are the Pauling coefficients.  $Ze$  is ionic charge.  $b$  and  $\rho$  are the range and hardness parameters, respectively.  $r_{ij}$  is the nearest neighbour separation. This potential has only three parameters  $b$ ,  $\rho$  and  $f(r)$ , which are determine from the equilibrium condition

$$b/r_0 [\beta_{ij} \exp(r_i + r_j - r_{ij})/r] + 2\beta_{ij} \exp[(2r_i - \sqrt{2}r_0)/r] \quad (59)$$

$$+ 2\beta_{ij} \exp[(2r_j - \sqrt{2}r_0)/r] = (2\alpha_{ij}/3) z^2 e^2 / 2V$$

Thermodynamically, a phase transition is said to occur when the changes in structure details of the phase are caused by the

variation of free energy. The thorium chalcogenides compound transform from their initial  $B_1(\text{NaCl})$  to  $B_2(\text{CsCl})$  structure under pressure. The difference between free energy of the two phases becomes zero at the phase transition pressure. The stability of a particular structure is decided by the minimum of the Gibbs energy which is given as:

$$G = U + PV - TS \quad (60)$$

where  $u$  is internal energy which at  $0^\circ\text{K}$  corresponds to cohesive energy,  $S$  is the vibrational entropy at absolute  $T$ , pressure  $P$  and volume  $V$ .

The Gibbs free energies  $G_{B_1}(r) = u_{B_1}(r) + 2Pr^3$  for the  $\text{NaCl}(B_1)$  phase and  $G_{B_2}(r') = u_{B_2}(r') + 8\sqrt{3}/3 Pr'^3$  for the  $\text{CsCl}(B_2)$  phase become equal at the phase transition pressure  $P$  at temperature  $0\text{K}$  i.e.  $\Delta G (= G_{B_1} - G_{B_2})$  becomes zero. There the abbreviations  $u_{B_1}$  and  $u_{B_2}$  represent cohesive energies for the  $B_1$  and  $B_2$  phases, respectively and are written as:

$$u_{B_1}(r) = -1.7475e^2 z(z + 6f(r)/r + 6V_{ij}(r) + 6V_{ij}(r') + 8V_{ij}(r')) \quad (61)$$

and

$$u_{B_2}(r') = -1.7627e^2 z(z + 8f(r)/r' + 8V_{ij}(r') + 8V_{ij}(r') + 8V_{ij}(r')) \quad (62)$$

Here  $r$  and  $r'$  are nearest neighbour ( $nn$ ) separation corresponding to  $\text{NaCl}$  and  $\text{CsCl}$  phases respectively. For predicting transition pressure we have minimized the Gibbs free energies with respect to inter-atomic separations and calculated  $\Delta G (= G_{B_1} - G_{B_2})$ , for various pressures. The pressure at which  $\Delta G$  approaches zero corresponds to the phase transition.

The first order phase transition involving a discontinuity in volume takes place at the phase transition pressure. Experimentally the phase diagram obtained by plotting relative volume as a function of pressure.

### Debye Temperature variation:

The specific heat at constant volume ( $C_V$ ), at temperature  $T$  is expressed as

$$C_V = 3Nk_B \frac{\int_0^{\nu_m} \left\{ \left( \frac{h\nu}{k_B T} \right)^2 e^{\frac{h\nu}{k_B T}} \right\} G(\nu) d\nu}{\int_0^{\nu_m} G(\nu) d\nu} \quad (63)$$

where,  $\nu_m$  is the maximum frequency,  $N$  is the Avogadro's number,  $h$  is the Planck's constant and  $k_B$  is the Boltzmann's constant. The equation (63) can be written as a suitable form for a computational purpose as

$$C_V = 3Nk_B \frac{\sum_{\nu} \left\{ \left( \frac{h\nu}{k_B T} \right)^2 e^{\frac{h\nu}{k_B T}} \right\} G(\nu) d\nu}{\sum_{\nu} G(\nu) d\nu} \quad (64)$$

where  $E = h\nu/k_B T$  is the Einstein function, defined by

$$E(x) = x^2 \frac{\exp(x)}{(\exp(x) - 1)^2} \quad (65)$$

Also,  $\sum_{\nu} G(\nu) d\nu = \text{Total number of frequencies considered.}$

= 6000 for  $\text{NaCl}$  structure.

Hence, equation (21) can be written for  $\text{NaCl}$  structure type crystals, as

$$C_V = \frac{3Nk_B}{6000} \sum_{\nu} E(x) G(\nu) d\nu \quad (66)$$

The contribution of each interval to the specific heat is obtained by multiplying an Einstein function corresponding to mid-point of each interval (say  $0.1 \text{ THz}$ ) by its statistical weight. The statistical weight of the interval is obtained from the number of frequencies lying in that interval. The contributions of all such intervals when summed up give  $\sum_{\nu} E(x) G(\nu) d\nu$ . The specific heat  $C_V$  is then calculated by expression (66).

### COMPUTATIONS

The calculations on the  $\text{ThSe}$  have been performed with our models TRSM and TRIM described earlier. The parameters of the models have been determined from the knowledge of experimental values of the equilibrium inter-atomic separation ( $r_0$ ), the elastic constants ( $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ) and the vibration frequencies  $\nu_{LO}(T)$  and  $\nu_{TO}(T)$ .

The input data along with their relevant references and calculated model parameters using TRSM and TRIM for  $\text{ThSe}$  are given in tables 1.

The model parameters of both TRSM and TRIM have been used to compute the phonon spectra for  $\text{NaCl}$  structure  $\text{ThSe}$  for the allowed 48 non-equivalent wave vectors in the first Brillouin zone at Computer Center, Banaras Hindu University, Varanasi. The frequencies along the symmetry directions have been plotted against the wave vector to obtain the phonon dispersion curves (PDCs) from both the models. These curves have been compared with each other. Measured data on PDC of these compounds are not available as yet. Since the neutron scattering experiments provide us only very little data for the symmetry directions, we have studied the specific heat variation and 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, 1955) sampling technique and have been plotted against the absolute temperature ( $T$ ) in the same figure for  $\text{ThSe}$ . They have not been compared with the experimental data because no such measurements are available as yet.

The complete phonon spectra have been used to calculate the combined density of states (CDS),  $N(\nu_j + \nu_j)$  corresponding to the sum modes ( $\nu_j + \nu_j$ ), following the procedure of (Smart et al.,

1965). A histogram between  $N(\nu_j + \nu_j)$  and  $(\nu_j + \nu_j)$  has been plotted and smoothed out to obtain the CDS curves. These curves show well defined peaks which correspond to two-phonon Raman scattering peaks. Since no observed data on two-phonon IR/Raman spectra are available, these CDS peaks have been compared with the assignments calculated by using our present theoretical data. Furthermore, 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., 1965). Besides above properties, the third order elastic constants (TOEC) and fourth order elastic constants (FOEC) and their pressure derivatives have also been calculated.

For the study of phase transition at high pressure for ThSe, we have calculated equilibrium lattice constant and phase transition pressures, using equations (58) to (62).

**Table 1** Input data and model parameters for ThSe [ $C_{ij}$  (in  $10^{12}$  dyne  $\text{cm}^{-2}$ ),  $\nu$  (in THz),  $r_0$  (in  $10^{-8}$  cm),  $\alpha_i$  (in  $10^{-24}$   $\text{cm}^3$ )

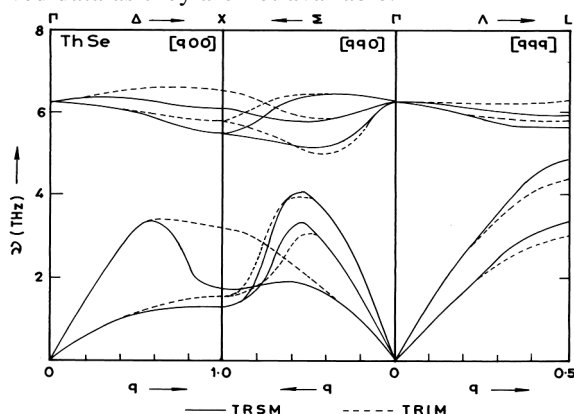
Input Data		Model Parameters		
Properties	Values	Parameters	TRIM	TRSM
$C_{11}$	2.8304 <sup>a</sup>	$A_{12}$	5.1425	11.4990
$C_{12}$	0.4353 <sup>a</sup>	$B_{12}$	-0.6063	-0.6063
$C_{44}^*$	0.2221 <sup>b</sup>	$Z_m^2$	2.0819	2.0819
$r_0$	2.9448 <sup>c</sup>	$r_0 f_0$	0.0206	0.0206
$\nu_{\text{TO}}(\Gamma)$	6.232 <sup>d</sup>	$d_1$	—	0.3962
$\alpha_1$	1.570 <sup>e</sup>	$d_2$	—	1.0467
$\alpha_2$	7.00 <sup>f</sup>	$Y_1$	—	-2.2131
$\epsilon_\infty$	8.087 <sup>g</sup>	$Y_2$	—	-3.7349

a-(Mahendra et.al, 2002); b- Extrapolated value for model parameters calculations; c-( D'Eye et.al.1952); d-(Mahendra et.al, 2005); e- Calculated by using Clausius Mossotti equation; f-(Kittel, 2006); g-( Dollins, 1978).

## RESULTS

### Phonon dispersion relations for ThSe

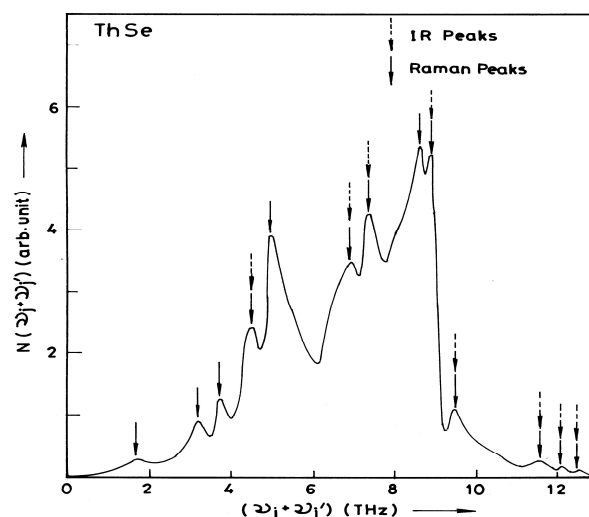
The phonon spectra for NaCl structure ThSe for the allowed 48 non-equivalent wave vectors in the first Brillouin zone with a comparative result on their phonon dispersion curves (PDCs) for the two models have been shown in figures 1. These results have not been compared with the observed data as they are not available.



**Fig 1** Phonon Dispersion Curve for ThSe

### Combined density of states and their assignments from two-phonon IR and Raman Spectra of ThSe:

The combined density of states for ThSe has been presented in figures 2. The comparison of CDS peaks and their assignments from two-phonon IR and Raman scattering spectra with the help of present study have been shown in tables 2. No observed data are available for thorium selenide (ThSe) crystal.



**Fig 2** Combined density of states curve for ThSe

**Table 2** Comparison of CDS peaks with their assignments of two-phonon Raman and infrared peaks for ThSe

CDS peaks ( $\text{cm}^{-1}$ )	Raman Peaks		IR Peaks	
	Assignments	Values ( $\text{cm}^{-1}$ )	Assignments	Values ( $\text{cm}^{-1}$ )
57	LA-TA(L)	50	—	—
107	2LA(X)	110	—	—
125	TO-LA(X)	127	—	—
151	LA + TA( $\Delta$ )	151	LA + TA( $\Delta$ )	151
165	LO - TO( $\Delta$ )	168	—	—
235	TO + TA( $\Delta$ )	235	TO + TA( $\Delta$ )	235
247	LO + TA( $\Delta$ )	248	LO + TA( $\Delta$ )	248
288	TA + TA( $\Delta$ )	272	—	—
298	TO + LA( $\Delta$ )	306	TO + LA( $\Delta$ )	306
317	LO + LA( $\Delta$ )	319	LO + LA( $\Delta$ )	319
388	2TO( $\Delta$ )	390	2TO( $\Delta$ )	390

### Third and fourth order elastic constants and pressure derivatives of SOEC, TOEC and the values of Cauchy discrepancy for ThSe

The third order and fourth order elastic constants for thorium selenide (ThSe) is shown in table 3. The pressure derivatives of TOEC calculated by TRSM for ThSe have been presented in table 4 and further the values of Cauchy discrepancy are also being shown in table 5 with the application of our models. No experimental results are available on these elastic constants and their pressure derivatives and Cauchy discrepancy TOEC and FOEC. This theoretical investigation is probably the first report of its kind on these compounds.

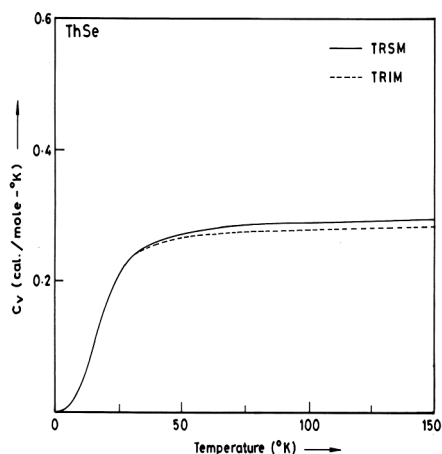
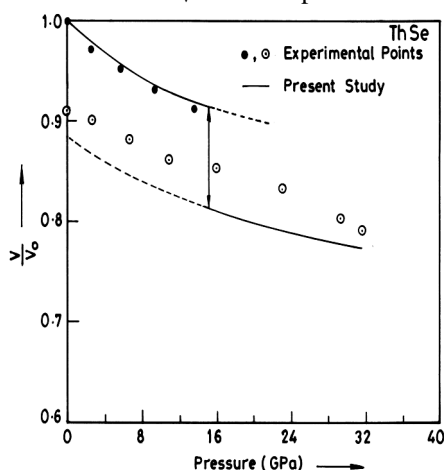
Fig 3 Variation of  $C_V$  with temperature for ThSe

Fig 4 Equation of state of ThSe

Table 3 Third and Fourth order elastic constants (in units:  $10^{12}$  dyne  $\text{cm}^{-2}$ ) for ThSe

Properties	Values	Properties	Values
$C_{111}$	1493.51	$C_{1122}$	14.26
$C_{112}$	-3.21	$C_{1266}$	16.33
$C_{123}$	1.84	$C_{4444}$	19.30
$C_{144}$	1.77	$C_{1123}$	-4.20
$C_{456}$	1.73	$C_{1144}$	-3.92
$C_{166}$	-4.17	$C_{1244}$	4.10
$C_{1111}$	1926.26	$C_{1456}$	-3.98
$C_{1112}$	12.09	$C_{4456}$	-2.86
$C_{1166}$	15.61	—	—

Table 4 Values of pressure derivatives of SOEC and TOEC (dimensionless) for ThSe

Properties	Values	Properties	Values
$dK'/dP$	10.46	$dC'_{166}/dP$	-2.05
$dS'/dP$	10.80	$dC'_{123}/dP$	2.91
$dC'_{44}/dP$	1.41	$dC'_{144}/dP$	-3.59
$dC'_{111}/dP$	-1734.63	$dC'_{456}/dP$	0.66
$dC'_{112}/dP$	-9.59	—	—

Table 5 Values of Cauchy discrepancy of TOEC and FOEC (in the units  $10^{12}$  dyne  $\text{cm}^{-2}$ ) for ThSe

Properties	Values	Properties	Values
$C_{112}-C_{166}$	0.95	$C_{1122}-C_{4444}$	-5.03
$C_{123}-C_{456}$	0.10	$C_{1123}-C_{4456}$	-1.33
$C_{144}-C_{456}$	0.03	$C_{1123}-C_{1144}$	-0.27
$C_{1112}-C_{1166}$	-3.52	$C_{1123}-C_{1456}$	-0.22
$C_{123}-C_{144}$	0.07	$C_{1123}-C_{1244}$	-8.30
$C_{1122}-C_{1266}$	-2.07	—	—

### Variation of specific heat for ThSe

Variation of  $C_V$  with  $T$  for ThSe has been plotted in figure 3 using TRIM and TRSM. This curve has not been compared with the experimental data because they are not available as yet.

### Phase Transition Study at High Pressure:

The input and output parameters used in phase transition study at high pressure for ThSe is shown in Table 6. We have calculated phase transition pressure from present model which are shown in table 7 also. The equation of state for ThSe is plotted between pressure and relative volume changes which shown in Figure 4.

Table 6 Input and Output parameters used in phase transition study for ThSe

Input parameters		Output parameters	
Properties	Values	Properties	Values
$r_+$ ( $10^{-8}$ cm)	0.99 <sup>h</sup>	$b(10^{-12}$ erg)	19.569
$r_-$ ( $10^{-8}$ cm)	1.19 <sup>h</sup>	$\rho$ ( $10^{-8}$ cm)	0.288
$B_T$ (GPa)	125 <sup>i</sup>	$f(r)$	0.0698

<sup>h</sup>-(Kittel, 2006); <sup>i</sup>-(Menoni et.al.,1983).

Table 7 Phase transition properties of ThSe

Properties	Predicted values	Experimental values
Equilibrium lattice constant ( $10^{-8}$ cm)	$R_1(B_1)$ $R_2(B_2)$	2.950 3.160
Phase transition pressure (GPa)	$P_t$	15.12 15.0 <sup>j</sup>
Relative volume change (%)	$(V/V_0)$	9.15 9.0 <sup>j</sup> 7.5 <sup>i</sup>

<sup>j</sup>-(Menoni et.al.,1983); <sup>j</sup>-(D'Eye et.al.1952)

## CONCLUSION AND DISCUSION

This paper presents a systematic theoretical investigation of the thorium Selenide (ThSe). The models proposed for this purpose, TRSM and TRIM have been developed by incorporating three body interactions (TBI) effects in the framework of rigid shell model (RSM) originated by (Cochran et.al, 1959). The present models, TRSM is reasonably better for describing the phonon dispersion curves, variation of specific heat with temperature and two-phonon infra-red and Raman spectra anharmonic elastic properties of these crystals and study of phase transition at high pressure. The overall success achieved by TRSM over TRIM reveals that the physical effects underlying in these crystals are almost the same as those occurring in the interaction system of the present model TRSM. The definite improvements achieved from the TRSM over RSM clearly indicates that the interaction mechanism beyond the dipolar approximation is mainly the charge transfer mechanism (Singh, 1982) which manifests the many-body interactions with most significant contribution from their three-body component. In view of its adequacies, the TRSM may be understood to provide a powerful and simple approach for a comprehensive study of the harmonic as well as anharmonic properties of the crystals under consideration. The only limitation of the model is the requirement of the knowledge of certain experimental information to be used as input data.

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 (Kellermann, 1940). From the symmetry, these 1000 points are reduced to 48 non-equivalent points for NaCl structure at which the variation frequencies have been obtained by solving the secular determinant. These frequencies represent the complete vibration (or phonon) spectra. The physical properties derived from these spectra have been discussed below.

The phonon dispersion relations are obtained by solving the secular equation for the six vibration frequencies corresponding to each phonon wave vector ( $\vec{q}$ ) along the principal symmetry directions  $[q,0,0]$ ,  $[q,q,0]$  and  $[q,q,q]$ . The phonon dispersion curves have been obtained by plotting these vibration frequencies ( $\nu$ ) against the wave vector  $q$  and displayed in figure 1 for ThSe. Since the present approach has two diversifications i.e. TRSM and TRIM and results reported from TRSM for uranium compounds (carbide, pnictides and chalcogenides) (Jackman, 1986) are comparatively more close to the measured data on PDC, therefore, further studies like variations of specific heat, two phonon IR/Raman data, CDS curves and anharmonic elastic constants for these crystals, we have used only phonon spectra of TRSM. It is seen from the figure 1 that the phonon dispersion curve (PDC) for thorium Selenide is similar but there are certain features in PDC of these crystals which deserve special mention. The three body interactions have influenced both LO and TO branches much more than acoustic branches (LA and TA) in these crystals. It is a matter of great interest that there is degeneracy of optical phonon frequencies at zone center (like uranium compounds) which do not show a LST-splitting of longitudinal optic and transverse optic phonon modes. Another striking feature of the present model is 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. Also, the results obtained from present models are almost identical in  $[qqq]$  direction and slightly differ in other directions. This may be particularly because the zone-center vibration frequencies have been used as input data in the calculation of their model parameters. A quantitative interpretation of general features of PDC is also obvious from the present models when they predict the gap between the acoustic and optic branches similar to forbidden gap between the valence and the conduction band. This gap is large in ThSe. Consequently, the values of frequencies in phonon dispersion are largest in ThSe. The reported theoretical investigations from various models are made for individual crystal in the following tables 8.

**Table 8** Comparison of frequencies by TRSM and TRIM at different points for ThSe

Points	Branches	TRIM Values (THz)	TRSM (THz)	Improvement (THz)	% Improvement
X	LO	6.53	6.06	0.47	7.19
	TO	5.76	5.46	0.30	5.21
	LA	3.20	1.66	1.54	48.12
	TA	1.53	1.26	0.27	17.64
L	LO	6.26	5.90	0.36	5.75
	TO	5.76	5.60	0.16	2.77
	LA	4.36	4.83	-0.47	10.78
	TA	3.00	3.33	-0.33	11.00

Table 8 predicts that the improvement in the PDCs of ThSe by TRSM is upto a maximum of 48% along LA(X) as compared to TRIM. In figure 3 we have presented the calculated low temperature specific heats of ThSe. We do not observe any anomalous behaviour in this property. The measured data of two phonon IR and Raman spectra are not available as yet. The assignments of two phonon IR and Raman peaks shown in tables 2 give a good interpretations of the CDS peaks (figure 2). The basic aim of detailed study of the two phonon infra-red and Raman spectra in the present work is to correlate the theoretical PDCs and optical experimental results for thorium chalcogenides. It is expected that this study will be useful in deducing the values of individual phonon frequencies of thorium chalcogenides to explain the considerable coupling between the modes of vibration of their ions.

The results on third and fourth order elastic constant tables 3 is probably the first report and as such it is not possible to comment on their reliability in the absence of experimental data. However, it is interesting that they show a close resemblance in signs with those obtained from NaCl structure crystals. A similar comment holds true for pressure derivatives of SOEC and TOEC 4 and calculated Cauchy discrepancy 5 for this crystal. These results on anharmonic elastic properties are, however, of only academic importance.

The calculated values of compressibility  $B_T$  is given in table 6 for ThSe, do not follow any trend of variation. This fact can be attributed to very large value of bulk-modulus and very small magnitude of ionic radius of negative ions. It is seen from the table 6 that structural properties of ThSe have been predicted most satisfactorily from the present calculations. The equilibrium values of lattice constants, both in  $B_1$  and  $B_2$  phases are in good agreement with experimental results. This fact suggests that the rock-salt ( $B_1$ ) structure in these compounds are most suitable and at high pressure they transform to body centred CsCl ( $B_2$ ) structure, similar to ionic (Rao and Sanyal, 1990) and several other rare earth compounds (Sakalle et.al, 1999). The calculated values of phase transition ( $B_1$ - $B_2$ ) pressure for ThSe agree reasonably well with the measured ones. However, from our calculations based on TRSM, it predicts 15.12 GPa for ( $B_1$ - $B_2$ ) transition for ThSe. The percentage of the relative volume change at the phase transition are in II excellent agreement with the experimental finding (Gerward, 1988), suggesting that the pressure volume characteristics for these crystals, is nicely reproduced by the present model TRSM.

This study is strongly supported by the published work of our research group (Bilz and Kress, 1979); (Singh, 1982) and research papers (Mahendra et. al, 2002; mahendra et. al, 2005; Pandey et.al, 2002; Sanyal and singh, 2003; Upadhyay et. al. 2001, 2002, 2004, 2005; pandey et.al. 2006; Upadhyay, 2006, Singh et.al. 2006; Srivastava et. al., 2006; Ojha et.al., 2007; Upadhyaya et.al. 2003, 2003; Chaubey et.al, 2004; Tiwari et.al., 2004; Pathak et.al. 2004; Singh et.al., 2004; Pandey et.al., 2004; Singh et. al., 2004; Dwiwedi et.al. 2004; Pandey et.al., 2004; Srivastava et.al, 2005; Srivastava et.al., 2005; Upadhyay et.al., 2005; Pandey et.al, 2005; Pandey et.al., 2005, 2005; Singh et.al. 2005; Tripathi et.al, 2005; Srivastava et.al., 2005; Dwiwedi et.al., 2005; Upadhyay et.al., 2005; Tiwari et.al, 2007; Singh et.al. 2007; Tiwari et.al., 2007, Tiwari et.al. 2009, 2011, Mishra et.al. 2012). It is concluded that our theoretical results predicted by TRSM on



phonon dynamics and phase transition will be very much close to their measured data whenever reported in future. These are probably the first reports of its kind and they will certainly help the experimental workers to analyze their data in future.

In view of overall achievements discussed, above, it may be concluded that the inclusion of the effect of three-body interactions in the frame work of rigid shell model is important and significant for the study of structural properties at high pressure and phonon dynamics of thorium chalcogenides. The scope of inclusion of other effects like van der Waals interactions are still open for theoretical workers if the measured data are reported in future.

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