



Pressure dependent elastic and structural ($B3-B1$) properties of Ga based monpnictides

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ABSTRACT

By formulating an effective interionic interaction potential that incorporates the long-range Coulomb, the covalency effects, the charge transfer caused by the deformation of the electron shells of the overlapping ions, the Hafemeister and Flygare type short-range overlap repulsion extended up to the second neighbour ions and the van der Waals (vdW) interaction, the pressure dependent elastic and thermodynamical properties of the III–V semiconductors as GaY (Y = N, P, As) are studied. The estimated values of phase transition pressure of GaY (Y = N, P, As) are in reasonably good agreement with the available data on the phase transition pressures ($P_t = 41, 22, 17$ GPa). The vast volume discontinuity in pressure–volume phase diagram identifies a structural phase transition from zinc-blende ($B3$) to rock salt ($B1$) structure. Later on, the Poisson's ratio ν , the ratio $R_{S/B}$ of S (Voigt averaged shear modulus) over B (bulk modulus), elastic anisotropy parameter, elastic wave velocity, average wave velocity and Debye temperature as functions of pressure is calculated. From Poisson's ratio and the ratio $R_{S/B}$ it is inferred that GaY (Y = N, P, As) is brittle [ductile] in zinc-blende ($B3$) [Sodium Chloride ($B1$)] phase. To our knowledge this is the first quantitative theoretical prediction of the pressure dependence of ductile (brittle) nature of GaY compounds and still awaits experimental confirmations.

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1. Introduction

The Ga monpnictides: GaY (Y = N, P, As) exhibit some interesting properties, such as large band gap, high thermal conductivity, strong interatomic bonds, the pressure induced structural phase transition and are ideal materials for optoelectronic and high-temperature and/or high-power devices [1–3]. Numerous efforts have been made in establishing links between macroscopic properties of solids and their atomic-scale features. Most of the activities are focused to characterize these compounds in exploiting their usage in optoelectronic devices and less attention has been paid regarding the elastic properties.

Elastic properties as elastic moduli is important in assessing the competition between the ductile and brittle failures, have been investigated in relation to various microscopic characteristics of different sorts of materials, such as metals and covalently bonded

crystals. The elastic modulus of simple and complex materials is usually evaluated following the *ab initio* calculation techniques. The limitation is the rationalization of the first principles calculations often requires profound understanding of the nature of the chemical bonding and its attributes in various solid systems. Henceforth, the lattice model calculations need to be elaborated in concert with computational approaches and estimations.

While computing the pressure and structure dependent mechanical properties as ductility (brittleness) and wave velocities of Ga monpnictides, we need to first understand the pressure dependent structures and thus the pressure dependent structural phase transition is of importance. The GaAs, GaP and several other III–V semiconductors have been observed to transform from the cubic zinc-blende type structure to more densely packed phases at very high-pressures. The stable configuration of GaN under the ambient conditions is the wurtzite structure with mainly covalent, partly ionic tetrahedral bonding and a direct electronic gap of 3.5 eV at the Γ point [4].

At ambient conditions these compounds crystallize in the cubic zinc-blende structure and under hydrostatic pressure, a structural phase transition to Sodium Chloride phase appears. There exists a number of experimental and theoretical calculations for the structural and elastic constants of these compounds using different

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methods. Weil and Groves reported the elastic constants of GaP using the ultrasonic measurements [5]. The transit times of ultrasonic waves associated with piezoelectrically inactive modes have been measured in sulfur-doped, n-type GaP using hydrostatic pressures up to 5 kbar [6]. Furthermore, the elastic constants of GaP have been obtained from measurements of the effect of hydrostatic and uniaxial pressures on ultrasonic wave velocities and the valence force field model has been used to obtain the bond-bending and stretching force constants [7]. Apart from the ultrasonic measurements to elucidate the elastic properties of III–V semiconductors, progress has been made in theoretical understanding of these compounds.

The *ab initio* calculations [8] using density functional method indicate that at zero pressure the stable crystal structure of GaN has wurtzite structure and at high-pressures the rocksalt and the NiAs structures are stable. Structural parameters, cohesive energy, ground state and electronic properties of low- and high-pressure phases of GaY using first principle calculations are performed by various groups and we shall refer them later on. These calculations for $E(V)$ equation of state show that the zinc-blende structure is higher to wurtzite structure by only 15 meV/atom. Recently, Bouhemadou et al. [9] studied the structural and elastic properties of BP, AlP, GaP and InP the zinc-blende compounds under pressure effect by employing FP-APW + lo approach based on density functional theory, within both the local-density approximation and the generalized gradient approximation to the exchange-correlation approximation energy. Earlier Singh and Singh [10] employed a charge transfer effect through three-body interactions to depict the phase diagram and elastic properties of III–V semiconducting compounds as GaAs, GaSb, GaP, InAs, InSb, and InP. The electrical resistivities of GaAs and GaP drops discontinuously to several orders of magnitude at the transition pressures; therefore the phase transitions in GaAs and GaP can be conveniently studied by resistivity measurements [11,12]. Experimentally, all three compounds adopt the zinc-blende structure at low and moderate pressures.

The IIIA–VA compounds, GaY, (Y = N, P, As) are found to exhibit a structural phase transition at the pressures of 47–50 [13,14] in GaN by Perlin and Gorcza following EXAFS, 20–24 [15] in GaP, and 16–19 [15] GPa in GaAs, respectively. Ueno et al. has performed the high-pressure *in situ* X-ray diffraction study on GaN using an imaging-plate technique and a diamond-anvil cell identifying the phase transition at 52.2 ± 3.0 GPa and volume collapse of 17.9 in GaN [13,14]. The X-ray diffraction patterns of high-pressures GaP and GaAs were obtained using the energy dispersive diffraction technique and the synchrotron radiation. The phase transition started at 21.5 and 17.2 GPa respectively and volume collapse 17.5 and 17.3, for GaP (GaAs), respectively [16].

The mechanical properties of crystalline solids provide valuable information about their interatomic forces. It is known that GaN is characterized by its high ionicity of 0.4–0.6 among the materials in the III–V series. Thus, it contains admixtures of ionic and covalent bonds and it is convenient to consider them as partially ionic or partially covalent compounds. Also, the chemical bonds are strong in GaY and possess a small lattice constant. The high-pressure structural aspects of GaY can be an interesting test for different theoretical predictions concerning the general structural behavior of III–V and II–VI materials [17].

One way to establish the structure of the binary compounds is to determine the competition between the energy gain obtained by formation of sp^3 bonds (as in the zinc-blende, $B3$ structure) and the gain in Madelung energy due to a larger coordination number. The $B3$ structure is fourfold coordinated (CN4), and $B1$ (rocksalt) is sixfold coordinated (CN6). Most of the semiconducting alloys undergo structural transformations when pressure is applied, and some of the compounds transform to the rocksalt structure under pressure. This is ascribed to the fact that the reduction of the lattice dimen-

sions causes the interionic Coulomb interaction to favor the CN6 structure over the CN4 structure. The covalent energy increases less rapidly in magnitude than the Madelung term [17].

The experimental investigations regarding the structural phase transition and scarcity of pressure dependent elastic properties as ductile (brittle) nature on III–V semiconductors therefore pose a strong need to study the structural properties of GaY compounds theoretically at high-pressure, which can predict at least the extent of pressure one should generate to observe a structural phase transition and its pressure dependent ductile and brittle nature. In addition, the structural and mechanical studies on III–V semiconducting compounds have further widened the scope of future theoretical and accurate experimental investigations of crystallographic phase transition from $B3 \rightarrow B1$ in IIIA–VA semiconductors.

The modelling of lattice models in binary III–V semiconducting compounds is a complicated task and, in many instances, must be guided by experimental evidence of the low degree of freedom in order to obtain a correct minimal model, which will capture the observed effect and will make useful predictions. The first principle calculations are widely and successfully used to address the electronic, and structural ground state properties. Extensive efforts have been made to reveal the phase transition and anharmonic properties of solids by means of different forms of cohesion. On the other hand, the phenomenological lattice models [18–25] have proved very successful in obtaining the qualitative and quantitative understanding with proper parameterisation.

Motivated from these remarks and the versatility of many-body interactions approach for the successful description of the high-pressure phase transition in binary semiconductors, we thought it pertinent to make a comprehensive study of covalency and charge transfer effects on mechanical properties of GaY semiconducting compounds. Physically, the relevance of many-body interactions arose from the charge transfer mechanism caused by the deformation of the electron shells of the overlapping ions, to explain the various mechanical properties and we experienced that it still needs detailed investigations.

The main focus of the present investigation is to discuss the pressure dependent elastic properties as ductility (brittleness), elastic anisotropy and sound velocity of Ga monpnictides as no systematic efforts have been made so far. To our knowledge this is the first attempt to reveal the pressure dependence of ductile (brittle) nature of GaY compounds and still awaits experimental confirmations. The theory and technical details to estimate the pressure dependent structure are given in Section 2. In a next step, the phase transition pressures are deduced within the framework of Shell model that incorporates the long-range Coulomb, charge transfer effects, covalency effects, van der Waals (vdW) interaction, and short-range overlap repulsive interaction up to second neighbour ions within the Hafemeister and Flygare approach. In Section 3, we present our results and the comparison with the experimental and other theoretical studies. Finally, conclusions are presented in Section 4.

2. The method of computation

Pressure dependent mechanical properties as ductility and brittleness, longitudinal and transverse velocity, elastic anisotropy and thermodynamical property as Debye temperature of Ga monpnictides are important and can be known from second-order elastic constants. In doing so, we first need to evaluate pressure dependent structural properties. Many-body interaction approach is successful in description of the high-pressure phase transition. Usually the applied pressures cause an increase in the overlap of adjacent ions in a crystal and hence, charge transfer takes place between the overlapping electron shells. The transferred charges interact with all

others of the lattice via Coulomb's law and give rise to many-body interactions, of which the most significant is three-body interaction. It is well known that three-body interactions come from the covalent bonding in tetrahedral semiconductors. The increased effect due to covalent nature and of charge transfer, thus obtained, lead to an obvious necessity of their inclusion in the high-pressure study of materials.

The III–V binary compounds are known to transform from their initial $B3 \rightarrow B1$ structure under pressure. Usually, the thermodynamical properties are described by the appropriate thermodynamical potential relevant to the given ensemble. Either variable pressure or temperature acting on the system is altered, the free energy changes smoothly and continuously. The stability of a particular structure is decided by the minima of Gibbs's free energy. The relevant potential, e.g. Gibbs free energy (G) can be written as $G = U + PV - TS$, U being the internal energy, which at 0 K corresponds to the cohesive energy, S is the vibrational entropy at absolute temperature T , pressure P and volume V .

We must mention that the calculations presented here assume zero temperature, i.e. the frozen ionic degrees of freedom. Although, the experimental results are obtained at ambient temperature inferring a certain small temperature dependence of the transition pressures in the range of low temperatures. Nevertheless, it is safe to consider the lattice model calculation results as representative of the results that would be obtained under the actual experimental conditions. At zero temperature, the thermodynamically stable phase at a given pressure P is the one with lowest enthalpy, and the thermodynamical potential is the Helmholtz free energy (H).

The Gibbs's free energies

$$G_{B3}(r) = U_{B3}(r) + PV_{B3} \quad (1)$$

$$G_{B1}(r') = U_{B1}(r') + PV_{B1} \quad (2)$$

at $T = 0$ K for ZnS ($B3$, real) phase and NaCl ($B1$, hypothetical) phase become equal at the phase transition pressure P . Here, $V_{B3} (=3.08r^3)$ ($V_{B1} (=2r'^3)$) as the unit cell volume and r (r') being the nearest neighbour distance for $B3$ ($B1$) phase. The notations $U_{B3}(r)$ and $U_{B1}(r')$ denote cohesive energies for $B3$ and $B1$ phases and are expressed as:

$$U_{B3} = \left(\frac{-\alpha_M Z e^2}{r} \right) [Z + 2nf_T(r)] - \sum_{ij} C r_{ij}^{-6} - \sum_{ij} D_{ij} r^{-8} + nb\beta_{ij} \exp \left[\frac{(r_i + r_j - r_{ij})}{\rho} \right] + \left(\frac{n'b}{2} \right) \left[\beta_{ii} \exp \left(\frac{(2r_i - kr_{ij})}{\rho} \right) + \beta_{jj} \exp \left(\frac{(2r_j - kr_{ij})}{\rho} \right) \right] \quad (3)$$

$$U_{B1} = \left(\frac{-\alpha'_M Z e^2}{r'} \right) [Z + 2mf_T(r')] - \sum_{ij} C r'_{ij}{}^{-6} - \sum_{ij} D r'_{ij}{}^{-8} + mb\beta_{ij} \exp \left[\frac{(r_i + r_j - r'_{ij})}{\rho} \right] + \left(\frac{m'b}{2} \right) \left[\beta_{ii} \exp \left(\frac{(2r_i - k'r'_{ii})}{\rho} \right) + \beta_{jj} \exp \left(\frac{(2r_j - k'r'_{jj})}{\rho} \right) \right] \quad (4)$$

Here the first term is the potential energies due to long-range Coulomb, and the second term is due to the charge transfer caused by the deformation of the electron shells of the overlapping ions and the covalency effects. The III–V semiconducting compounds contain covalent bonds so that some electrons are distributed over the region between neighbouring atoms; in such a situation, the ionic charge for each atom cannot be determined uniquely and

hence the calculation of the Madelung energy is modified by incorporating the covalency effects [26]. We thus need to incorporate the effective charge arose due to the polarization of a spherical shaped dielectric in displacing the constituent positive ions. The third and fourth terms are the short-range (SR) vdW attraction energies due to dipole–dipole and dipole–quadrupole interaction. The C and D are the overall vdW coefficients, which are evaluated from the variational approach [25].

The vdW coefficients due to dipole–dipole and dipole–quadrupole interactions are calculated from the Slater and Kirkwood variational approach and are

$$c_{ij} = \frac{3}{2} \frac{e\hbar}{\sqrt{m_e}} \alpha_i \alpha_j \left[\left(\frac{\alpha_i}{N_i} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right)^{1/2} \right]^{-1}, \quad (5)$$

$$d_{ij} = \frac{27}{8} \frac{\hbar^2}{m_e} \alpha_i \alpha_j \left[\left(\frac{\alpha_i}{N_i} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right)^{1/2} \right]^2 \times \left[\left(\frac{\alpha_i}{N_i} \right) + \frac{20}{3} \left(\frac{\alpha_i \alpha_j}{N_i N_j} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right) \right]^{-1}. \quad (6)$$

$$c_{ii} = \frac{3}{2} \frac{e\hbar}{\sqrt{m_e}} \alpha_i \alpha_i \left[\left(\frac{\alpha_i}{N_i} \right)^{1/2} + \left(\frac{\alpha_i}{N_i} \right)^{1/2} \right]^{-1}, \quad (7)$$

$$d_{ii} = \frac{27}{8} \frac{\hbar^2}{m_e} \alpha_i \alpha_i \left[\left(\frac{\alpha_i}{N_i} \right)^{1/2} + \left(\frac{\alpha_i}{N_i} \right)^{1/2} \right]^2 \times \left[\left(\frac{\alpha_i}{N_i} \right) + \frac{20}{3} \left(\frac{\alpha_i \alpha_i}{N_i N_i} \right)^{1/2} + \left(\frac{\alpha_i}{N_i} \right) \right]^{-1} \quad (8)$$

$$c_{jj} = \frac{3}{2} \frac{e\hbar}{\sqrt{m_e}} \alpha_j \alpha_j \left[\left(\frac{\alpha_j}{N_j} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right)^{1/2} \right]^{-1}, \quad (9)$$

$$d_{jj} = \frac{27}{8} \frac{\hbar^2}{m_e} \alpha_j \alpha_j \left[\left(\frac{\alpha_j}{N_j} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right)^{1/2} \right]^2 \times \left[\left(\frac{\alpha_j}{N_j} \right) + \frac{20}{3} \left(\frac{\alpha_j \alpha_j}{N_j N_j} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right) \right]^{-1}. \quad (10)$$

where m , e and Z are the electron mass, charge and valence of the constituent metallic element respectively (α_i , α_j) are the polarizabilities of i th and j th ion respectively; N_i and N_j are the effective number of electrons responsible for polarization. The overall vdW coefficients C and D are then expressed in terms of c_{ij} and d_{ij} , by a appropriate lattice sums (S_{ij} and T_{ij}) the values of which are taken from [24] such that and the expression is given by,

$$C = c_{ij} S_{ij} + c_{ii} S_{ii} + c_{jj} S_{jj} \quad (11)$$

$$D = d_{ij} T_{ij} + d_{ii} T_{ii} + d_{jj} T_{jj} \quad (12)$$

The last two terms are SR repulsive energy due to the overlap repulsion between ij , ii and jj ions. α_m (α'_m) are the Madelung constants for $B3$ ($B1$) phases. β_{ij} is the Pauling coefficient defined as $\beta_{ij} = 1 + (Z_i/n_i) + (Z_j/n_j)$ with Z_i (Z_j) and n_i (n_j) as the valence and the number of electrons in the outermost orbit. Ze is the static charge of the ion, k (k') is the structure factor for $B3$ ($B1$) structures, and $b(\rho)$ are the hardness (range) parameters. r (r') are the nearest neighbour ion separations for $B3$ ($B1$) structures.

The second term in Eq. (2) is an algebraic sum of three-body force parameters $f(r)$ and the force parameter arises due to covalent nature, i.e. $f_T(r) = f(r) + f_{cov}(r)$. The three-body force parameter $f(r)$ is expressed as [18,19,21]

$$f(r) = f_0 \exp\left(\frac{-r}{\rho}\right) \quad (13)$$

$r_i(r_j)$ are the ionic radii of ions $i(j)$. Keeping in mind that the III–V semiconducting compounds are partially ionic and partially covalent in bonding, and the attractive forces due to covalency are important that modifies the effective charge. The polarization effects originates from changes in covalency due to electric fields and the covalency term is expressed as [26]

$$f_{cov}(r) = \frac{4e^2 V_{sp\sigma}^2}{r_0 E_g^3} \quad (14)$$

$V_{sp\sigma}$ is the transfer matrix element between the outermost p orbital of anion and the lowest excited of s state of cation, E_g is the transfer energy of electron from anion to cation. The effective charge e_s^* of the host crystal is related with the number of electrons transferred to the unoccupied orbitals of a cation from its surrounding anions at the nearest neighbour and is $n_c = 1 - e_s^*/e$. Furthermore, $n_c/12 \cong V_{sp\sigma}^2/E_g^2$ and the transfer matrix element $V_{sp\sigma}$ and the transfer energy E_g is related to effective charge e_s^* following [26]

$$\frac{V_{sp\sigma}^2}{E_g^2} = \frac{1 - e_s^*}{12} \quad (15)$$

The transfer energy E_g is further expressed as

$$E_g = E - I + (2\alpha - 1) \frac{e^2}{r} \quad (16)$$

Here E is the electron affinity for N, P and As, i.e. for the non metal atoms and I is the ionisation potential of the constituent metal atom.

The optical static dielectric constant ϵ_s and the high frequency dielectric constant ϵ_∞ are intimately related to Sziget effective charge $e_s^* (=Ze)^*$ [21] as follows:

$$e_s^{*2} = \frac{9\mu\omega_{T0}^2(\epsilon_s - \epsilon_\infty)}{4\pi N_k(\epsilon_\infty + 2)^2} \quad (17)$$

and

$$\frac{e_s^{*2}}{e^2} = \frac{9V\mu\omega_{T0}^2(\epsilon_s - \epsilon_\infty)}{4\pi e^2(\epsilon_\infty + 2)^2} \quad (18)$$

Here, μ is the reduced mass, N_k is the number of atoms present per unit cell volume, i.e. $N_k = 1/V$, ω_{T0} is the long wavelength transverse optical phonon frequency. For partially ionic as well partially covalent crystals as III–V semiconductors, e_s^* deviates from Ze due to covalency effects.

In the absence of any barrier, a transition occurs when the thermodynamical potential relevant to the given ensemble of the lower-pressure phase equals that for some other structure, which becomes the stable phase above this coexistence pressure. As a next step, we have investigated the pressure variations of the second-order elastic constants (SOECs) and its derivatives. The relevant expressions for the SOECs are given elsewhere [27]. We shall now compute numerically the high-pressure phase transition, the associated volume collapses of GaY compounds which shows the first-order phase transition and mechanical properties for B3 and B1 phases in the next section.

3. Results and discussion

New crystal phases appear in materials under the influence of applied pressure and the relative stability of two crystal structures

requires an extremely accurate predictions. The effective interionic interaction potential incorporating the charge transfer effect and the covalency contribution as discussed in previous section has been applied to investigate the structural phase transitions and elastic properties in III–V semiconductors GaY (Y = N, P and As) materials. The phase transition pressure is determined by calculating the Gibbs free energy $G = U + PV - TS$ for the two phases. The Gibbs free energy becomes equal to the enthalpy $H = U + PV$ at $T = 0$ K.

Usually the high-pressure experiments results huge pressures that causes a reduction of the material volume and the temperature variations will normally produce much smaller changes in the relative stabilities of different phases. It is thus physically meaningful to concerned with the Gibbs free energy at zero temperature, which is the enthalpy H . At $T = 0$ K, the thermodynamically stable phase at pressure P is the one with the lowest enthalpy and the zero-temperature theory results in consistent agreement with experiment, however, the effects of finite temperature may be significant. We have undertaken such structural and elastic properties in an ordered way.

The values of thermodynamical potential G or H have been computed using the values of the three material dependent parameters, namely, range, hardness and force parameter (b , ρ and $f_T(r)$), which have been evaluated from the equilibrium condition [27]

$$\left. \frac{dU(r)}{dr} \right|_{r=r_0} = 0 \quad (19)$$

and the bulk modulus (B_T):

$$\left. \frac{d^2U(r)}{dr^2} \right|_{r=r_0} = (9kr_0)^{-1} B_T \quad (20)$$

The values of the overall vdW coefficient C and D involved in Eqs. (3) and (4) have been evaluated from the well-known Slater–Kirkwood variational method [25] and are listed in Table 1. We consider that the GaY compounds to be partially ionic and covalent to discuss their structural and mechanical properties in a systematic manner. We shall use the experimental values of lattice constant ($2a$), Bulk modulus (B_T), ionic (Ze) and effective charge (e_s^*).

It is perhaps worth mentioning that we have deduced the values of hardness (ρ), range (b) and force parameters ($f_T(r)$) from the knowledge of equilibrium distance and the bulk modulus following the equilibrium conditions. The input data along with their relevant references and the deduced model parameters from the knowledge of equilibrium distance (r_0), the bulk modulus (B_T) is given in Table 2. The values of electronic polarizabilities for GaN, GaP, and GaS have been directly taken from the experimental data [28,29]. While estimating the effective charge e_s^* , the values of optical dielectric constant ϵ_s and the high frequency dielectric constant ϵ_∞ , and the long wavelength transverse optical phonon frequency ω_{T0} are taken from [30] to have the covalency contribution.

In an attempt to reveal the structural phase transition of the test materials, we minimise the Gibbs's free energies $G_{B3}(r)$ and $G_{B1}(r')$ for the equilibrium interatomic spacing (r) and (r'). Fig. 1(a–c) shows the in Gibbs's free energies $G_{B3}(r)$ and $G_{B1}(r')$ as functions of pressure (P). Let us summarize the results of the plots. At zero pressure, the Gibb's free energy for B3 crystal phase is more negative therefore it is thermodynamically and mechanically stable, while

Table 1

The values of van der Waals coefficients of GaY compounds. c_{ij} ($i, j = 1, 2$) [in unit of 10^{-60} erg cm⁶], d_{ij} ($i, j = 1, 2$) [in units of 10^{-76} erg cm⁸] and overall van der Waals coefficients (C, D).

Compound	c_{11}	c_{12}	c_{22}	C	d_{11}	d_{12}	d_{22}	D
GaN	65.11	51.44	40.89	264.4	42.5	31.24	22.84	135.68
GaP	65.11	55.69	47.75	285.5	42.5	34.59	28.09	149.99
GaAs	65.11	72.11	79.95	369.3	42.5	48.72	55.83	211.16

Table 2

Input crystal data and model parameters for GaY compounds.

Compound	Input parameters				Model parameters		
	r_i (Å)	r_j (Å)	a_0 (Å)	B_T (GPa)	b (10^{-12} erg)	ρ (10^{-1} Å)	f_T (10^{-4})
GaN	1.07	0.82	4.52 [30]	190	4.29	2.97	53.56
GaP	1.07	0.6	5.451 [30]	88	15.07	3.78	-9.121
GaAs	1.07	0.61	5.653 [30]	74.8	16.99	3.93	-8.222

the B1 is not. As pressure increases, beyond the phase transition pressure (P_t), the Gibb's free energy for B1 system becomes more negative than B3 phase, so B1 will be more stable. All compounds in GaY shows the zinc-blende structure at low and moderate pressures and a crystallographic transition from B3 \rightarrow B1 occurs.

The phase transition pressure (P_t) thus obtained are listed in Table 3 and compared with experimental [14–17] and other theoretical [30–33] results. It is worth to comment that the transition pressure decreases in going from GaN to GaAs. The consistency between experimental data and lattice model calculation is attributed to the formulated effective interionic potential, which considers the various interactions as well proper usage of material parameters from the reported experimental data.

We further check the validity of the effective interionic interaction potential EIoIP, by estimating the values of the relative volumes $V(P)/V(0)$ associated with various compressions have also been cal-

culated from the Murnaghan equation of state [34]

$$\frac{V}{V_0} = \left(1 + \frac{B'}{B_0}P\right)^{-1/B'} \quad (21)$$

with V_0 as the cell volume at ambient conditions.

The estimated values of the pressure dependent radii $r(P)$ for both the structures (B3 and B1) have been used to compute the values of $V(P)/V(0)$ and are plotted them against the pressure (P) as illustrated in Fig. 2(a–c) for GaN, GaP and GaAs semiconductors. It is evident from the plot that our approach has predicted correctly the relative stability of competitive crystal structures, as the values of ΔG are positive. The magnitudes of the discontinuity in volume collapse [$-\Delta V(P_t)/V(0)$] at the transition pressure are obtained from the phase diagram and the values are listed in Table 3.

We note that the volume discontinuity $\Delta V/V$ at B3 \rightarrow B1 transition is lower than that of experimental [14–17] and other theoretical [30–33] results. We admit that the developed EIoIP considers only the overlap repulsive interactions significant up to the second nearest neighbours and does not incorporate the thermal fluctuations, which does not leads to a consistent prediction of the

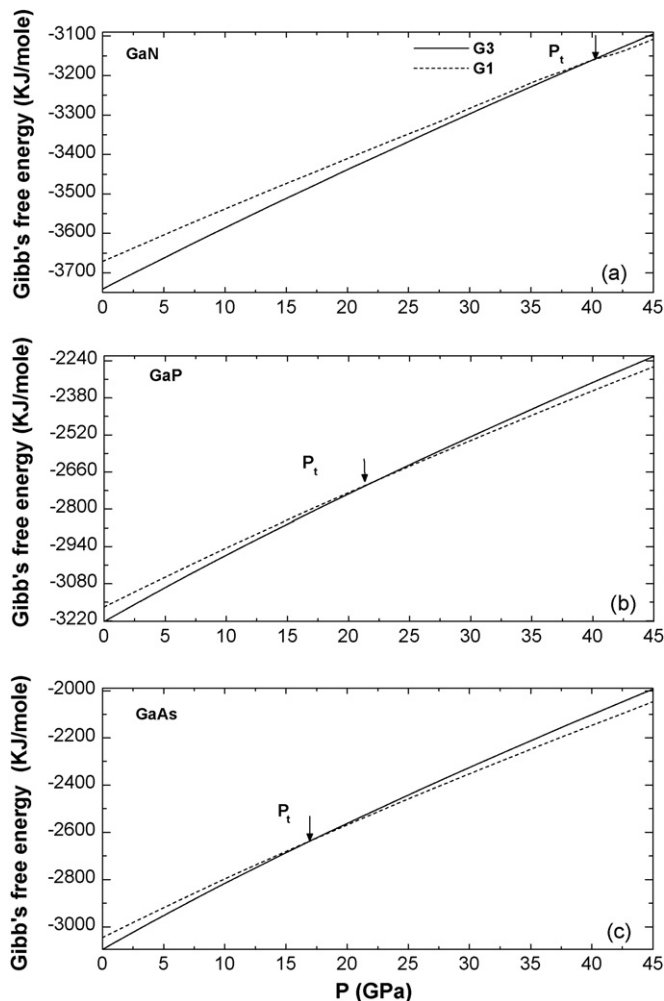
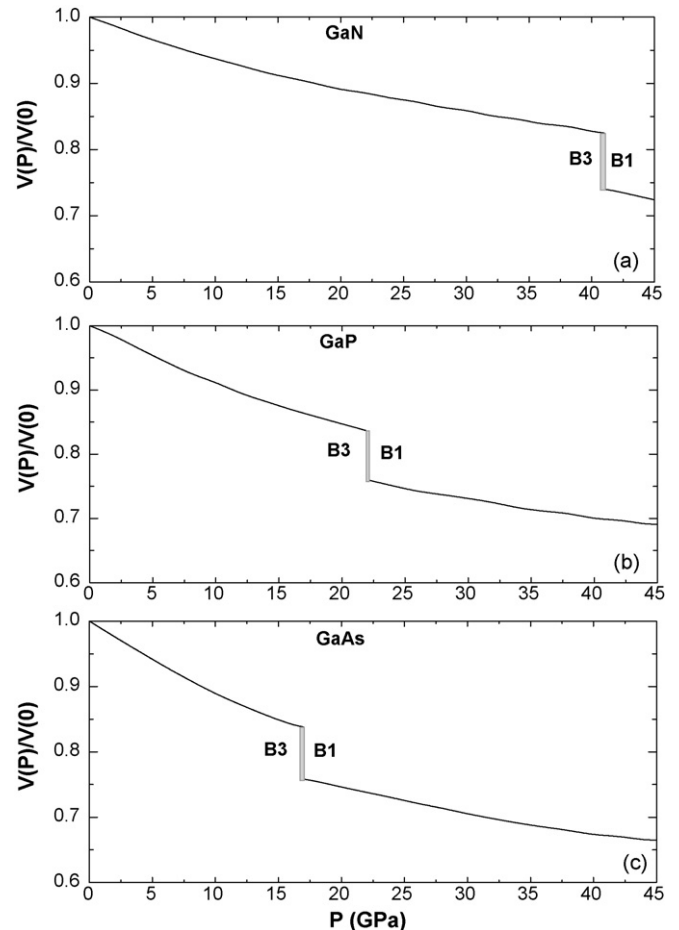
**Fig. 1.** (a–c) Variation of Gibbs free energy with pressure.**Fig. 2.** (a–c) Variation of volume collapse with pressure.

Table 3
Calculated transition pressures and volume collapse of GaY.

Compounds	Transition pressure (GPa)	Transition pressure (GPa)			Volume collapse (%)		
		Present	Experiment	Other calculations	Present	Experiment	Other calculations
GaN	B3 → B1	41	52.2 ± 3.0 [14] 47–50 [15]	37–53.6 [30] 37 [31]	8.5	13 [14,15]	
GaP	B3 → B1	22	21.5 ± 0.8 [16] 21.5 [17]	17.1 [10] 21.5 [30]	7.5	17.5 [17]	15.5 [33]
GaAs	B3 → B1	17	17.2 ± 0.7 [16] 16.6–17.3 [17]	17.0 [10] 10.5 [30]	8.6	15.0 [16] 17.3 [17]	13.8 [32] 17.4 [33]

volume change associated with the phase transition. Although the transition pressures may be well reproduced up to certain extent, the idea is to incorporate both the issues such that a balance of P_t and $\Delta V/V$ must yield the equilibrium of the systems under investigations.

To study the high-pressure elastic behavior of these compounds, we have computed the second-order elastic constants and their variation with pressure as shown in Fig. 3(a–c) for GaY compounds. We note that C_{44} decrease linearly with increasing pressure, away from zero at the phase transition pressures. On the contrary, the values of C_{11} and C_{12} increase linearly with pressure and in accordance with the first-order character of the transition for these compounds. It is useful to mention that the Born criterion for a lattice to be in the mechanically stable states is that the elastic energy density must be a positive definite quadratic function of the strain. This requires that the principal minors (alternatively the eigen values) of the elastic constant matrix should all be positive.

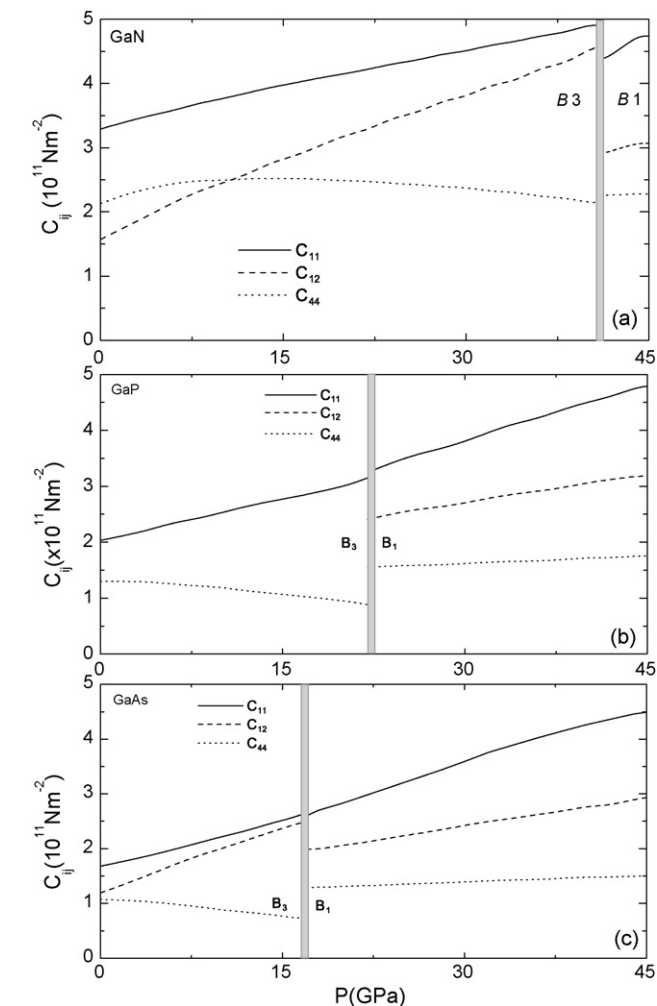


Fig. 3. (a–c) Variation of second-order elastic constants with pressure for GaY (Y = N, P and As) compounds.

We must mention that the elastic constant C_{11} is a measure of resistance to deformation by a stress applied on (1, 0, 0) plane with polarization in the direction (1 0 0), and the C_{44} refers to the measurement of resistance to deformation with respect to a shearing stress applied across the (1 0 0) plane with polarization in the (0 1 0) direction. Henceforth, the elastic constant C_{11} represents elasticity in length and a longitudinal strain produces a change in C_{11} . No doubt, the elastic constants C_{12} and C_{44} are intimately related to the elasticity in shape, which is a shear constant. However, a transverse strain causes a change in shape without a change in volume. Thus, the second-order elastic constants as C_{12} and C_{44} are less sensitive of pressure as compared to C_{11} [27].

Further the stability of a cubic crystal is expressed in terms of elastic constants [35]:

$$B_T = \frac{(C_{11} + 2C_{12})}{3} > 0, \quad (22)$$

$$C_{44} > 0, \quad (23)$$

and

$$C_S = \frac{(C_{11} - C_{12})}{2} > 0. \quad (24)$$

Here, C_{ij} are the conventional elastic constants.

Estimated values of bulk modulus (B_T), shear moduli (C_{44}) and tetragonal moduli (C_S), well satisfied the above elastic stability criteria for GaY compounds. The calculated values of second-order elastic constants, bulk modulus (B_T) and tetragonal moduli (C_S) are given in Table 4 and are also compared with various experimental [36–43] and other theoretical works [8,30–33,44–54]. Furthermore, Vukcevic [55] proposed a high-pressure stability criterion for ionic crystals, combining mechanical stability with minimum energy conditions. In accordance, the stable phase of the crystal is one in which the shear elastic constant C_{44} is nonzero (for mechanical stability) and which has the lowest potential energy among the mechanically stable lattices.

Further, C_{44} is a very small quantity, the calculated value of $[(4r_0/e^2)C_{44} - 0.556Z_m^2]$ is found to be a negative quantity so that $(A_2 - B_2)$ is negative and infers that these terms belong to an attractive interaction and possibly arise due to the van der Waals energy. The van der Waals energy converges quickly, but the overlap repulsion converges much more quickly. This means that the second neighbour forces are entirely due to the van der Waals interaction and the first neighbour forces are the results of the overlap repulsion and the van der Waals attraction between the nearest neighbours in semiconducting chalcogens and pnictides [27].

Furthermore, the mechanical properties as ductility and brittleness of Ga mononictides are of substantial importance and can be known from second-order elastic constants. A simple relationship, empirically linking the plastic properties of materials with their elastic moduli has been mentioned [56]. The thermodynamical property as the Voigt averaged shear modulus S representing the resistance to plastic deformation, while the bulk modulus B represents the resistance to fracture. Accordingly, the ratio $R_{S/B} < 0.5$, the material behaves in a ductile manner, otherwise the material behaves in a brittle manner. From Fig. 4(a–c) the ratio $R_{S/B}$ shows the brittle nature in ZnS phase while the compounds show ductile behavior after phase transition in NaCl phase.

Table 4
Second-order elastic constants (C_{11} , C_{12} and C_{44}), bulk modulus (B_T), tetragonal moduli (C_2) (10^{10} N m $^{-2}$), and pressure derivatives of SOECs (dB_T/dP , dC_{44}/dP and dC_2/dP) for GaV in B3 phase.

Properties	GaN			GaP			GaAs		
	Present	Expt.	Other calculations	Present	Expt.	Other calculations	Present	Expt.	Other calculations
C_{11}	32.9	39.0 [36], 37.4 [37]	40.77 [45], 31.69 [46], 26.40 [48], 29.60 [52], 29.30 [53], 27.70 [54]	20.3	14.12 [5], 14.05 [6], 14.05 [36]	14.08 [9], 17.88 [45], 15.07 [46]	16.8	12.23 [39]	12.30 [44], 14.76 [45], 12.42 [46]
C_{12}	15.7	14.5 [36], 10.6 [37]	13.8 [45], 15.2 [46], 15.3 [48], 15.4 [52], 15.9 [53], 15.6 [54]	14.2	6.25 [5], 6.20 [6]	6.57 [9], 6.20 [38], 5.63 [45], 6.28 [46]	11.9	5.71 [39]	5.30 [44], 4.60 [45], 5.14 [46]
C_{44}	21.30	10.5 [36], 10.1 [37]	10.23 [45], 19.76 [46], 16.80 [48], 20.60 [52], 15.50 [53], 15.00 [54]	13.0	7.047 [5], 7.03 [6]	8.22 [9], 7.03 [37], 5.12 [45], 7.63 [46]	10.7	6.00 [39]	6.20 [44], 4.24 [45], 6.34 [46]
B_T	21.44		23.7 [42], 19.0 [45,47], 20.3 [51], 17.6 [48], 24.0 [49], 18.4 [50], 17.3 [51]	16.2		8.82 [30], 8.68 [33], 8.87 [43]	13.5		7.55 [30], 7.08 [33], 7.48 [43]
C_2	8.6		7.15 [30]	3.05		3.745 [9], 3.92 [30], 4.4 [45]	2.45		3.25 [30]
dB_T/dP	4.39	2.92 [37], 3.64 [38]	3.93 [8], 2.66 [48], 4.6 [49], 3.8 [50], 3.98 [51]	3.69		3.68			
dC_{44}/dP	3.78				1.137	3.20 [9], 0.92 [30]	0.977		1.1 [30]
dC_2/dP	-0.5			-0.4		0.596 [9], 0.553 [45]	-0.43		
ξ	0.6			0.78			0.81		

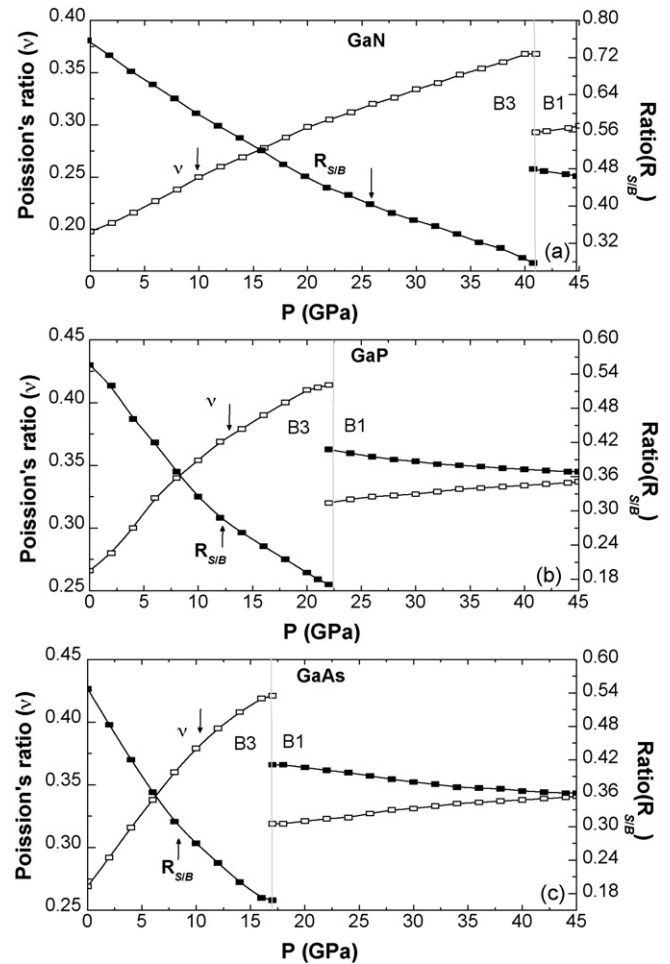


Fig. 4. (a–c) Variation of Poisson's ratio ν and ratio $R_{S/B}$ with pressure.

We may also refer to Frantsevich [57] who distinguish the ductility and brittleness of materials in terms of Poisson's ratio. According to Frantsevich rule the critical value of a material is 0.33. For brittle materials, the Poisson's ratio is less than 0.33, otherwise the material behaves in a ductile manner. It is identified from Fig. 4(a–c) that at low pressures, the Poisson's ratio shows the brittle nature and with the further increase in pressure the compounds in ZnS phase show ductile behavior and after phase transition in NaCl phase the compounds show brittle behavior. We can observe that there is a contradiction in between Pugh [56] and Frantsevich [57] empirical rules.

The Poisson's ratio ν in terms of the bulk modulus B and the Voigt averaged shear modulus S as [58]

$$\nu = \frac{1}{2} \left[3 \frac{B}{S} - 2 \right] \left[3 \frac{B}{S} + 1 \right]^{-1} \quad (25)$$

It follows that the empirical Pugh's critical value corresponds to $\nu = 0.26$, so that both the Pugh and Frantsevich empirical rules only differ on the exact border between the two types of behavior. Therefore the Ga monopnictides that are semiconducting compounds are brittle in nature in ZnS phase and ductile in nature in NaCl phase. The brittle nature is also observed in face centered cubic intermetallic compounds as Ir and Ir $_3$ X (X = Ti, Ta, Nb, Zr, Hf, V) [59] and in III–V Ga $_{1-x}$ In $_x$ As semiconducting and other compounds [60].

We may add that the value of the ratio $R_{C/B} < 0.57$ is used for the ductile behavior of intermetallics as MgCNi $_3$, otherwise the material behaves in a brittle manner [58]. If we follow this critical value of $R_{C/B}$ that acts as a performance indicator to distinguish ductile

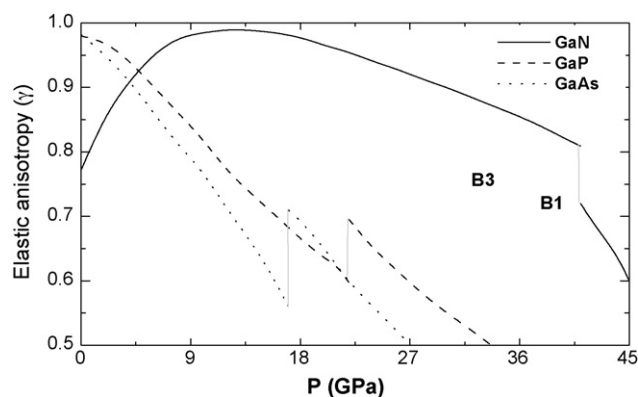


Fig. 5. Variation of elastic anisotropy with pressure.

tile and/or brittle transition of materials, then there is an obvious contradiction in between Pugh [56] and Frantsevich [57] empirical rules.

It is known that anisotropic parameter A is unity for isotropic elasticity but still the cubic crystal which is isotropic structure, has elastic anisotropy other than unity as a result of a fourth rank tensor property of elasticity. The elastic anisotropic parameter of a cubic crystal is defined as [61].

$$\gamma = \frac{2C_{44} + C_{12}}{C_{11}} - 1 \quad (26)$$

Through the calculated elastic constants, we can obtain the elastic anisotropic parameter γ at various pressures for GaY ($Y=N, P$ and As) compounds. Fig. 5 shows the pressure dependence of the elastic anisotropic parameter γ up to 45 GPa. It is clear from the plot that the anisotropy decreases with increase in pressure, which indicates that the anisotropy is more obvious under pressure. We have plotted the elastic anisotropy for both phases. The anisotropy factor drops rapidly with pressure and then decrease more slowly at higher pressures. The values of anisotropic parameter γ for these compounds are given in Table 5 at zero temperature and pressure.

Usually, the elastic constants relates the properties of material that undergo stress, deform and then recover after returns to its original shape after stress ceases. The elastic constants are emphasized in solids because they are closely intimated to various fundamental solid-state phenomena such as interatomic bonding, equations of state, and phonon spectra [9]. It is worth to mention that the elastic properties are also linked thermodynamically with specific heat, thermal expansion, Debye temperature, the relative positions of the cation and anion sublattices under volume-conserving strain distortions, and Grüneisen parameter in semiconducting chalcogens and pnictides [27]. Most importantly, knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermoelastic stress, internal strain, sound velocities, and fracture toughness.

As suggested by Bouhemadou et al. [9], the above is applicable for III–V semiconducting compounds, we have attempted to understand the Kleinman parameter, ξ , which describes the

relative positions of the cation and anion sublattices under volume-conserving strain distortions for which positions are not fixed by symmetry. A low value of ξ implies a large resistance against bond-bending or bond-angle distortion and vice versa [62,63]. We used the following relation [64]:

$$\xi = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}} \quad (27)$$

The Kleinman parameter, ξ , is calculated for III–V semiconducting compounds GaY ($Y=N, P, As$) and are illustrated in Table 4 at zero temperature and pressure for zinc-blende phase. An increasing trend in ξ values is noticed on going from GaN to GaAs. Concerning GaP, the calculated value of ξ is consistent with the available experimental [45] and theoretical calculations [9]. For other compounds because of unavailability of data we could not compare them and can be considered as a prediction of elastic properties.

The average wave velocity v_m has been approximately calculated from [65]:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-1/3} \quad (28)$$

where v_l and v_t are the longitudinal and the transverse elastic wave velocity respectively, which are obtained from Navier's equation in the following forms:

$$v_l = \left[\frac{3B + 4S}{3\rho} \right]^{1/2} \quad (29)$$

$$v_t = \left[\frac{S}{\rho} \right]^{1/2} \quad (30)$$

where S is the Voigt averaged shear modulus, B is the bulk modulus, and ρ is the density.

The pressure dependence of the sound velocity is documented in Fig. 6(a–c). It is noticed that v_l increases in both phases while v_t decreases in B3 phase and increases in B1 phase. The values of longitudinal, transverse and average sound velocities are given in Table 5 at zero temperature and pressure consistent with the available experimental [5] and theoretical calculations [9].

We have further attempted to compute the pressure dependence of Debye temperature (θ_D) estimated from the knowledge of elastic constants by defining θ_D as

$$\theta_D^3 = \frac{3.15}{8\pi} \left(\frac{h}{k_B} \right)^3 \left(\frac{r}{M} \right)^{3/2} \left(\frac{C_{11} - C_{12}}{2} \right)^{1/2} \times \left(\frac{C_{11} + C_{12} + 2C_{44}}{2} \right)^{1/2} C_{44}^{1/2}, \quad (31)$$

Here, M is the acoustic mass of the compound; h and k_B are the Planck and Boltzmann constants, respectively. The Debye temperature as functions of pressure is plotted in Fig. 7(a–c). It is inferred from the figure that θ_D increase with increasing in pressure for GaAs, while, reverse is true for GaN and GaP at higher pressures. To explain the variation of θ_D with the pressure, we attempt to analyze our results in the framework of dynamics of lattice with pressure. The change of the force constants induced by pressure increases θ_D . On the other hand, the pressure dependence of θ_D in

Table 5
Calculated elastic anisotropic parameter, longitudinal, transverse and average elastic wave velocity of GaY in m/s.

Compounds	γ	v_l			v_t			v_m		
		Present	Other calculations	Expt.	Present	Other calculations	Expt.	Present	Other calculations	Expt.
GaN	0.772	9200			5650			1330		
GaP	0.98	8540	6345 [9]	6280 [5]	4820	3759 [9]	3466 [5]	1140	4163 [9]	445 [5]
GaAs	0.982	6890			3870			919.69		

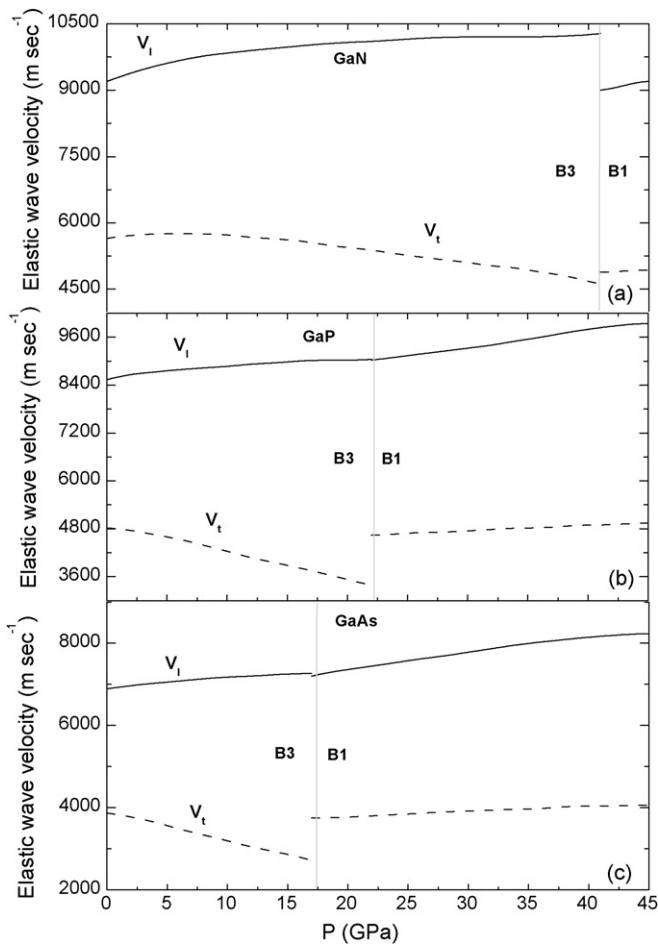


Fig. 6. (a–c) Pressure dependence of elastic wave velocity v_l and v_t .

GaN and GaP at higher pressure suggests that decreasing of Debye temperature drives the system effectively toward the softening of lattice with increasing pressure.

The Debye temperature also allow us to correlate Cauchy discrepancy C^* with elastic constant following

$$C^* = \frac{C_{12} - C_{44}}{C_{12} + C_{44}}, \quad (32)$$

at zero pressure. We have observed negative Cauchy discrepancy for GaN, while to that positive Cauchy discrepancy of 0.044 and 0.053 for GaP and GaAs, respectively. It is worth to mention that the III–V semiconductors with zinc-blende structure (B3 to B1 structural phase transition), rare earth chalcogenides with NaCl-type (B1) to CsCl-type (B2) structure, alkaline earth chalcogenides and yttrium and scandium antimonides [NaCl-type (B1) to CsCl-type (B2) structure], II–VI semiconductors and diluted magnetic semiconductors with zinc-blende (B3) to Rocksalt (B1) structure [27] and most of the body centered cubic transition metals shows a positive Cauchy deviation C^* . However, negative Cauchy discrepancy for AlY (Y = N, P, As) is also noticed [60]. It should be pointed out that the significance of this work is not only in calculating the high-pressure phase transition but also in predicting the sound velocity, the relative positions of the cation and anion sublattices under volume-conserving strain distortions, the Grüneisen parameter, the Poisson ratio, and the Debye temperature for GaY (Y = N, P and As).

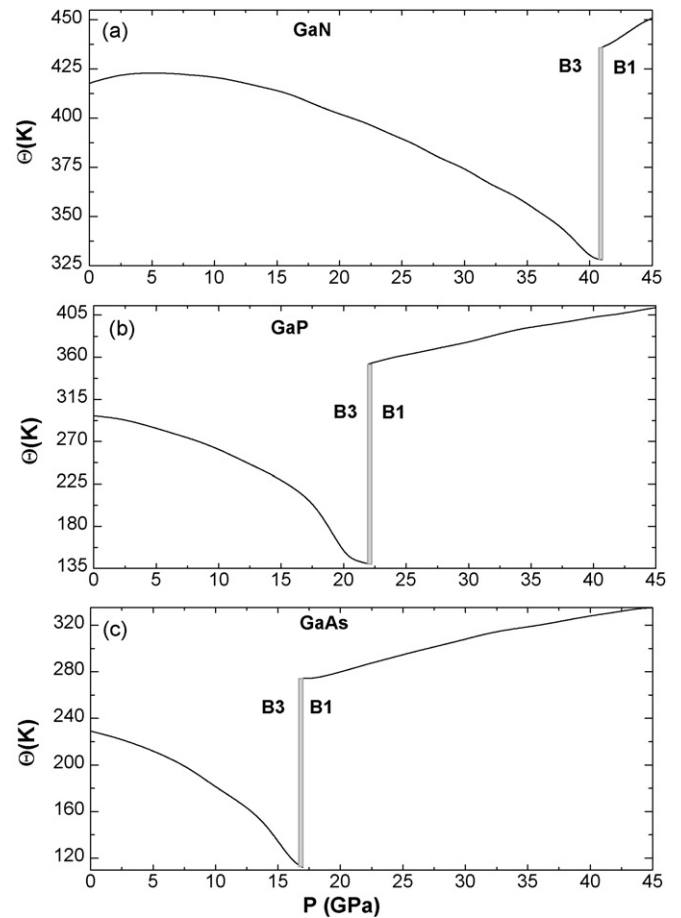


Fig. 7. (a–c): Variation of Debye Temperature (θ_D) with pressure.

4. Conclusion

The present study addresses for the first time, the pressure dependent ductile and brittle nature of III–V compound GaY (Y = N, P and As) by formulating an effective interionic interaction potential incorporating the long-range Coulomb, the covalency effects, the charge transfer caused by the deformation of the electron shells of the overlapping ions and the Hafemeister and Flygare type short-range overlap repulsion extended up to the second neighbour ions and the van der Waals interaction. As a first step, we exercise for identifying the pressure dependent structures.

Deduced value of materials parameter allows us to predict phase transition pressure and associated volume collapse consistent with the available data. We stress that the vast volume discontinuity in pressure–volume phase diagram is ascribed in terms of the structural phase transition from ZS (B3) to RS (B1) structure. It is thus obvious from the overall achievements that present charge transfer phenomena and covalency effects are essential for the description of the phase transition phenomena and mechanical properties. We stress that the charge transfer mechanism and covalency effects in III–V semiconductors that are partially ionic and partially covalent yields a realistic representation of effective interionic interaction capable of explaining the elastic behavior.

From the computed values of pressure dependent Poisson's ratio ν and the ratio $R_{S/B}$ we conclude that GaY (Y = N, P, As) is brittle [ductile] in zinc-blende (B3) [Sodium Chloride (B1)] phase. We stress that to the best of our knowledge the pressure dependence of ductile (brittle) nature of mixed valent compounds have not been calculated and measured yet, hence the present calculations will inspire further experimental research on these compounds.

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