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Debye temperature variation in thallium fluoride (TIF)

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ABSTRACT

Thallium halides have CsCl structure except TlF which has an orthorhombically distorted variant NaCl-type structure. At the normal room temperature it has a distorted rock salt structure. The nature and the physical properties of the thallous halides have attracted an increased interest in the study of their lattice dynamics. The dynamical behavior of thallium fluoride (TlF) have been studied by using van der Waals three-body force shell model (VTBFSM), which incorporates the effects of the van der Waals interaction with long-range Coulomb interactions, three-body interactions and short-range second neighbour interactions in the framework of rigid shell model (RSM). In present paper the variations of Debye temperature with absolute temperature have been theoretically calculated for thallium fluoride using (VTBFSM).

Keywords: Phonon; Debye Temperature & Van Der Waals Interaction

INTRODUCTION

The monoflourides of thallium, potassium, rubidium, cesium and silver constitute a class of binary fluorides for which CsCl-type structures would be excepted if the radius-ratio criterion obtained [1]. Availability of the measured data on Debye temperature variations [2,3] along with their theoretical values[4] and their interpretations by means of theoretical models[5-10] with successfully describe their interesting properties. This has motivated to author for incorporation of the effects of van der Waals & three-body interactions in the framework of ion polarizable (RSM) by Dick and Overhauser[11] and Woods et al[12] by two different groups of workers has given for study of lattice property with short-range interactions effective up to the second neighbour. Therefore, it is concluded that the most realistic model for study of complete harmonic dynamical behaviour of the crystals can be developed by introducing the effect of van der Waals interactions (VWI) and expression for the contribution of (TBI) to the dynamical matrix has been rigorously derived and exactly evaluated by Verma and Singh [13] for NaCl-structure in the framework of RSM. The present model is known as van der Waals three-body force shell model (VTBFSM). Here a theoretical study of Debye temperatures variation of TIF has been presented in terms of ΘD and T (K) that are consistent with experimental data observed by various workers.

In Figure-1 shows the atomic structure of TIF with three dimensional space vectors.



Figure 1. Atomic Structure of TIF

2. Theory

The necessity of including the (VWI) and (TBI) effects in the framework of (RSM)[14] has already been discussed above. The van der Waals interaction (VWI) potential owes its origin to the correlations of the electron motions in different atoms. The electrons of each atom shift with respect to the nucleus in the presence of other atoms and consequently an atom becomes an electric dipole. The instantaneous dipole moment of a closed shell atom induces as the van der Waals interaction potential. 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,TBI and the short-range overlap repulsion operative upto the second-neighbour ions in thallous halides. The general formalism of VTBFSM can be derived from the crystal potential whose relevant expression per unit cell is given by

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

Where, First term Φ^{C} is Coulomb interaction potential. This interaction potential is long-range in nature. Thus, total Coulomb energy for the crystal is

$$\Phi^{C}(r) = \sum_{j} \Phi^{C} \alpha_{M} \frac{Z^{2} e^{2}}{r_{0}} (r_{ij})$$

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.

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

Where, a (or b) and $\eta(or\rho)$ are the Born exponents called the strength and hardness parameters, respectively. Third term Φ^{TBI} is three-body interactions potential. As a natural consequence of the anti-symmetry requirement on the wave function[15], 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[16] and Lundqvist[17]. This interaction potential is expressed as

$$\boldsymbol{\Phi}^{TBI} = \boldsymbol{\alpha}_{m} \frac{Z^{2} e^{2}}{r_{0}} \left[\frac{2n}{Z} f(r)_{0} \right]$$

Where, the term $f(r)_0$ is a function dependent on the overlap integrals of the electron wave-functions. Φ^{TBI} is also long-range in nature hence it is added to the Φ^{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 closely the method used by Wood et.al[12]. By using the potential energy expression (1), the equations of motion of two cores and two shells can be given as.

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$$\omega^2 M U = (R + Z_m C Z_m) U + (T + Z_m C Y_m) W$$

$$0 = (T^T + Y C Z_m) U + (S + K + Y C Y_m) W$$
(2)
(3)

Here, U and W are vectors describing the ionic displacements and deformations respectively, Zm and Ym are the diagonal matrices of modified ionic charges and shell charges, respectively, M is the mass of the core, T and R are the repulsive Coulombian matrix respectively; C' and Ym are the long-range interaction matrices which includes Coulombian and three-body interaction respectively; S and K are core-shell and shell-shell repulsive interaction matrices respectively T^{T} is the transpose of the matrix T. All these variables are as described in [14]. The introduction of VWI and TBI in the framework of RSM with the elimination of W from eqs (2) and (3) leads to the secular determinant:

$$\left|\underline{D}(\vec{q}) - \omega^2 \underline{MI}\right| = 0 \tag{4}$$

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

$$\underline{D}(\vec{q}) = (\underline{R}' + \underline{Z}_m \underline{C'Z}_m) - (\underline{T} + \underline{Z}_m \underline{C'Y}_m) \times (\underline{S} + \underline{K} + \underline{Y}_m \underline{C'Y}_m)^{-1} (\underline{T}^T + \underline{Y}_m \underline{C'Z}_m)$$
(5)

Where R, T and S are short ranges forces appear in the form of matrices defined by[10].

$$\underline{\mathbf{C}}' = \underline{\mathbf{C}} + (\mathbf{Z}_{\mathrm{m}}^{-2} \operatorname{Z} \mathbf{r}_{0} f_{0}') \, \underline{\mathbf{V}}$$
(6)

Where $f_0^{'}$ is the first –order space derivative and Z_m modified ionic polarizability.

3. Computations

Specific heats are compared with that computed from the phonon spectra. This comparison is usually done by plotting the Debye temperatures against the temperature. At high temperatures, quantum consideration carry almost no significance but at low temperature the validity of Debye's approximation proved. For calculating Debye temperature at low and high temperature case given by formula. Disagreement has been observed at the higher temperature side may be ascribed to the non-inclusion of the harmonic interactions in the present model. The Specific heat constant volume (C_V), at temperature T is expressed as Debye's model define the frequency distribution function which is given by

$$\Theta D = h \nu m/K \tag{7}$$

For calculating the exact variation of Debye temperatures we have used the Blackmann's[18] sampling technique. In this technique, the frequency spectrum is divided into a suitable number of equal intervals and the specific heat is expressed as a sum over Einstein functions corresponding to the mid point of each interval. Thus,

$$C_{v} = \frac{3R}{6000} \sum_{v} g(v) E(v) dv$$
(8)

where E(v) is the Einstein function, R is the gas constant and g(v)dv are the number of frequencies lying in the interval (v-dv/2) to (v+dv/2). In given Figure-2 shows the Debye temperature variation graph between T temperature and Θ_{D} .

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Figure 2. Debye Temperature Variation of Thallous Fluoride

RESULTS AND DISCUSSION

In the present study the variation of Debye temperatures (Θ D) at different temperatures T have been calculated and plotted by the availability of experimental data of Pistorius and Clark [19]. Despite the lower symmetry of TIF and the uncertainty as to the exact nature of the distortion of the lower–temperature structure, a heat capacity determination of the deviation from the harmonic model of lattice vibration is of great interest because of extremely large disparity in ion masses [1]. Due to this available data it crate much interest to author for theoretical studies of TIF . If we start from the lowest temperature first decreases to a minimum, then increases to a flat maximum and finally decreases slowly .At lower value side of Θ D no deviation observed but at increasing value of Debye temperature the mix nature of curve clearly observable near 350K. The initial slope of the melting curve of TIF is considerably lower .This is similar to the behaviour encountered for potassium, rubidium and sodium halides .The thermo dynamical functions have a probable error of less than 10% above 100K and 200 K in this graph, relative to other fluorides, significant deviation beyond the harmonic limits begins to appear.

CONCLUSION

Relativistic effects in dissociation energies are large. Part of these large effects is due to atomic spin-orbit coupling in thallium and the heavier halides, only TIF shows such large effect. Thallium halides are thermodynamically stable if we neglect entropy effects. Thus, it may be possible for these species to be trapped by matrix isolation techniques at low temperatures for spectroscopic investigations. Our study shows a better agreement at lower temperature side but slight disagreement at the higher temperature side may be ascribed to the non-inclusion of the an harmonic interactions in the present model, which it may be inferred that the incorporation of van der Waals interactions is essential and appropriate for the complete description of dynamical behaviour of thallium fluorides. Complete lattice dynamical property of alkali halides of NaCl and CsCl-type structure like potassium and thallous halides theoretically reported by some researcher[20-33], create much interest for further study of such crystals.

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