

A Theoretical study of Debye Temperature Variations of Gallium Pnictides

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Abstract: The Gallium Pnictides are one of the several groups III-V compounds with zinc-blende structure (ZBS) which have been widely studied because of their important semiconducting properties. A study of Debye temperature variations of Gallium Pnictides (GaP, GaAs and GaSb) have been presented using an interionic potential, which consists of a long-range Coulomb and three-body interactions (TBI), short-range overlap repulsion and van der Waals (vdW) interactions. Our study shows a better agreement at lower temperature side. Slight disagreement at the higher temperature side may be ascribed to the non-inclusion of the anharmonic interactions in the present model. To conclude, we can say that our present model gives a better interpretation of the lattice dynamical studies of these crystals.

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Index Terms— Phonon; Debye Temperature, Combined densities of states, gallium antimonide, van der Waals interaction.

1. Introduction

The compound semiconductors of zinc-blende structure (ZBS) crystals are the promising candidate materials for numerous experimental and theoretical investigations. These investigations are the consequence of efforts devoted to understand the interesting crystal property and interaction mechanisms exhibited by these compounds. Gallium Pnictides are one of the several groups III-V compounds which have been widely studied because of their important semiconducting properties. The lattice vibrations play an important role in determining the dielectric and infrared optical properties of these crystals as well as their free carrier transport. Hence it is of considerable interest to study the phonon dispersion curves of Gallium Pnictides (GaP, GaAs and GaSb) whose experimental data [1 to 6] of different spectra are available. A good agreement of our results for phonon dispersion curves and Raman assignments for these crystals has been shown in the previous paper published earlier [7 and 19]. Here a study of Debye temperatures variation of GaP, GaAs and GaSb has been presented in terms of Θ_D and T(K). In addition, the results have been analysed with the aid of the Three Body Force Shell model (TSM) which have been found applicable to zincblende materials (R.K.Singh et al) [8 to 12]. For each material, a set of Debye temperatures variation has been obtained that are consistent with experimental data observed by various workers.

2. Theory

2.1. Three Body Crystal Potential

In order to describe the cohesion in ZBS semiconductors, we have employed a three-body potential to express the crystal energy for a particular lattice separation (r) as

$$\Phi(r) = \Phi_{LR}(r) + \Phi_{SR}(r) \quad (1)$$

where the first $\Phi_{LR}(r)$ consists of the long-range Coulomb and three-body interaction (TBI) energies given by

$$\begin{aligned} \Phi_{LR}(r) &= - \sum_{\substack{ij \\ i \neq j \neq k}} \frac{Z_i Z_j e^2}{r_{ij}} \left\{ 1 + \sum_k f(r_{ik}) \right\} \\ &= - \frac{\alpha_M Z^2 e^2}{r} \left\{ 1 + \frac{4}{Z} f(r) \right\} \end{aligned} \quad (2)$$

where α_M is the Madelung constant (= 1.63805), $Z_i e$ the ionic charge of the i-th ion, r_{ij} the separation between ith and jth ions, and $f(r_{ik})$ the TBI parameter dependent on nearest neighbour distances (r_{ik}) and being a measure of ion size differences.

The second term in equation (1) consist of the short-range energy contributions from the overlap repulsive and van der Waals interaction (VDWI) as

$$\begin{aligned} \Phi_{SR}(r) &= Nb \sum_{i,j=1}^2 \beta_{ij} \exp \left[r_i + r_j - \frac{r_{ij}}{\rho} \right] \\ &\quad - \sum_{ij} \frac{c_{ij}}{r_{ij}^6} - \sum_{ij} \frac{d_{ij}}{r_{ij}^8} \end{aligned} \quad (3)$$

where the first term is the Hafemeister and Flygare (HF) potential [13] as used in Singh and coworkers[8 and 9] . The second and third order terms represent the energy due to van der Waals dipole- dipole (d-d) and dipole- quadrupole interaction, respectively.

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

$$\omega^2 M U = (R + Z_m C' Z_m) U + (T + Z_m C' Y_m) W \quad (4)$$

$$O = (T' + Y_m C' Z_m) U + (S + K + Y_m C' Y_m) W \quad (5)$$

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; M is the mass of the core; T and R are repulsive Coulombian matrices, respectively; C' and Y_m are long-range interaction matrices, that include Coulombian and TBI respectively; S and K are core-shell and shell-shell repulsive interaction matrices, respectively and T^T is the transpose of matrix T. The elements of matrix \underline{Z}_m consists of the parameter \underline{Z}_m giving the modified ionic charge.

$$Z_m = \pm Z \sqrt{1 + \frac{Z}{Z} f(r)} \tag{6}$$

The elimination of \underline{W} from eqns. (4) and (5) leads to the secular determinant:

$$|D \underline{C} - \omega^2 \underline{M} I| = 0 \tag{7}$$

for the frequency determination. Here $\underline{D}(q)$ is the (6x6) dynamical matrix given by

$$\underline{D} \underline{C} = \underline{C}' + \underline{Z}_m \underline{C}' \underline{Z}_m - \underline{C} + \underline{Z}_m \underline{C}' \underline{Y}_m \underline{X} \tag{8}$$

$$\underline{C} + \underline{K} + \underline{Y}_m \underline{C}' \underline{Y}_m - \underline{C}^T + \underline{Y}_m \underline{C}' \underline{Z}_m$$

The numbers of adjustable parameters have been largely reduced by considering all the short-range interactions to act only through the shells.

2.2 Specific Heat and Debye Temperature:

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

$$C_V = 3Nk_B \frac{\int_0^{v_m} \left\{ \left(\frac{h\nu}{k_B T} \right)^2 e^{\frac{h\nu}{k_B T}} \right\} G(\nu) d\nu}{\int_0^{v_m} G(\nu) d\nu} \left(e^{\frac{h\nu}{k_B T}} - 1 \right)^{-2} \tag{9}$$

Where, v_m is the maximum frequency, N is the Avogadro's a number, h is the Planck's constant and k_B is the Boltzmann's constant. The equation (9) can be written as a suitable form for a computational purpose as

$$C_V = 3Nk_B \frac{\sum_v \left\{ \left(\frac{h\nu}{k_B T} \right)^2 e^{\frac{h\nu}{k_B T}} \right\} G(\nu) d\nu}{\sum_v G(\nu) d\nu} \tag{10}$$

Where $E\left(\frac{h\nu}{k_B T}\right)$ is the Einstein function, defined

$$\text{by } E(x) = x^2 \frac{\exp(x)}{\exp(x) - 1} \tag{11}$$

With $x = \left(\frac{h\nu}{k_B T} \right)$.

Also,

$\sum_v G(\nu) d\nu$ = Total number of frequencies considered.

= 6000 for zinc-blende structure.

Hence, equation (9) can be written for zinc-blende structure type crystals, as

$$C_V = \frac{3Nk_B}{6000} \sum_v E(x) G(\nu) d\nu \tag{12}$$

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 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 $\sum_v E(x) G(\nu) d\nu$. The specific heat C_V is then calculated by expression (12).

3. Result and Discussion:

3.1 Gallium Phosphide (GaP):

Specific heat of GaP was measured from 300⁰K to 10⁰K by Tarassov and Demidenko [14]. Kushwaha and Kushawaha [6] calculated C_V values for this compound using bond-bending force model and obtained a good agreement with experimental results at higher temperature. C_V values calculated on the basis of present model have given a better agreement at low temperatures also upto 1⁰K which shows predominant with the other zinc-blende semiconductor structure crystals. Calculated Θ_D Vs T curve for GaP as plotted in figure 1 shows a very good agreement in the entire temperature range.

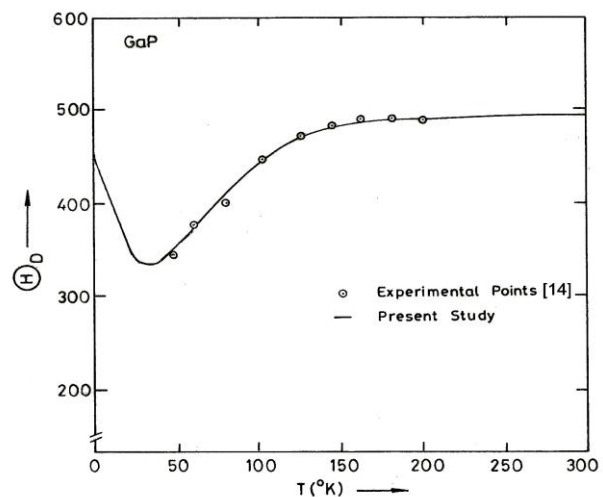


Fig. 1: Debye Temperature variation of GaP

3.2 Gallium Arsenides (GaAs):

Specific heat at constant pressure (C_P) of this compound has been measured by Piesbergen [15] and Lundin et al[16]. Specific Heat at constant volume (C_V) has been calculated by Cetas et al [17] and Holste [18]. Specific Heat C_V values calculated on

the basis of present model have presented with better agreement at low temperatures also upto 1^0K which shows predominant with the other zinc-blende semiconductor structure crystals. Calculated Θ_D Vs T curve for GaP as plotted in figure 2 shows a very good agreement in the entire temperature range.

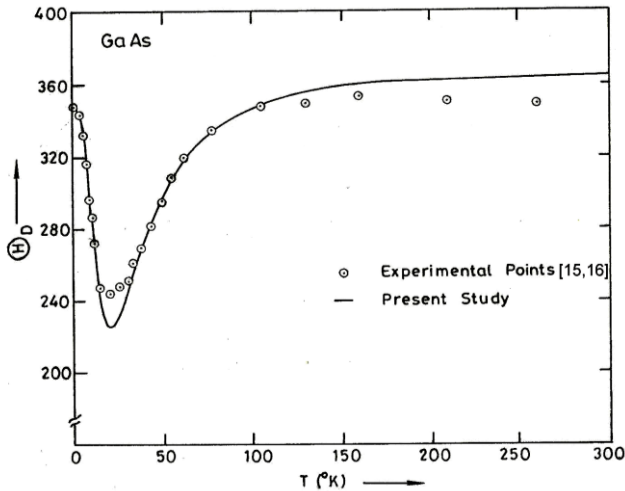


Fig.2: Debye Temperature variation of GaAs

3.3 Gallium Antimonide (GaSb):

C_V Values as obtained on the basis of present model have been shown in figure 3. The experimental data as obtained by Farr et al [4] has been included. The calculated Θ_D values differ slightly at high temperature from the experimental values, maximum discrepancy being 12% at 300^0K .

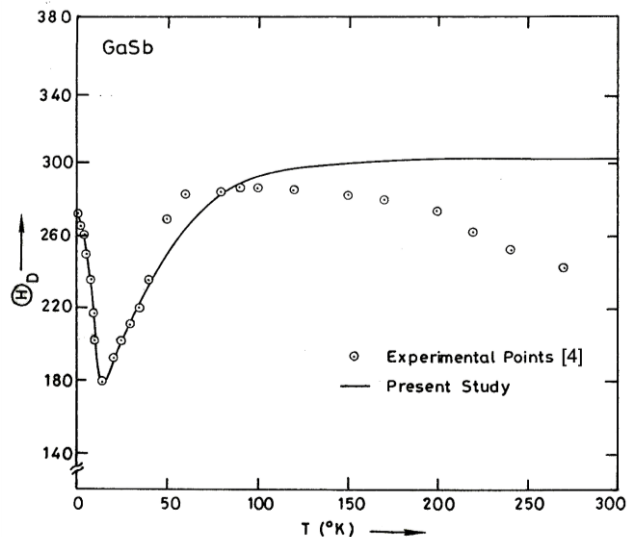


Fig.3: Debye Temperature variation of GaSb

4. Conclusion:

Our study shows a better agreement at lower temperature side. Slight disagreement at the higher temperature side may be ascribed to the non-inclusion of the anharmonic interactions in the present model. To conclude, we can say that our

present model gives a better interpretation of the lattice dynamical studies of these crystals.

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