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Lattice Dynamics of III-V Compounds of Semiconducting crystals (GaP-InP)

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Abstract

To study the lattice dymamics of GaP-InP having Zinc-blende structure in a new non-central rigid ion model (NC-RIM) which in corporates three types of interactions (i) Non-coulombic forces (ii) Coulombic forces (iii) Bond bending forces has been used developed. The model involves seven model parameters; we used six critical point phonon frequencies, two elastic constants. The applications of the present model (NC-RIM) have been made to calculate the phonon dispersion relations, Debye characteristic temperature and specific heat of GaP-InP. The comparision of theoretical results with the available experimental data has been made along the three sysmmetry direction [100], [110] and [111]. A reasonably good agreement observed between theory and experiments.

Keywords: Secular determinant, Ionic rigidity, non-coulombic interaction, phonon dispersion.

Introduction

The lattice dynamics of semi conductor compounds have been extensively studied in recent years. With the development of inelastic neutron scattering experiments, a vast amount of data has been accumulated for phonon dispersion curves of various II-VI and III-V compounds[1-4]. The phenomenological models which have been used to calculate the frequencies of zinc-blende structure crystals can be broadly classified into two categories. (i) Rigid Ion Model (RIM) [5-7](ii) Shell Model[8-9]. The rigid ion model involves the ion rigidity hypothesis; whereas the shell model takes into account the ionic polarizability.

In developing a model for a crystal having covalent bonding there is a fundamental difficulty related to the introduction of noncentral forces. In the usual definition of a noncentral forces. In the usual definition of noncentral interation the corresponding force parameters noncentral forces can be due to the rotation of on e atom about another, but must be due to a change in the configuration of the atoms (or bonds), and these force parameters must take into account at least two coordination spheres. The Rigid ion model (RIM) and its various ramifications have been widely used to explain several lattice dynamic properties of perfect and imperfect zinc-blende crystals[10,11]. These models, although economical in force parameters, ignore completely the non-central interaction in the lattice. The valence Force Fild Model (VFFM) as used by Price et al incorporate bond-bending, bond stretching and point coulombic interactions[12]. Later on the original 14 parameter VFFM was modified on the lines of shell model by Vageletos et al. and Feldkamp et al.[4, 13]. In addition to RIM, SNIM (Second Neighbour Ionic Model) and VFFM, some other models e.g., the bond charge model (BCM) and deformable dipole model (DDM) have also been used for zinc-blende crystals[14-16].

The present article is devoted to making use of a seven parameters non-central rigid ion model (NC-RIM). Recently proposed with its application on compounds for studying, the vibrational properties of GaP-InP crystals. Since a fairly good agreement was found between theory and experiment we thought it work while to study the lattice dynamics of other chemically crystals. It is however, no longer interesting to study the phonons in one isolated crystals. We have to examine as many members of zinc-blende (Z-B) family as possible. In this paper is to give details of NC-RIM with into crystals Ga-In pnictides.

The Dynamic Model: The potential energy Φ of the compounds possessing the Zinc-blende structure is expressed as

$$\Phi_{kk'} = \Phi^{N}_{kk'} + \Phi^{C}_{kk'}$$

Where superscripts N and C refer to the non-coulombic and coulombic parts.
The non-coulombic potential energy of the Zinc-blende structure Φ^N using Taylor's series can be written as

$$\Phi^N = \sum_{lmn}\left[\frac{1}{r}\left(\frac{d\phi^N}{dr}\right)_{|r|=r_1}\left\{\gamma^0_{lmn}\left(S_{lmn}-S_0\right)+\frac{1}{2}\left|S_{lmn}-S_0\right|\right\}+\frac{1}{2}\left\{\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi^N}{dr}\right)\right\}_{r=r_1} x\left\{\gamma^0_{lmn}\left(S_{lmn}-S_0\right)^2\right\}\right] \quad (2)$$

Where S_o and S_{lmn} are the displacement of the crystal ion and its first neighbour ions form their normal positions, r_{lmn} represents the position coordinates of neighbouring ions in equilibrium. *l*, m, n represent the direction cosines of the line joining the central ion and a nearest neighbour.

$|r_1|$ is the nearest neighbour distance. In our work we have considered the non-columbic interaction between central ion its two nearest neighbour. Let us define force constants A and B in terms of the derivatives of potential energy ϕ^N.

$$\left.\frac{d^2\phi^N}{dr^2}\right|_{r=r_1} = \frac{e^2}{V}A\,,\ \left.\frac{d^2\phi^N}{dr^2}\right|_{r=r_2} = \frac{e^2}{V}A_k\,,\ \left.\frac{1}{r}\frac{d\phi^N}{dr}\right|_{r=r_1} = \frac{e^2}{V}B$$

$$\left.\frac{1}{r}\frac{d\phi^N}{dr}\right|_{r=r_2} = \frac{e^2}{V}B_k \qquad (3)$$

Where K = 1, 2. r_1 refers to first neighbour and r_2 refers to second neighbour, e is electronic charge and ($V=2a^3$) volume per unit cell.

The first nearest neighbour we have taken the force constant B and A equal to zero for the first derivative of the potential energy. In the second neighbour however, there are two types of different atoms (KK) or (K'K'). As result B_1, B_2 are the force constants for the second neighbour corresponding to first derivative of potential energy for K, K type or K', K' type of interatomic interactions. Likewise A_1, A_2 are the force constants corresponding to the second derivative of potential energy. X and e_s^* effective ionic charge parameters, e_L^* and e_T^* Longitudinal and Transverse effective charge parameters.

The secular determinant for determining the angular frequency of modes of vibrations is usually written as

$$\left|D(\vec{q},kk') - \omega^2\delta_{\alpha\beta}\delta_{kk'}\right| = 0 \qquad (4)$$

Where K, K' = 1, 2………..S, label the ions per unit cell $\vec{q}$ denotes the wave vector whose allowed values range over the first brillouin zone. α and β = x, y or z designating the coordinate axes and δ is the usual Kronecker-delta symbol. m_K is the mass of the ion K in the *l* th cell.

The elements of the dynamical matrix are defined as

$$D_{\alpha\beta}(\vec{q},kk') = \sum_{l'} \frac{1}{\sqrt{m_k m_{k'}}}\phi_{\alpha\beta}(lk,l'k')\exp\, i\left[\vec{q}\cdot\vec{\gamma}(lk,l'k')\right]$$

Where $\vec{\gamma}^o(lk,l'k') = \vec{\gamma}(lk) - \vec{\gamma}(l'k')$ denotes the coupling parameters between ions (lK) and (l'K'). The dynamical matrix $D(\vec{q},kk')$ is constructed from constituents, Cochran et al.[17].

$$D(\vec{q},kk') = D^N(\vec{q},kk') + D^C(\vec{q},kk') \qquad (5)$$

The first term $D^N(\vec{q},kk')$ of the dynamical matrix is the non-columbic interaction part which is introduced to stimulate the contributions from non-coulombic interaction to the potential energy. The second term is coulombic interaction part due to undeformable ion interaction, and we can write it conventional matrix form as

$$F^C = -ZQZ \qquad (6)$$

Where Z is a diagonal matrix specifying the effective dynamical charges Z_K. The matrix elements of Z are given.

$$Z_{\alpha\beta kk'} = \delta_{\alpha\beta}\delta_{kk'}Z_k$$

Likewise the element of Q is expressed as

$$Q = Q_{\alpha\beta kk'}(\vec{q}) - \delta_{kk'}\sum_{k''}\left(Z_{k''}/Z_k\right)Q_{\alpha\beta kk'}(0)$$

Where Q is the coulombic coefficient matrix representing the coulombic range electrostatic interaction.

In view of these observations our model essentially reduces to the rigid ion model incorporating non-coulombic and coulombic interactions.

We shall obtain matrix element $D_{\alpha\beta}$ (q,KK') for such interactions. In the Zinc-blende structure the dynamical matrix $D(\vec{q},kk')$ is a (6×6) matrix usually written as

$$D(\vec{q},kk') = \begin{vmatrix} D(\vec{q},11) & D(\vec{q},12) \\ D^*(\vec{q},12) & D(\vec{q},22) \end{vmatrix} \qquad (7)$$

Where $D(\vec{q},11)$ and $D(\vec{q},12)$ are 3×3 submatrices and $D^*(\vec{q},12)$ is the complex conjugate of $D(\vec{q},12)$. The element of submatrices can be written as the sum of the non-coulombic (N) range and Coulombic (C) range contribution, Thus

$$D_{\alpha\beta}(\vec{q},kk) = D^N_{\alpha\beta}(\vec{q},kk) + D^C_{\alpha\beta}(\vec{q},kk)$$
$$D_{\alpha\beta}(\vec{q},kk') = D^N_{\alpha\beta}(\vec{q},kk') + D^C_{\alpha\beta}(\vec{q},kk') \qquad (8)$$

Where superscript N and C refer to non-coulombic and coulombic contribution, respectively, suffix α and β (=X, Y, Z) used with the submatrices represent their elements.

The potential energy ϕ^N giving rise to the NC-RIM has been assumed to be of the form

$$\phi^N = \frac{1}{2}\left(\frac{e^2}{V}\right)\gamma_\theta(\delta\theta)^2$$

Where ($\delta\theta$) is the change in the angle under consideration and γ_θ is the corresponding force constant. Where e is the electronic charge and volume V ($=2a^3$) of the unit cell. The change in the angle ($\delta\theta$) is calculated geometrically figure 1 as

$$(\delta\theta) = \frac{\left(\vec{S}_A - \vec{S}_O\right)\in_{nA}}{|\overrightarrow{OA}|} + \frac{\left(\vec{S}_B - \vec{S}_O\right)\in_{nB}}{|\overrightarrow{OB}|}$$

where $\vec{S}_A$, $\vec{S}_O$ and $\vec{S}_B$ are the displacement vectors of the respective atom A, O and B. $\vec{\in}_{nA}$ and $\vec{\in}_{nB}$ are the unit vectors perpendicular to the vectors $\overrightarrow{OA}$ and $\overrightarrow{OB}$, respectively and lying in the plane OAB (figure 1). The details is of all such angles have been given by CGW.

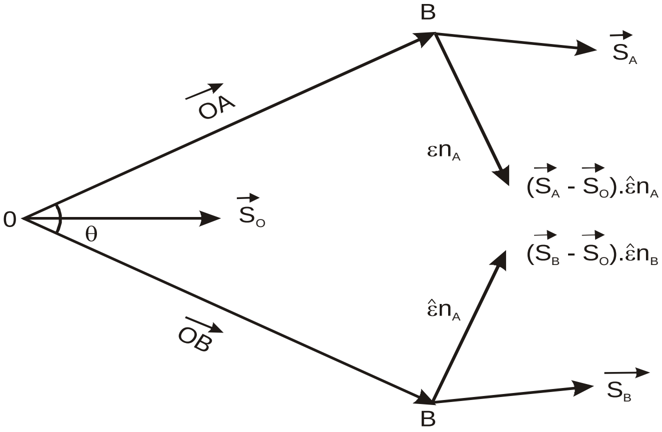

Figure-1
Geometrical interpretation bond-bending interaction

The matrix elements for the non-coulombic interaction are

$$D_{xx}^{N}(\vec{q},11)=\frac{e^2/v}{m_1}\left[\frac{4}{3}(A+2B)+4(A_1+B_1)\left\{2S_x^2+(1-2S_x^2)(S_y^2+S_z^2)\right\}+8B_1(S_y^2+S_z^2+2S_y^2S_z^2)\right]$$

$$D_{xx}^{N}(\vec{q},22)=\frac{e^2/v}{m_1}\left[\frac{4}{3}(A+2B)+4(A_2+B_2)\left\{2S_x^2+(1-2S_x^2)(S_y^2+S_z^2)\right\}+8B_2(S_y^2+S_z^2+2S_y^2S_z^2)\right]$$

$$D_{xy}^{N}(\vec{q},11)=\frac{e^2/v}{m_1}\left[8(A_1-B_1)\right]S_xS_yC_xC_y$$

$$D_{xx}^{N}(\vec{q},22)=\frac{e^2/v}{m_2}\left[8(A_2-B_2)\right]S_xS_yC_xC_y$$

$$D_{xx}^{N}(\vec{q},12)=-\frac{e^2/v}{\sqrt{m_1m_2}}\left[4(A+2B)(C_xC_yC_z+iS_xS_yS_z)\right]$$

$$D_{xy}^{N}(\vec{q},12)=-\frac{e^2/v}{\sqrt{m_1m_2}}\left[\frac{4}{3}(A-B)(S_xS_yC_z+iC_xC_yS_z)\right] \quad (9)$$

Where $S_x=\sin\frac{\vec{q}_x a}{2}, C_x=\cos\frac{\vec{q}_x a}{2}$ $\vec{q}_x$, $\vec{q}_y$ and $\vec{q}_z$ are components of the propagation vector $\vec{q}$ along x, y and z axis respectively '2a' is the semilattice constant other elements of the matrix can be written using cyclic permutation for changing the Cartesian indices.

Coulombic Interaction Behaviour: The expression for the matrix elements due to coulombic interaction were first derived by, Kellermann for alkalihalides. Cochran et al., modified them for the diamond structure and Merten for zinc-blende structure[18]. The potential energy ϕ^C, giving rise to such coulombic interaction between the ions, is of the form.

$$\phi^C=\frac{1}{2}\sum_{lk}\sum_{l'k'}\frac{Ze_{k'}Ze_{k'}}{\vec{\gamma}^o(l'k')-\vec{\gamma}^o(lk)} \quad (10)$$

Where the symbol have their usual meaning. The matrix element due to such coulombic interaction are, (Banerjee et al.[10]).

For $\vec{q}=0$

$$D_{xy}^{C}(\vec{q},kk')=\frac{1}{\sqrt{m_km_{k'}}}\frac{Ze_kZe_{k'}}{V}\left(\frac{4}{3}\pi\delta_{xy}\right)$$

For $\vec{q}\neq 0$

$$D_{xy}^{C}(\vec{q},kk')=\frac{1}{m_k}\frac{Z^2e_k^2}{V}\left[-G_{xy}(kk)+H_{xy}^{1}-\frac{8\in^3}{3\sqrt{\pi}}\delta_{xy}\right]$$

$$D_{xy}^{C}(\vec{q},kk')=\frac{1}{m_km_{k'}}\left(\frac{Ze_kZe_{k'}}{V}\right)\left[-G_{xy}(kk')+H_{xy}^{n}\right]$$

Where

$$G_{xy}(kk)=4\pi\sum_{\vec{h}}\frac{(\vec{h}_x+\vec{q}_x)(\vec{h}_y+\vec{q}_y)}{|\vec{h}+\vec{q}|^2}\times\exp\left(\frac{-\pi^2}{4e^2}|q+h|^2\right)$$

$$G_{xy}(kk')=4\pi\sum_{\vec{h}}\frac{(\vec{h}_x+\vec{q}_x)(\vec{h}_y+\vec{q}_y)}{|\vec{h}+\vec{q}|^2}\times\exp\left[\left\{\frac{-\pi^2}{4e^2}|q+h|^2\right\}\times\exp\left(i\pi(h_x+h_y+h_z)\right)/2\right]$$

$$f(\vec{l})=\frac{2\in}{\sqrt{\pi}l^2}\exp\left(-\in^2 l^2\right)+\frac{l}{l^3}\Psi(\in l)$$

$$g(\vec{l})=3f(l)+\frac{4\in^3}{\sqrt{\pi}}\exp\left(-\in^2 l^2\right)$$

g(n) and f(n) can be written analogously and

$$\Psi(\in l)=1-\frac{2}{\sqrt{\pi}}\int_0^{\in l}\exp\left(-t^2\right)dt$$

Where, $\in$ is an arbitrary parameter usually taken to be unity l (l_x, l_y, l_z) and n(n_x, n_y, n_z) are the lattice vectors and h(h_x, h_y, h_z) are the reciprocal lattice vectors. The present calculations of the coulombic matrix elements have been made by taking summation over 137 values of, h generated in the units of π/a, in the reciprocal space. Both of the submatrices, due to coulombic range force, hence have been calculated as the independent of the factor (Z^2e^2/a^3), where Z has been treated as disposable parameter. Furthermore, the long wave length limit method used to calculate the elastic constants in terms of the force constants, and the methods of parameter determination have widely been discussed in the Thesis. However, we would still like to state briefly that model parameters in the present NC-RIM have been determined by making use of four critical point phonon frequencies $\nu_{LO}^{(\Gamma)}\nu_{TO}^{(\Gamma)}\nu_{LO}^{(X)}\nu_{LA}^{(X)}$, two elastic constants (C_{11} and C_{12}) and the lattice equilibrium condition. The use of lattice equilibrium condition makes the parameters lie within their physical significance. The experimental input data used for the evaluation are listed in table 1. The expression used for calculation of the specific heat at constant volume C_v, after solving few thermodynamics relations can be written as

$$C_v = \frac{3R}{2mn}\sum_{q_i}\frac{x^2}{\left[\exp(x)-1\right]^2}\, g\left(\nu_i(q)\right) \qquad (11)$$

Where R(=NK$_b$) is the universal gas constant. The term $x = \left(\frac{h\nu_i(\vec{q})}{K_b T}\right)$ where h is Planck's constant, K$_b$ is Boltzmann's constant, and T the absolute temperature in Kelvin's $\left(g\nu_i(\vec{q})\right)$ is correct statistical weight of the mode having the vibrational frequency $\nu_i(q)$, where the subscript i stands for the branches 1 to 6 and q is the propagation wave vector in the reciprocal space. The symbol m (=2) and n (=1000) stand, respectively, for the number of atoms per unit cell and the number of subdivisions in the first brillouin zone. The use of the calculated specific heat Cv has been made to calculate the Debye characteristic temperature (θ_D) using the standard Cv V_s θ_D /T[10].

Results and Discussion

The numerical values of the model parameters listed in the Table-1 have been used to solve the secular determinant (eqution4) for determining the phonon frequencies. For this purpose we have divided the first brillouin zone into a mesh of 1000 points, but because of the cubic symmetry they reduce 48 nonequivalent point (including origin) lying in the (1/48)th part of brillouin zone. When the proper statistical weight is assigned to them, we get 6000 frequencies.

Table-1
Experimental values of lattice constants (2a) in the unit of Angstrom, elastic constants in the units of 10^{11} dyne / cm, and frequencies in the units of terahertz masses of compound unti 10^{-24}gm, The numerical values of the parameters are in the unit of 10^3dyne/cm

Quantities	GaP	InP	Parameters	GaP	InP
2a	5.45	5.87	A	89.44	90.03
C_{11}	14.11	10.22	A_1	10.21	6.86
C_{12}	6.19	5.76	A_2	13.47	13.92
m_1	51.42	51.42	B	23.08	9.69
m_2	115.74	190.61	B_1	-3.33	-1.71
$\nu_{LO}(\Gamma)$	12.05	10.38	B_2	-3.33	-1.71
$\nu_{TO}(\Gamma)$	10.96	9.12	X	5.62	6.25
$\nu_{LO}(X)$	11.06	9.95			
$\nu_{LA}(X)$	7.75	5.85			

Conclusion

The phonon dispersion relations for GaP-InP along the principal symmetry directions [100], [110] and [111] are displayed in figure-2, 3. The experimental points due to neutron scattering measurements have also been plotted in respective figures for comparison. It is observed that there is in general a good agreement between theory and experimental except at few point.

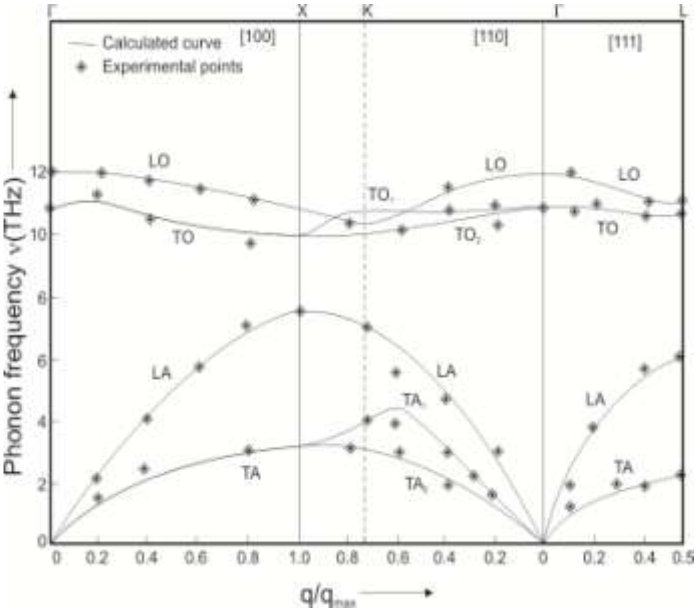

Figure-2
Phonon dispersion relation of GaP

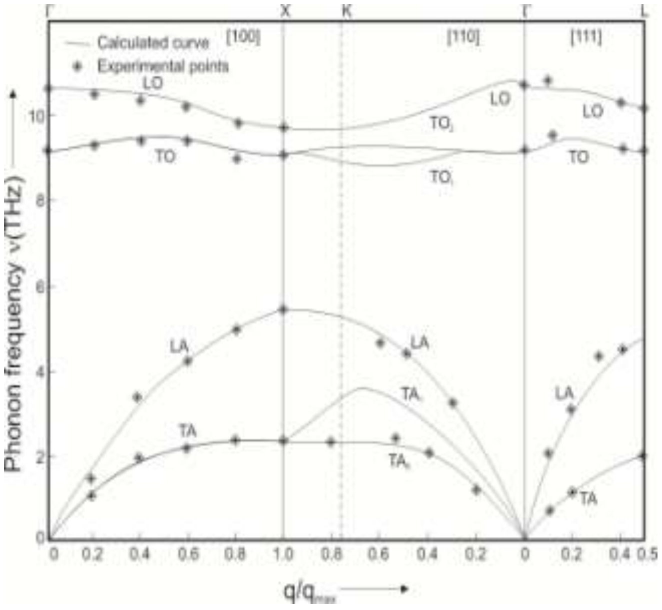

Figure-3
Phonon dispersion relation of InP

The frequency spectrum for this purpose was divided into the frequency interval of Δν=0.1 THz for Ga-In pnictides, four major peaks at frequencies 2.0 THz, 4.3 THz, 5.3 THz and 11.65 THz are dut to TA, LA, TO and LO modes respectively for GaP. The peaks are observed four major frequencies 0.15THz and 5.4THz are due to transverse and longitudinal acoustic modes, while peaks frequencies 9.0THz and 10.8THz correspond to transverse and longitudinal optic modes for InP.

Calculated specific heat values for GaP and InP using the present model have been shown in table II. θ_D values of InP have been plotted in figure-5. Calculated θ_D vs T curve for GaP and InP as plotted in figure-4, 5 shows a very good agreement in entire temperature range.

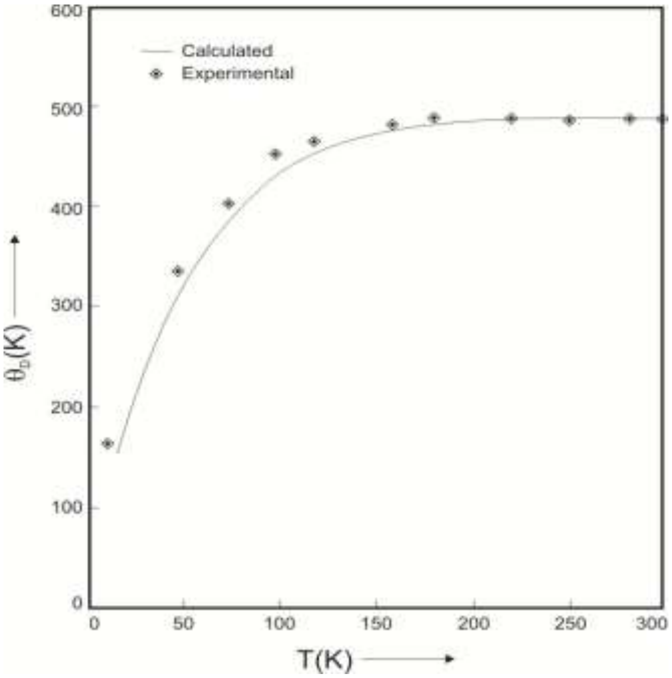

Figure-4
(θ_D-T) curve for GaP

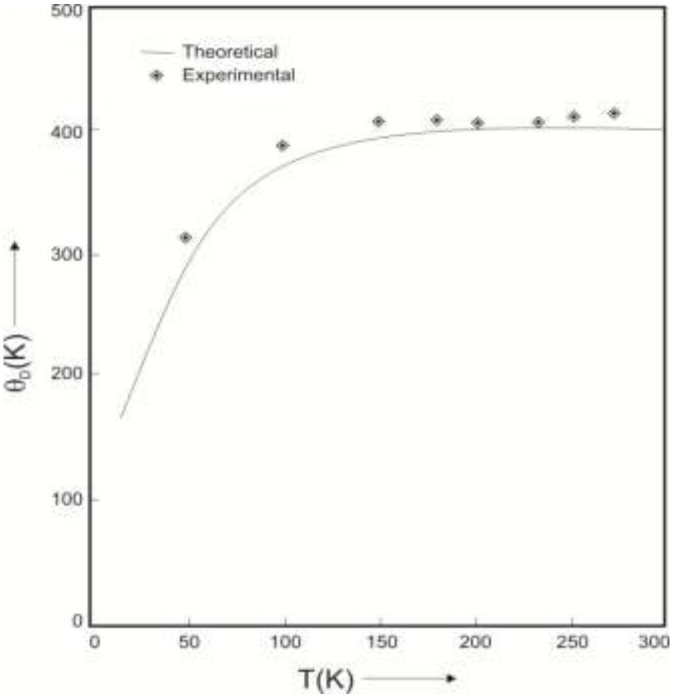

Figure-5
(θ_D-T) Curve for InP

Table-2
The calculated and measured experimental values of specific heat of Ga-In pnictide crystals units J/Mole-ºK and temperatures in Kelvin

Temp. (ºK)	GaP C_v(J/mole ºK)		InP C_v(J/mole ºK)	
	Calculated	Exp.	Calculated	Exp.
20	5.8	-	6.8	5.2
30	6.2	-	9.6	-
50	8.4	6.8	14.0	12.8
60	10.8	-	16.0	-
75	15.9	15.6	-	-
80	18.4	-	19.9	-
100	24.4	22.0	24.0	22.8
110	29.4	-	26.0	-
120	31.0	30.0	29.7	-
150	35.2	35.0	33.4	33.0
175	40.0	40.0	36.2	-
180	40.4	-	38.8	38.6
200	41.8	42.0	38.8	38.0
230	42.0	-	41.2	40.8
250	42.0	-	41.6	40.0
270	42.2	-	41.6	40.0

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