

# Study of effect of temperature on phase transition pressure of GaAs and GaSb

Pooja Pawar<sup>1</sup>, Abdul Shukoor V<sup>1</sup>, Sadhna Singh<sup>1</sup>

<sup>1</sup>High Pressure Research Lab, Department of Physics, Barkatullah University Bhopal, MP 462026, India

Corresponding author Email: poojapawarphy@gmail.com

**Abstract.** We have presented the pressure induced phase transition of GaAs and GaSb from zinc blende (ZB) to rocksalt (NaCl) structure associated by using realistic interaction potential model (RIPM), which is modified by taking effect of temperature. This model consists of coulomb interaction, three body interaction and short range overlap repulsive interaction up to second neighbor. Phase transition pressures are associated with a sudden collapse in volume showing the occurrence of first order phase transition. The phase transition pressure ( $P_t$ ) and volume collapse obtained from this model show a reasonable agreement with experimental and theoretical results.

## 1. Introduction

During the last generation, III-V semiconductors have been broadly served as substances for electronic and optoelectronic devices. These applications make them as vital elements in an advanced information society [1]. The III-V compounds generally crystallize in zinc-blend (ZB) and wurtzite (W) structure. In this group GaAs has wide applications due to its direct band gap and having a higher saturated electron velocity as well as higher electron mobility, especially where the reliability is a major concern. [2]. Among III-V compounds, the narrow band gap antimonide based compound semiconductors (ABCS) are broadly regarded as the first nominee materials for the manufacturing of the third generation infrared photon detectors and ICs with ultra-high speed and ultra-low power consumption. Their distinctive physical aspects and band gap structures provide a large space to design varied unique devices [3]. They differ structurally only in their third-nearest-neighbour atomic arrangement. Even the difference in total energy between these two phases is very small. The study of materials at high pressure by high pressure technique like diamond anvil technique [4] exhibits new crystal phases and novel behaviour under pressure.

Among these materials, GaAs shows complicated phases under high pressure. As the pressure increased, the experimentally observed phase transition sequence in GaAs is GaAs-I, the ZB structure (space group F-43m), to GaAs- II, the orthorhombic phase (space group Pmm2) [5], which can be seen as a distortion of the rock-salt (RS) structure (space group Fm-3m) [6–8]. First-principles studies had predicted the existence of a field of stability for an sc16 phase (binary analog of the bc8 phase observed in Si and Ge), which was, however, close to the numerical precision of the calculations (9-10).

## 2. Methodology

The three body interaction effect [11] arising from the deformation of the overlapping electron shells of the adjacent ions in solids is important. This effect is introduced in the expression of Gibbs free



energy ( $G = U + PV - TS$ ), in order to obtain the stability condition for a crystal structure. Here  $U$  is the internal energy, which at  $T = 0K$  is equivalent to the lattice energy,  $S$  is the vibrational entropy at absolute temperature  $T$ . Since the theoretical calculation are done at  $T = 0K$ , hence the Gibbs free energy is equivalent to enthalpy ( $H$ ). This is not a realistic approach because experiments are carried out at room temperature and not at  $T = 0K$ . This fact causes discrepancy in comparability of theoretical results with experimental data. To obtain better comparability with experimental results we have taken account of the room temperature (300K) in pressure induced theoretical calculations.

The Gibbs free energies for ZB (B3) and rock salt (B1) structures at room temperature  $T = 300K$  are given by:

$$G_{B3}(r) = U_{B3}(r) + PV_{B3} - TS_1 \quad (1)$$

$$G_{B1}(r) = U_{B1}(r) + PV_{B1} - TS_2 \quad (2)$$

With  $V_{B3} (= 3.08r^3)$  and  $V_{B1} (= 2.00r^3)$  and as the unit cell volume  $S_1$  and  $S_2$  are the entropies for B3 and B1 phases, respectively. In fact, the condition for a transition is that the difference in free energy between two phases approaches to zero.

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

The first term in energies of eq. (1) and (2) are lattice energies for B3 and B1 structures. As an isolated phase is stable only if its free energy is at minimum, we have adopted the method of minimization of free energies for both the phases. The pressure at which  $\Delta G \rightarrow 0$  is called the transition pressure, shows a sudden collapse in volume.

The first term in eq (1) and eq (2) are lattice energies for  $B_3$  and  $B_1$  structures and they are expressed as,

$$U_{B_3}(r) = -\frac{\alpha_m e^2 Z^2}{r} - \frac{4\alpha_m e^2 Z f(r)}{r} + 4b\beta_{ij} \exp\left[\frac{r_i + r_j - r_{ij}}{\rho}\right] + 6b\beta_{ii} \exp\left[\frac{2r_i - 1.63r_{ij}}{\rho}\right] - 6b\beta_{jj} \exp\left[\frac{2r_j - 1.63r_{ij}}{\rho}\right] \quad (4)$$

$$U_{B_1}(r) = -\frac{\alpha'_m e^2 Z^2}{r'} - \frac{6\alpha'_m e^2 Z f(r')}{r'} + 6b\beta_{ij} \exp\left[\frac{r_i + r_j - r'_{ij}}{\rho}\right] + 6b\beta_{ii} \exp\left[\frac{2r_i - 1.414r'_{ij}}{\rho}\right] + 6b\beta_{jj} \exp\left[\frac{2r_j - 1.414r'_{ij}}{\rho}\right] \quad (5)$$

Here  $\beta_{ij}$  is the Pauling coefficient,  $r_i$  ( $r_j$ ) is the ionic radii of  $i$ ( $j$ ) ions,  $\rho$  ( $b$ ) are the range (hardness) parameters.

### 3. Table

**Table 1.** Input parameters and Model parameters of GaAs and GaSb.

Input parameters		Model parameters		
r	B(GPa)	$b(\times 10^{-12} \text{ergs})$	$\rho(\text{\AA})$	$f(r)$
2.45 <sup>a</sup>	72.4 <sup>b</sup>	3.8012	0.748	0.007256
2.65 <sup>a</sup>	55.4 <sup>b</sup>	1.740	0.837	-0.0878

<sup>a</sup>Ref.[12], <sup>b</sup>Ref.[13]

**Table 2.** Calculated transition pressure and volume collapse of GaAs and GaSb.

Compounds	Transition Pressure (GPa)	Volume Collapse (%)
GaAs	11.8	17.34
	12 $\pm$ 1.5 <sup>a</sup> (exp.)	17.4 <sup>b</sup> (exp.)
	11.4 <sup>c</sup> (without temp.)	17.3 <sup>c</sup> (without temp.)
GaSb	7.6	18.59
	6-8 <sup>b</sup> (exp.)	18.6 <sup>b</sup> (exp.)
	8 <sup>c</sup> (without temp.)	18.5 <sup>c</sup> (without temp.)

<sup>a</sup>Ref. [14], <sup>b</sup>Ref. [15], <sup>c</sup>Ref. [13]

### 5. Figure

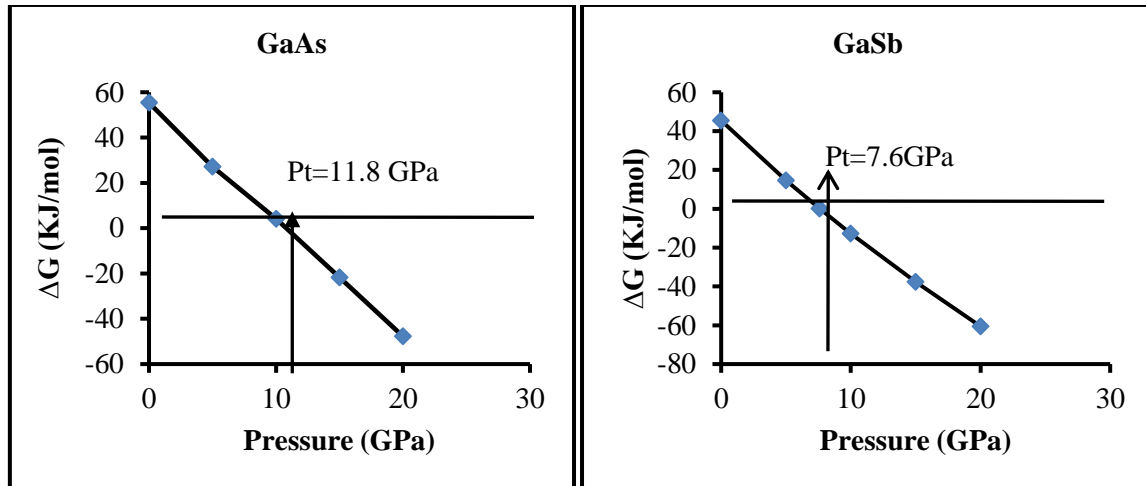


Figure 1. Variation of Gibb's free energy with pressure for GaAs and GaSb.

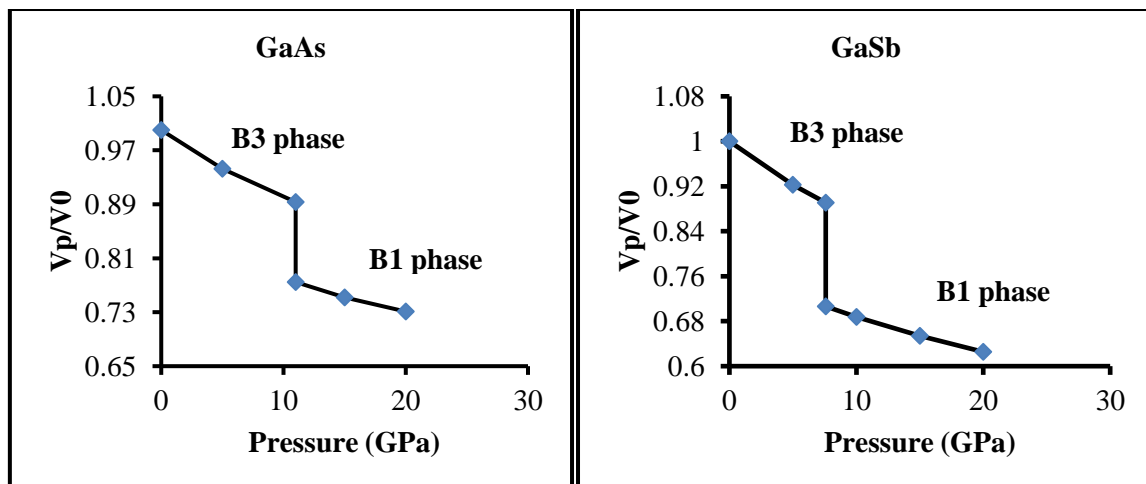


Figure 2. Variation of volume change  $V_p/V_0$  with pressure for GaAs and GaSb.

### 4. Results and Discussion

The stable phase is associated with minima of energy. The structural phase-transition pressures were calculated by minimizing the lattice energies given in Eqs. (4) and (5) at different pressures in order to obtain the inter-ionic separations  $r$  and  $r'$  corresponding to  $B_3$  and  $B_1$  phases. Now we have evaluated the corresponding Gibbs free energies  $GB_3(r)$  and  $GB_1(r')$  and their respective differences  $\Delta G = (GB_3(r) - GB_1(r'))$ . As the pressure increases this value of  $\Delta G$  decreases and approaches zero at the transition pressure ( $P_t$ ). Beyond this pressure,  $\Delta G$  becomes negative as the phase  $B_1$  becomes stable. This difference has been plotted against pressure ( $P$ ) as shown in Figure 1 and is indicated by arrows for GaAs and GaSb. It is clear from Figure 1 and Table 1 that phase transition  $B_3 \rightarrow B_1$  occurs at about 11.8 GPa for GaAs and 7.6 GPa for GaSb, which is close to experimental results. Besides, the values of relative volume change ( $V(P, T)/V(0, T)$ ) associated with various compressions have been obtained and plotted against pressure in Figure 2 the values corresponding to phase transition are well listed in Table 2. It is clear from Table 2 and Figure 2

that our calculated volume collapses from realistic interaction potential model are 17.34% for GaAs and 18.59% for GaSb, which are close to experimental values and reported by other works (without temperature).

## 5. Conclusion

Finally, from the present theoretical investigation we have noticed that the crystallographic pressure-induced phase transition from B3 to B1 structure analysis should be done at room temperature rather than at  $T = 0\text{K}$ . In order to meet the above defined condition, we obtained good comparative results regarding the phase transition pressure and the volume discontinuity in pressure–volume phase diagram with the experimental data using our realistic model.

## References

- [1] Adachi S 2004 *Handbook on Physical Properties of Semiconductors* (Boston : Kluwer Academic Publishers)
- [2] Ferhat M and Zaoui A 2006 *Appl. Phys. Lett.* **88** 161902
- [3] Liu C, Li Y and Zeng Y 2010 *Engineering* **2** 617–624
- [4] Schilling J S and Shelton R N 1981 *Physics of Solids under Pressure* (New York:North-Holland)
- [5] Weir S T, Vohra Y K, Vandenborgh C A and Ruoff A L 1989 *Phys. Rev. B* **39** 1280
- [6] Mujica A, Rubio A, Munoz A and Nedds R J 2003 *Rev. Mod. Phys.* **75** 863
- [7] Garcia A and Cohen M L 1993 *Phys. Rev. B* **47** 6751
- [8] Rino J P, Chatterjee A, Ebbsjo I, Kalia R K, Nakano A, Shimojo F and Vashishta P 2002 *Phys. Rev. B* **65** 195206
- [9] Crain J, Piltz P O, Ackland G J, Clark S J, Payne M C, Milman V, Lin J S, Hatton P D and Nam Y H 1994 *Phys. Rev. B* **50** 8389
- [10] Mujica A, Needs R J and Munoz A 1995 *Phys. Rev. B* **52** 8881
- [11] Singh R K 1982 *Phys. Rep. (Neth.)* **85** 259
- [12] Verma A S, Singh R K and Rathi S K 2009 *J. Alloys Comp.* **489** 795
- [13] Sarwan M and Singh S 2012 *Computational Materials Science* **58** 167–174
- [14] Cai J, Chen N and Wang H 2007 *J. Phys. Chem. Solids* **68** 445
- [15] Zhang S B and Cohen M L 1987 *Phys. Rev. B* **35** 14