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

Raju Sapkale$^{1,a)}$, Sanjay Jain$^{2,b)}$ and Swarna Shriya$^3$ 

$^1$Department of Physics, Pt. Jawaharlal Nehru Govt. College, Nepanagar-45022, India. 
$^2$Department of Physics, IES, IPS Academy Indore-452012, India 
$^3$School of Physics, Vigyan Bhavan, Devi Ahilya University, Khandwa Road Campus, Indore 452001, India. 

$^a)$Corresponding author: sapkale.raju@rediffmail.com 
$^b)$sanjay_rjain@rediffmail.com 

Abstract. The high-pressure structural phase transition and pressure as well temperature induced elastic properties of cubic zincblende to rocksalt structures of Ga$_{1-x}$In$_x$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 $\nu$ and Pugh ratio $\phi$ ($= B_T/G_H$), heat capacity ($C_v$), thermal expansion coefficient ($\alpha_{th.exp}$) the Ga$_{1-x}$In$_x$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 Ga$_{1-x}$In$_x$P is formed by randomly replacing a fraction of the cations in compound semiconductor alloys with Indium ions and with generalized chemical formula A$^{III}_{1-x}$In$_x$C$^V$ [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 Ga$_{0.5}$In$_{0.5}$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 $\nu$ and Pugh ratio $\phi$ ($= B_T/G_H$), heat capacity ($C_v$), thermal expansion coefficient ($\alpha_{th.exp}$) of Ga$_{1-x}$In$_x$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:

\[
U_{11} = -\alpha_m \frac{Z e^2}{r} [Z + 2nf(r)] - \sum_i c_i r^{-\alpha_i} - \sum_i d_i r^{-\alpha_i} + nb \beta_i \exp \left( \frac{r_i + r_j - r_k}{\rho} \right) + \frac{\alpha' b}{2} \left[ \beta_i \exp \left( \frac{(2r_i - kr_j)}{\rho} \right) + \right] + \left[ \frac{\hbar}{\omega} > \frac{1}{2} \right]
\]

\[
U_{bb} = -\alpha_m \frac{Z e^2}{r} [Z + 2nf(r)] - \sum_i c_i r^{-\alpha_i} - \sum_i d_i r^{-\alpha_i} + nb \beta_i \exp \left( \frac{r_i + r_j - r_k}{\rho} \right) + \frac{\alpha' b}{2} \left[ \beta_i \exp \left( \frac{(2r_i - kr_j)}{\rho} \right) + \right] + \left[ \frac{\hbar}{\omega} > \frac{1}{2} \right]
\]

(1)

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-quadrupole 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. \( f(r) = f_{ca} + f_{cov} \). The charge transfer force parameter \( f_{ca} \) is expressed as [5-6]

\[
f(r) = f_{ca} \exp \left( \frac{-r}{\rho} \right)
\]

(3)

Keeping in mind that Ga\(_1-x\)In\(_x\)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

\[
f_{cov} (r) = 4e^2 V_{sp}^2 / r_0 E_g^3
\]

(4)

RESULTS AND DISCUSSIONS

Values of material parameters modified ionic charge \( (Z_m) \), range \( (\rho) \), 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 \( C_{12} = 0.57 \times 10^{11} \) Nm\(^2\), \( C_{44} = 0.73 \times 10^{11} \) Nm\(^2\), \( r_0 = 2.25 \) Å [5] and \( B_T = 88 \) GPa [8], ionic \( (Z_e) \), effective charge \( (e_*) \), Debye temperature \( (\theta_D) \) [5]. Deduced optimized value for Ga\(_1-x\)In\(_x\)P \([x = 0.25, 0.5\) and 0.75] as \( b = 0.12 \times 10^{-12}, 0.16 \times 10^{-12}, 0.21 \times 10^{-12} \) erg, \( \rho = 3.50 \times 10^9, 3.65 \times 10^9, 3.81 \times 10^9 \) cm and \( f(r) = 1.01 \times 10^3, -0.212 \times 10^3, -0.545 \times 10^3 \) equilibrium interatomic spacing in \( B3 \) \([r_0 = 2.47, 2.52, 2.56 \) Å] and \( B1 \) \([r_0 = 2.75, 2.79, 2.83 \) Å] phases, respectively.

Figure 1 shows the Gibbs’s free energies \( G_{B1}(r) \) and \( G_{B3}(r) \). It is noticed that at zero pressure, the Gibb’s free energy for Ga\(_1-x\)In\(_x\)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 Ga\(_1-x\)In\(_x\)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 \( v \) behaviour as a function of temperature. The Poisson’s ratio at room temperature is 0.293, 0.314, 0.317 for Ga\(_1-x\)In\(_x\)P \([x = 0.25, 0.5, 0.75] \). It is noticed that \( v \) is insensitive for temperature variations even at \( T = 1000 \) K. Deduced values of Poisson’s ratio \( v \) infer the brittle manner of Ga\(_1-x\)In\(_x\)P. Figure 2 also showed that the Pugh ratio \( \phi = B_P / G_H > 1.75 \) shows that at zero as well at high pressures Ga\(_1-x\)In\(_x\)P \([x = 0.25, 0.5\) and 0.75] is brittle and the Poisson’s ratio \( v \) also shows that at zero as well
as at high-pressure Ga$_{1-x}$In$_x$P [$x = 0.25$, 0.5 and 0.75] is brittle. Thus, both Pugh and Frantsevich rule confirms the brittle/ductile nature of Ga$_{1-x}$In$_x$P. Furthermore, at zero pressure, the value of $\nu$ is 0.38, 0.46, and 0.47 for Ga$_{1-x}$In$_x$P [$x = 0.25$, 0.5 and 0.75].

**FIGURE 1**: Variation of Gibb’s free energy and Equation of state of Ga$_{1-x}$In$_x$P with pressure and temperature.

**FIGURE 2**: Variation of Pugh ratio ($\Phi$) and Poisson’s ratio ($\nu$) 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 Ga\(_{1-x}\)In\(_x\)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 Ga\(_{1-x}\)In\(_x\)P lattice gets stiffened due to bond compression as functions of pressure at variable temperatures. For higher temperatures \(T \to T_D\), the variation in heat capacity with pressure becomes weak.

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 Ga\(_{1-x}\)In\(_x\)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 Ga\(_{1-x}\)In\(_x\)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 Ga$_{1-x}$In$_x$P [$x = 0.25, 0.5$ and $0.75$]. However, the temperature dependent $\alpha_{\text{th,exp}}$ increases rapidly (nonlinearly) at low temperatures and remains independent of temperature away from room temperature at all pressures. The $\alpha_{\text{th,exp}}$ suppresses with enhanced pressures at higher temperatures.

To an end Ga$_{1-x}$In$_x$P [$x = 0.25, 0.5$ and $0.75$] showed that the volume collapse ($V_p/V_0$) in terms of compressions in Ga$_{1-x}$In$_x$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.

ACKNOWLEDGMENTS

We would like to thank late Dr. Dinesh Varshney, School of Physics, Devi Ahilya University, Indore for his guidance in our carrier and research work.

REFERENCES