

Pressure and Temperature Dependent Thermodynamical Properties of $\text{Ga}_{1-x}\text{In}_x\text{P}$

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Abstract. The high-pressure structural phase transition and pressure as well temperature induced elastic properties of cubic zincblende to rocksalt structures of $\text{Ga}_{1-x}\text{In}_x\text{P}$ ($x = 0.25, 0.5$ and 0.75) alloy have been performed using effective interionic interaction potential with emphasis on charge transfer interactions and covalent contribution. Estimated values of phase transition pressure and the volume discontinuity in pressure-volume phase diagram indicate the structural phase transition from ZnS to NaCl structure. From the investigations of elastic constants the pressure (temperature) dependent volume collapse/expansion, Poisson's ratio ν and Pugh ratio ϕ ($= B_T/G_H$), heat capacity (C_v), thermal expansion coefficient (*ath.exp*) the $\text{Ga}_{1-x}\text{In}_x\text{P}$ lattice infers mechanical stiffening, thermal softening, and brittle nature.

INTRODUCTION

The III–V semiconductors experienced great research activity because of their wide ranged device applications and rich physics as well chemistry such as mixed bonding features. The mixed valence compound $\text{Ga}_{1-x}\text{In}_x\text{P}$ is formed by randomly replacing a fraction of the cations in compound semiconductor alloys with Indium ions and with generalized chemical formula $\text{A}^{\text{III}}_{1-x}\text{In}_x\text{C}^{\text{V}}$ [1].

The II–VI and III–V compounds possess tetrahedrally coordinated zinc blende (ZB) or wurtzite (W) type phases as probed from experiments and theoretical findings. As pressure increases, III – V semiconductors discerns the sequence of ZB (B3) \rightarrow NaCl (B1) \rightarrow Sn (A5) structural transitions [1]. A high-pressure NaCl (B1) type phase and a metallic (Sn) type phase in III–V semiconductors have been earlier reported [2].

Optical absorption measurement shows the phase-transition pressure of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ at 17 GPa [3]. Inelastic neutron scattering experiment determines phonon frequencies in InP. The phonon dispersion curve shows longitudinal modes have higher frequency than the transverse modes [4].

Motivated from the available information on structural phase transition, we intended to seek the role of pressure and temperature dependent volume collapse/expansion, Poisson's ratio ν and Pugh ratio ϕ ($= B_T/G_H$), heat capacity (C_v), thermal expansion coefficient (*ath.exp*) of $\text{Ga}_{1-x}\text{In}_x\text{P}$ with B3 to B1 structure.

THE MODEL

The stability of a particular structure is decided by the minima of Gibbs's free energy, $G = U + PV - TS$, U being the internal energy, which at $T = 0$ K is the cohesive energy, S is the entropy at temperature T , pressure P and volume V . The cohesive energy is:

$$U_{B3} = (-\alpha_M Ze^2 / r)[Z + 2nf(r)] - \sum_{ij} c_{ij} r^{-6} - \sum_{ij} d_{ij} r^{-8} + nb\beta_{ij} \exp[(r_i + r_j - r_{ij}) / \rho] + (n'b/2) \left[\frac{\beta_{ii} \exp((2r_i - kr_{ij}) / \rho) + \beta_{jj} \exp((2r_j - kr_{ij}) / \rho)}{\beta_{ij} \exp((2r_j - kr_{ij}) / \rho)} \right] + [\hbar < \omega^2 >^{1/2} / 2] \quad (1)$$

$$U_{B1} = (-\alpha_M Ze^2 / r)[Z + 2nf(r)] - \sum_{ij} c_{ij} r^{-6} - \sum_{ij} d_{ij} r^{-8} + nb\beta_{ij} \exp[(r_i + r_j - r_{ij}) / \rho] + (m'b/2) \left[\frac{\beta_{ii} \exp((2r_i - kr_{ij}) / \rho) + \beta_{jj} \exp((2r_j - kr_{ij}) / \rho)}{\beta_{ij} \exp((2r_j - kr_{ij}) / \rho)} \right] + [\hbar < \omega^2 >^{1/2} / 2] \quad (2)$$

The pressure causes an increase in the overlap of adjacent ions in a crystal and charge transfer takes place between the overlapping electron shells. In equation 1 and 2, the first two terms are the potential energies including long-range Coulomb and charge transfer effect. The third and fourth terms are the short-range (SR) van-der Waals (vdW) attraction energies due to dipole-dipole and dipole-quadruple interaction. Last term is short-range repulsive energy due to the overlap repulsion between ions. The second term in Eq. (1 and 2) is an algebraic sum of central force part of the charge transfer force parameter and the force parameter arises due to covalent nature *i.e.* $f(r) = f_{cti} + f_{cov}$. The charge transfer force parameter f_{cti} is expressed as [5-6]

$$f(r) = f_0 \exp(-r / \rho) \quad (3)$$

Keeping in mind that $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75] lead to partially ionic and partially covalent in bonding, and attractive forces due to covalency are important that modifies the effective charge. The covalency term is

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

RESULTS AND DISCUSSIONS

Values of material parameters modified ionic charge (Z_m), range (ρ), hardness (b) and charge transfer parameter $f(r)$ are obtained from the equilibrium distance, bulk modulus and second order aggregate elastic constant C_{12} (C_{44}) [5, 6]. For the computation purpose, we have used the input parameters as $C_{12} = 0.57 \times 10^{11} \text{ Nm}^2$, $C_{44} = 0.73 \times 10^{11} \text{ Nm}^2$, $r_0 = 2.25 \text{ \AA}$ [5] and $B_T = 88 \text{ GPa}$ [8], ionic (Ze), effective charge (e_s^*), Debye temperature (θ_D) [5]. Deduced optimized value for $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75] as $b = 0.12 \times 10^{-12}$, 0.16×10^{-12} , $0.21 \times 10^{-12} \text{ erg}$, $\rho = 3.50 \times 10^{-9}$, 3.65×10^{-9} , $3.81 \times 10^{-9} \text{ cm}$ and $f(r) = 1.01 \times 10^{-3}$, -0.212×10^{-3} , -0.545×10^{-3} equilibrium interatomic spacing in $B3$ [$r_0 = 2.47, 2.52, 2.56 \text{ \AA}$] and $B1$ [$r_0 = 2.75, 2.79, 2.83 \text{ \AA}$] phases, respectively.

Figure 1 shows the Gibbs's free energies $G_{B3}(r)$ and $G_{B1}(r)$. It is noticed that at zero pressure, the Gibb's free energy for $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75] in $B3$ crystal phase is more negative therefore it is thermodynamically and mechanically stable, while 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. Figure 1 showed the relative volumes associated with a change in either P or T . The magnitude of the discontinuity in volume at the P_t is obtained from the phase diagram. A steep increase in the ratio V_T/V_0 with increasing temperature indicates net expansion and $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75] is susceptible to temperature

As a next step, we have evaluated pressure and temperature dependent of second order elastic constants: C_{11} , C_{12} , and C_{44} to estimate the Pugh and Poisson ratio. Figure 2 illustrates the Poisson's ratio ν behaviour as a function of temperature. The Poisson's ratio at room temperature is 0.293, 0.314, 0.317 for $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5, 0.75$]. It is noticed that ν is insensitive for temperature variations even at $T = 1000 \text{ K}$. Deduced values of Poisson's ratio ν infer the brittle manner of $\text{Ga}_{1-x}\text{In}_x\text{P}$. Figure 2 also showed that the Pugh ratio $\phi = B_T/G_H > 1.75$ shows that at zero as well at high pressures $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75] is brittle and the Poisson's ratio ν also shows that at zero as well

as at high-pressure $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75] is brittle. Thus, both Pugh and Frantsevich rule confirms the

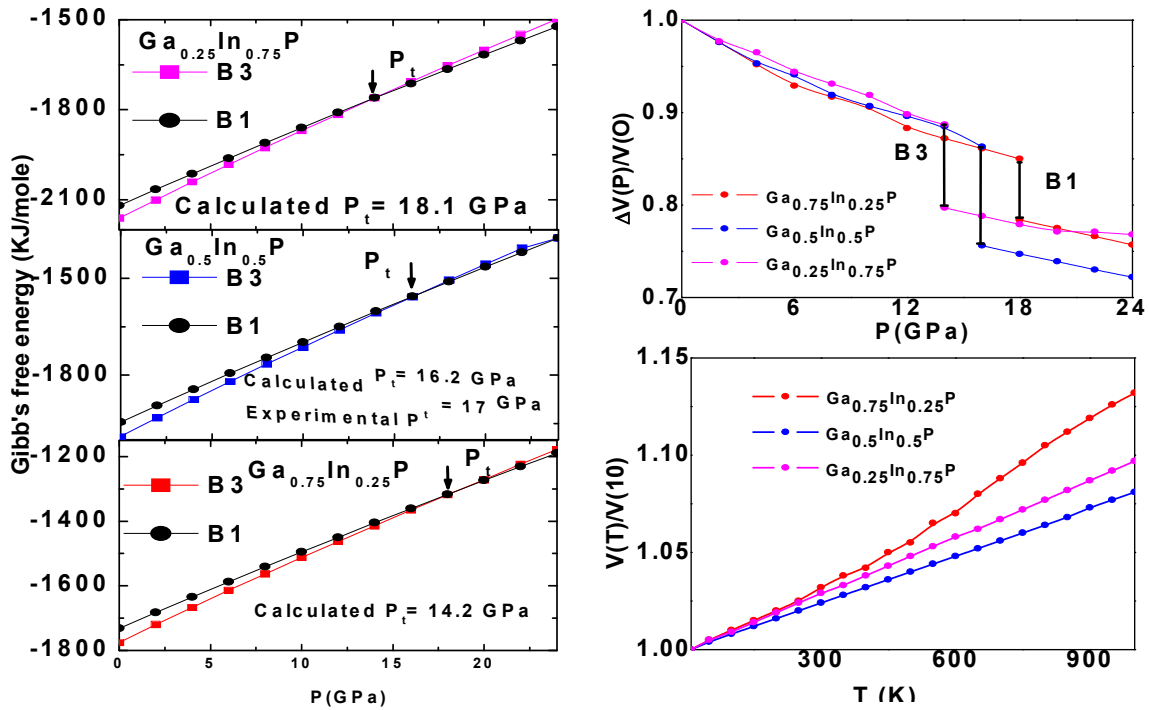


FIGURE 1: Variation of Gibb's free energy and Equation of state of $\text{Ga}_{1-x}\text{In}_x\text{P}$ with pressure and temperature. brittle/ductile nature of $\text{Ga}_{1-x}\text{In}_x\text{P}$. Furthermore, at zero pressure, the value of ν is 0.38, 0.46, and 0.47 for $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75].

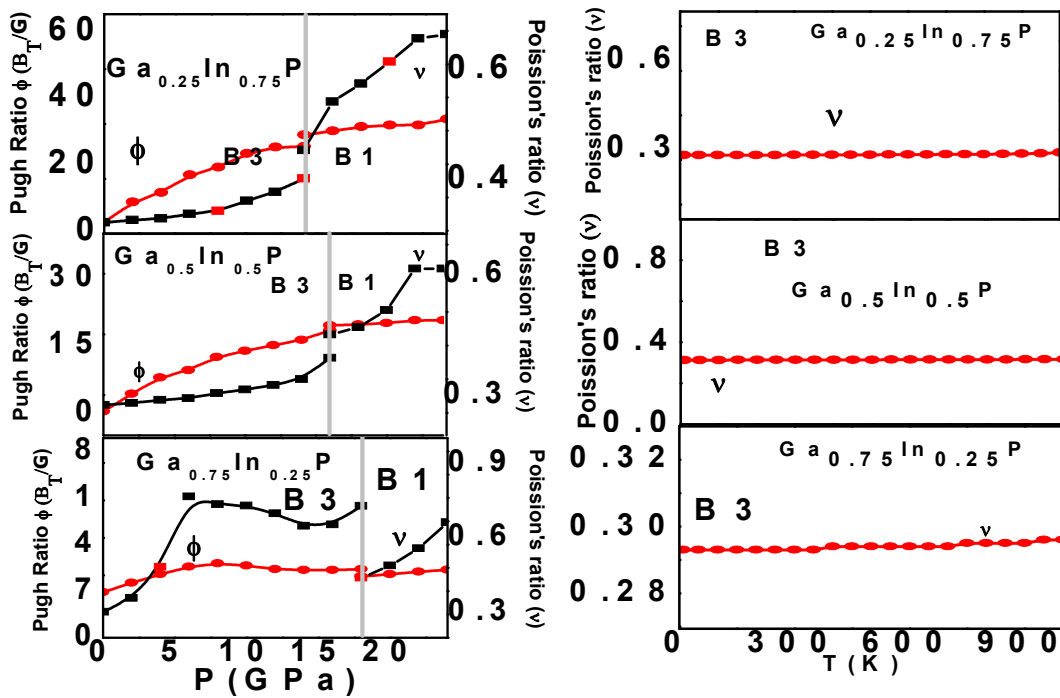


FIGURE 2: Variation of Pugh ratio (Φ) and Poisson's ratio (ν) with pressure and temperature.

Within the framework of quasi-harmonic Debye model, the normalized heat capacity, $[C_v - C_v(P=0)]/C_v(P=0)$ at constant volume with pressure P for $\text{Ga}_{1-x}\text{In}_x\text{P}$ is illustrated in Figure 3 at $T = 200, 400, 600$ and 800 K, respectively. Here, C_v and $C_v(P=0)$ are heat capacity at any pressure P and at zero pressure. The heat capacity at different temperatures decreases nonlinearly with the applied pressures. It infers that $\text{Ga}_{1-x}\text{In}_x\text{P}$ lattice gets stiffened due to bond compression as functions of pressure at variable temperatures. For higher temperatures $T \rightarrow \theta_D$, the variation in heat capacity with pressure becomes weak.

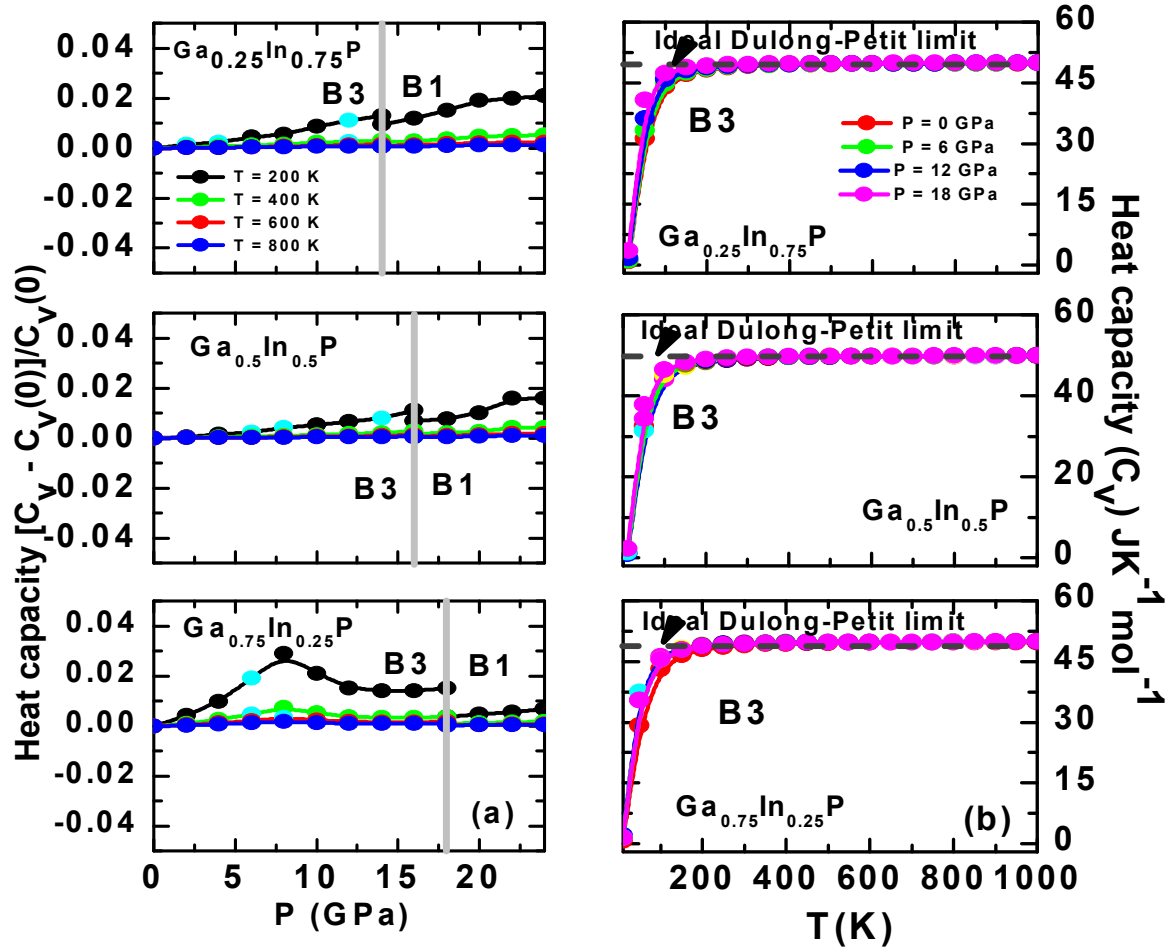


FIGURE 3: Variation of heat capacity (C_v) with pressure and temperature at different pressure/temperatures.

The pressure dependent Grüneisen parameter and Bulk modulus is required apart from heat capacity at constant volume C_v to determine thermal expansion coefficient ($\alpha_{th.exp.}$). We have determined the pressure dependence of $\alpha_{th.exp.}$ as shown in Figure 4 for $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75]. The pressure dependent thermal expansion coefficient $\alpha_{th.exp.}$ decreases nonlinearly with the pressure. The decreasing trend in $\alpha_{th.exp.}$ confirms the mechanical softening in $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75]. The variation of the C_v as functions of temperature for various $P = 0, 6, 12, 18$ GPa is shown in Figure 4. Below room temperature, C_v increases very rapidly with the temperature at all pressures. Above 300 K, C_v increases slowly with the temperature and it almost approaches a constant ideal gas limit $C_v(T) = 3R$, at higher temperatures.

As a next step, we have also plotted the variations of the thermal expansion, with temperature at various pressures and are illustrated in Figure 4 for $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75]. However, the temperature dependent $\alpha_{th.exp}$ increases rapidly (nonlinearly) at low temperatures and remains independent of temperature away from room

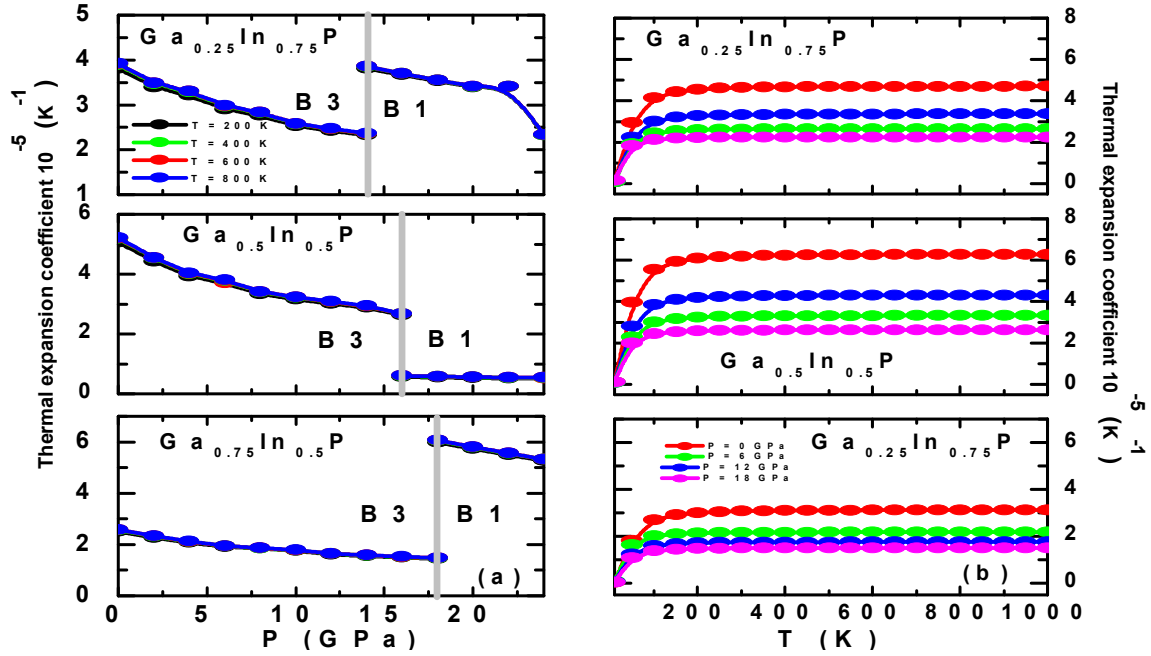


FIGURE 4: Variation of Debye Temperature (θ_D) as a function of pressure and temperature.

temperature at all pressures. The $\alpha_{th.exp}$ suppresses with enhanced pressures at higher temperatures.

To an end $\text{Ga}_{1-x}\text{In}_x\text{P}$ [$x = 0.25, 0.5$ and 0.75] showed that the volume collapse (V_p/V_0) in terms of compressions in $\text{Ga}_{1-x}\text{In}_x\text{P}$ ($x = 0.25, 0.5$ and 0.75) at higher pressure indicates the mechanical stiffening of lattice. These alloys are brittle on applied pressure and temperature and mechanically stiffened as a consequence of bond compression and bond strengthening and thermally softened due to bond expansion and bond weakening due to lattice vibrations.

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