



EFFECT OF MANY BODY INTERACTIONS ON OPTICAL DIELECTRIC CONSTANT OF LEAD CHALCOGENIDES

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ABSTRACT

A theoretical model for the optical dielectric constant of lead chalcogenides, incorporating the effect of many body interactions and Vander Waals interactions in the framework of rigid shell model is proposed. It is shown to yield accurate values for the optical dielectric constant of lead chalcogenides at room temperature. The computed values of optical dielectric constant of lead chalcogenides are compared with those in literature and measured by other researchers.

Key words: Lead chalcogenides, Rigid shell model, Optical dielectric constant.

INTRODUCTION

The lead chalcogenides (PbS, PbSe, PbTe and SnTe) are the IV-VI ionic semiconductors. The ionic model for crystal optical dielectric constant assumes that a crystal is composed of distinct polarizable ions which may be assigned individual polarizabilities. If such a crystal has cubic symmetry, the high frequency dielectric constant is related to the polarizabilities of its constituent ions by the Clausius-Mosotti relation.

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\alpha_m}{3v_m}$$

Here ϵ is the dielectric constant, v_m is the volume per formula unit and α_m is the sum of the polarizabilities of the ions which compose a formula unit. A more sophisticated approach, developed by Wilson and Curtis¹ and extended and refined by Coker², allows the ionic polarizabilities to vary from crystal to crystal in systematic fashion, although at the expense of introducing additional variable empirical parameters. In view of extent of empirical work³⁻⁷, in this work, we present a simple interpretation of the effect of many body interactions and Vander Waals interactions in the framework of rigid shell model for the

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lead chalcogenides. A similar study has been reported for alkali halides by the author⁸ and other researchers⁹. The optical dielectric constant of lead chalcogenides has been investigated at room temperature, in terms of additional three body interactions term ($Z_m, r_0 f_0'$). Z_m and $r_0 f_0'$ are determined by Upadhyaya et al.¹³ Since some of the vibration frequencies of zone-boundary points have been used to determine the model parameters, therefore, good agreement achieved for symmetry directions does not essentially guaranteed the agreement in the other general directions.

Theory

There has been always a continuing effort to obtain accurate interatomic potential functions. The interaction potential energy function is generally used to study the crystalline properties of diatomic crystal like lead chalcogenides. The first NaCl-structure like crystal potential, which gave a good fit to the lattice energy were obtained by Huggins and Mayer in 1933. The total potential for the lead chalcogenides can be written as

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

When first term Φ^C is coulomb interaction potential and is long-range in nature, second term is Φ^R short-range overlap repulsion potential, third term Φ^{TBI} is three-body interactions potential and the last term is Φ^{VWI} Vander Waals interactions potential and owes its origin to the correlations of the electron motions in different atoms. Thus the cohesive energy per mole is given by -

$$\Phi = N\Phi(r) = N(\Phi^C + \Phi^R + \Phi^{TBI} + \Phi^{VWI}) \quad \dots(2)$$

$$\text{where, } \Phi^c(r_0) = - \left[\sum_{n_1, n_2, n_3}^{+\infty} \frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2 + n_2^2 + n_3^2}} \right] \cdot \frac{e^2}{r_0}$$

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

$$\Phi_{dd}^{VWI}(r_{ij}) = -\frac{3}{2} \alpha_i \alpha_j \frac{E_i E_j}{E_i + E_j} \cdot \frac{1}{r_{ij}^6} \quad \text{and}$$

$$\Phi^{TBI} = e^2 \sum_{lk} \sum_{l'k'} \sum_{l''k''} Z_k f\{r(lk, l'k')\} \frac{Z_k''}{|\bar{r}(lk; l''k'')|}$$

and N is Avogadro number.

Using the crystal potential expression (1) the equations of motion of two cores and two shells can be written as

$$\omega^2 M U = (R + Z_m C' Z_m) U + (T + Z_m C' Y_m) W \quad \dots(3)$$

$$O = (T^T + Y_m C' Z_m) U + (S + K + Y_m C' Y_m) W \quad \dots(4)$$

Here U and W are vectors describing the ionic displacements and deformations, respectively. Z_m and 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.

$$Z_m = \{z(z + 12f_0 + 4r_0 f_0')\}^{1/2} \text{ for NaCl like structure} \quad \dots(5)$$

However, the core and shell charge parameters (X, Y) of RSM will be modified to ($X\xi$, $Y\xi$). These modifications lead to the following relation:

$$Z_m = Z\xi = X\xi + Y\xi \quad \dots(6)$$

Such that $X+Y=Z$; R, T and S are matrices describing various short-range interactions in the crystal. C' is the modified long-range interaction matrix given by

$$C' = C + (Z_m^{-2} Z r_0 f_0') V + (Z^2 Z_m^{-2}) D \quad \dots(7)$$

Here D is a matrix contributed by the Vander Waals interactions.

The elimination of W from equations (3) and (4) leads to the secular determinant:

$$\left| D(\vec{q}) - \omega^2 \underline{M} \underline{I} \right| = 0 \quad \dots(8)$$

Here D (q) is the (6×6) dynamical matrix given by

$$\underline{D}(\vec{q}) = (\underline{R}' + \underline{Z}_m \underline{C}' \underline{Z}_m) - (\underline{T} + \underline{Z}_m \underline{C}' \underline{Y}_m) \times (\underline{S} + \underline{K} + \underline{Y}_m \underline{C}' \underline{Y}_m)^{-1} (\underline{T}^T + \underline{Y}_m \underline{C}' \underline{Z}_m) \quad \dots(9)$$

Optical behaviors of lead chalcogenides

As mentioned earlier, the electron-shell deformation is included in form of charge-transfer in this model, so all the dielectric relations, except the macroscopic Lyddane-Sachs-

Teller (LST)-relation, are completely modified. Many body interactions and Vander Waals interactions in the framework of rigid shell model, providing more accurate values of several quantities, involved in these relations.

The LST-relation remains unchanged as

$$\frac{\epsilon_0}{\epsilon_\infty} = \left(\frac{\omega_{LO}}{\omega_{TO}} \right)^2 \quad \dots(10)$$

Which in turn requires that the values of static and high frequency dielectric constants ($\epsilon_0, \epsilon_\infty$) are given by -

$$\epsilon_\infty = \left[\left\{ 1 + \frac{\alpha_m}{\nu} \left(\frac{8\pi}{3} + \lambda \right) \right\} \left\{ 1 - \frac{\alpha_m}{\nu} \left(\frac{4\pi}{3} - \lambda \right) \right\}^{-1} \right] \quad \dots(11)$$

$$\epsilon_0 = \left[\left\{ 1 + \frac{\alpha_0}{\nu} \left(\frac{8\pi}{3} + \lambda \right) \right\} \left\{ 1 - \frac{\alpha_0}{\nu} \left(\frac{4\pi}{3} - \lambda \right) \right\}^{-1} \right] \quad \dots(12)$$

These values of high frequency dielectric constants ($\epsilon_0, \epsilon_\infty$) leads to the following modified Lorentz-Lorentz and Clausius-Mosotti relations are as follows:

$$(L-L) \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi\alpha_m}{3\nu} \left(1 + \frac{\lambda\alpha_m}{\nu} \right)^{-1} \quad \dots(13)$$

$$(C-M) \frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \frac{4\pi(\alpha_m + \alpha_I)}{3\nu} \left\{ 1 + \frac{\lambda(\alpha_m + \alpha_I)}{\nu} \right\}^{-1} \quad \dots(14)$$

Where $\lambda = \frac{8\pi p z r_0 f'_0}{9e_L^2}$ and $\alpha_0 = \alpha_m + \alpha_I$.

$p = 6$ (for NaCl)

With Lundqvist's effective charge-parameter for NaCl like structure

$$e_L = \{z(z + 12f_0 + 4r_0f'_0)\}^{1/2}$$

The total electronic polarizabilities of ions are

$$\alpha_m = \alpha_{m1} + \alpha_{m2}$$

While ionic polarizabilities are

$$\alpha_I = \frac{(Z' e)^2}{R'_0}$$

Table 1: Model parameters of lead chalcogenides [13]

Parameters	Values for PbSe	Values for PbTe
Z	2	2
f(r) ₀	-0.07832	-0.07819
r ₀ f' ₀	0.02820	-0.05353
A ₁	7.54391	8.18327
B ₁	-0.67878	-0.68284
A ₂	-0.42912	-0.45083
B ₂	-0.06130	0.06440
d ₁	0.36520	0.69271
d ₂	1.19310	1.04891
Y ₁	-3.91816	-1.99190
Y ₂	-1.71915	-2.39364

Computation

Calculated values of optical dielectric constant and its comparison with both theoretical and experimental data.

RESULTS AND DISCUSSION

Considering, the Vander Waals interactions and three body interactions in the frame work of rigid shell model, we have computed the optical dielectric constant for lead chalcogenides crystals. The results are presented with the known literature values¹⁰ of optical dielectric constant in the Table 2. The present values were found to be in a reasonable good agreement with the experimentally known optical dielectric constant of lead chalcogenides.

Table 2

Solids	Structure	Optical dielectric constant ϵ_0 (Present Study)	Optical dielectric constant ϵ_∞ (Present Study)	Optical dielectric constant ϵ_0 (measured values at room temp.) ¹⁰	Optical dielectric constant ϵ_∞ (measured values at room temp.) ¹⁰
PbSe	NaCl	208.67	21.24	210	22.9
PbTe	NaCl	411.12	30.90	414	33

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