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Theoretical Analysis of the Structural Phase Transformation from B3 to B1 in AlBi Under High Pressure

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Abstract: ***We report a phenomenological model- based calculation of pressure-induced structural phase transition of AlBi compound. Gibb's free energy is obtained as a function of pressure by applying an effective interionic interaction potential, which includes the long range Coulomb, van der Waals (vdW) interaction and the short-range repulsive interaction upto second-neighbor ions within the Hafemeister and Flygare approach. From the present study, we predict a structural phase transition from ZnS structure (B3) to NaCl structure (B1).***

Keywords: Structural phase transition, Gibbs free energy, Interionic interaction potential

1. Introduction

Aluminum bismuthide (AlBi) is a III-V semiconductor that has attracted significant interest due to its unique structural, electronic, and optical properties [1]. The incorporation of heavy bismuth atoms induces strong spin-orbit interaction and significantly alters the electronic band structure, making AlBi a promising material for applications in optoelectronic devices, infrared devices and spintronics [2,3]. Given the scarcity of available experimental data, first-principles calculations based on Density Functional Theory (DFT) have been widely used to investigate its structural stability, electronic structure, elastic properties, and optical behavior [1,4]. Consequently, the study of its physical properties is crucial for evaluating the potential of AlBi in next-generation semiconductor devices.

Among the lattice models, which have been invoked so far, to discuss the mechanical properties of several solids and alloys, charge transfer approach [5], following Hafemeister and Flygare [6] type overlap repulsion extended up to second neighbor ions besides short-range interactions. We refer to the pioneering work of Tosi [7], who properly incorporated van der Waals interaction along with dipole-dipole (*d-d*) and dipole-quadrupole (*d-q*) interactions to reveal the cohesion in several ionic solids. In trying to understand the structural aspects, we admit that the vdW attractions are the corner stone of lattice phenomenological models that is ignored in the first principle microscopic calculations. Motivated from the remarks on first principle studies [9&10] and the charge transfer effect approach [5] for the successful description of the phase transition and high pressure behavior of binary compounds, we have chosen two-body interaction potential because it includes vdW attractions, which are not well described by the standard methods currently used in first principle microscopic calculations. It is worth noting that vdW interaction appears to be effective in revealing the elastic and structural properties of binary compounds. Therefore, it is necessary to study fundamental properties, such as, lattice constants, structural stability and elastic properties of AlBi compound.

2. Theory and Method of Computation

The understanding of thermo dynamical properties for AlBi compound requires the formulation of an effective inter ionic potential. To begin with, we made the following assumptions: the change in force constants is small, the short range interactions are effective up to the second-neighbour ions, and the atoms are held together with harmonic elastic forces without any internal strains within the crystal. The effective inter ionic potential between pair of ions (i and jth) is expressed as

$$U(r) = \sum_{ij} \frac{Z_m e^2}{r_{ij}} + \sum_{ij} b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) + \sum_{ij} c_{ij} r_{ij}^{-6} + \sum_{ij} d_{ij} r_{ij}^{-8}. \quad (1)$$

Where, long-range Coulomb is represented by first term, second term correspond to Hafemeister and Flygare form of short-range repulsive energies [11] and vander Waals multipole are represented by third and fourth terms, respectively. The Pauling coefficients β_{ij} are 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 valencey and number of outermost electrons in the anions (cations), respectively. The symbols: c_{ij} and d_{ij} are representing the dipole-dipole (*d-d*) and dipole-quadrupole (*d-q*) vander Waals coefficients. $Z_m e$ is the modified ionic charge and parametrically includes the effect of Coulomb screening effects. b (hardness) and ρ (range) are short-range parameters. Thus, the effective interionic potential contains only three free parameters (Z_m, b and ρ) which can be determined from the crystal properties [11].

An isolated phase is stable only when its free energy is minimum for the specified thermodynamic conditions. As the temperature or pressure or any other variable acting on the systems is altered, the free energy changes smoothly and continuously. A phase transition is said to occur when the changes in structural details of the phase are caused by such variations of free energy. The test materials transform from their initial *B*3 to *B*1 structure under pressure. The structural stability of a particular structure is decided by the minima of Gibbs free energy:

$$G=U+PV-TS$$

U is the internal energy, which at 0K corresponds to the cohesive energy; S is the vibrational entropy at absolute temperature T, pressure P and volume V.

We have estimated the Gibbs free energy for both the *B*3 and *B*1 phases. The Gibbs free energies $GB3(r) = UB3(r) + 3.08Pr3$ for the zinc blende (*B*3) [real] phase and $GB1(r') = UB1(r') + 2Pr'^3$ for the NaCl (*B*1) [hypothetical] phase become equal at the phase-transition pressure *P* and at zero temperature *i. e.*, ΔG (= $G_{B3} - G_{B1}$). Here, U_{B3} and U_{B1} represent cohesive energies for *B*3 and *B*1 phases, and are

$$UB3(r) = -1.6381\frac{e^2 Z_m^2}{r} + 4V_{ij}(r) + 6V_{ii}(r) + 6V_{jj}(r), \quad (2)$$

and

$$U_{B1}(r') = -1.7475\frac{e^2 Z_m^2}{r'} + 6V_{ij}(r') + 6V_{ii}(r') + 6V_{jj}(r'). \quad (3)$$

Here r and r' are nearest-neighbor (*nn*) separations corresponding to ZnS and NaCl phases, respectively. The short-range potentials (V_{ij}) (in equations 2 and 3) for both the phases between the ions follow

$$V_{ij}(r) = b\beta_{ij}\exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) - c_{ij}r_{ij}^{-6} - d_{ij}r_{ij}^{-8}; \quad i, j = 1,2. \quad (4)$$

Where b and ρ being the short-range parameters. The effective interionic interaction potential can then have three material parameters: modified ionic charge (Z_m), range (b) and hardness parameters (ρ), which can be determined from the known crystal properties.

Table 1: The values of van der Waals coefficients c_{ij} (i, j = 1,2) [in units of 10^{-60} erg cm^6], d_{ij} (i, j = 1,2) [in units of 10^{-76} erg cm^8] and overall van der Waals coefficients (C, D) for AlBi compound

	vdW coefficients							
	c_{11}	c_{12}	c_{22}	C	d_{11}	d_{12}	d_{22}	D
AlSb	446.14	*507.6*	*671.92*	*2637*	*1393*	*1247*	*954*	*5383*

Table 2: Crystal data and model parameters for AlBi

	Material Parameters				Model Parameters		
	r_i (Å)	r_j (Å)	a (Å)	B_T (GPa)	Z_m^2	ρ (10^{-1} Å)	b(10^{12} erg)
AlBi	1.43	1.7	6.37 [8]	43.1915 [9]	5.29	4.63	2.074

Table 3: Calculated (reported) transition pressure and volume collapse in AlBi compound

Compound	Transition pressure P_t (GPa)	Volume collapses (%)
AlBi	2.6 (2.42[a], 2.01[b])	13.10%

[a]Ref. [9], [b]Ref. [10]

3. Results and Discussion

The effective interionic potential described in section (2) for the zinc blende (B3) and rock salt (B1) phases. We have undertaken such structural and elastic properties in an ordered way. For such purposes we have then three free parameters, namely, modified ionic charge, range and hardness parameters (Z_m, ρ and b). To estimate the free parameters, we first deduce the vdW coefficients from the Slater-Kirkwood variational method [12] and are listed in table 1. We consider that the AlBi compound to be partially ionic.

It is perhaps worth to remark that we have deduced the values free papameters modified ionic charge (Z_m), range (ρ) and hardness (b) from the knowledge of equilibrium distance and the bulk modulus following the equlibrium conditions [11]. The input data along with their relevant references and the model parameters for AlSb compounds are given in table 2.

In an attempt to reveal the structural phase transition of the test materials, we minimise the Gibbs's free energies $G_{B1}(r)$ and $G_{B3}(r')$ for the equilibrium interatomic spacing (r) and (r'). The Gibbs's free energy difference ΔG [= $G_{B3}(r)$ - $G_{B1}(r')$] have been plotted as functions of pressure (P) in Fig. 1 by using the inter ionic potential discussed above. Let us summarize the results of the plots. The pressure corresponding to ΔG approaching to zero is the phase transition pressure (P_t) [indicated by arrows in figure]. At zero pressure, the *B*3 crystal phase is thermodynamically and mechanically stable, while the *B*1 is not. As pressure increases, beyond the phase transition pressure (P_t), the *B*1 system becomes mechanically and thermodynamically stable (its ΔG function value is negative than that of *B*3 crystal). Eventually, and at a pressure higher than the theoretical thermodynamic transition pressure, the *B*3 crystal becomes thermodynamically unstable while the *B*1 phase remains stable up to the greatest pressure

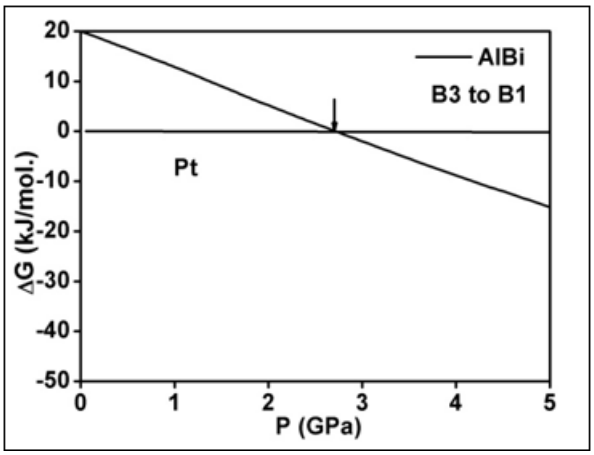

Figure 1: Variation of Gibbs free energy difference (ΔG) with pressure (P) for AlBi compound.

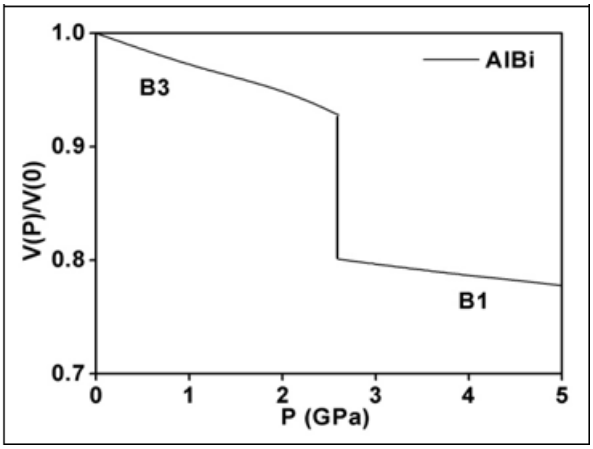

Figure 2: V(P)/V(0) as a function of pressure (P) for AlBi compound

studied (≈ 2.6 GPa). In AlBi compound a crystallographic transition from *B*3 to *B*1 occurs. These results may be successfully compared with those available reported data [9&10] and are tabulated in Table 3.

Let us now estimate the values of relative volumes associated with various compressions following Murnaghan equation of state [13]

$$\frac{V}{V_0} = \left(1 + \frac{B'}{B_0} P\right)^{-1/B'}, \qquad (15)$$

Where V_0 being the cell volume at ambient conditions. The estimated value of pressure dependent radius for both structures, the curve of volume collapse with pressure to depict the phase diagram is represented in Fig. 2. It is noticed from the plot that our approach has predicted correctly the relative stability of competitive crystal structures, as the values of ΔG are positive. The magnitude of the discontinuity in volume at the transition pressure is obtained from the phase diagram and its value is tabulated in Table 3.

4. Conclusion

An effective interionic interaction potential is formulated in analyzing the structural as well as elastic properties in AlBi compound. The obtained values of free parameters allow us to predict phase transition pressure and associated volume collapse. The main result of the paper is the vast volume discontinuity in pressure volume phase diagram identifies the structural phase transition from ZnS to NaCl structure. From our calculated results it can be emphasized that the present approach reproduced the structural properties at high pressure consistently, in terms of the screening of the effective Coulomb potential through modified ionic charge (Z^2m).

References

[1] A. M. Iqbal *et al*., Computational Materials Science, 110 (2016) 257–263.
[2] I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, Journal of Applied Physics, 89 (2001) 5815- 5875.
[3] K. Alberi *et al*., Physical Review B, 75, (2007) 045203.
[4] J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters, 77 (1996) 3865–3868.
[5] R. K. Singh, Phys. Rep. 85 (1982) 259.
[6] D. W. Hafemeister and W. H. Flygare, J. Chem. Phys. 43 (1965) 795.
[7] M. P. Tosi, Solid State Phys. 16 (1964) 1.
[8] B.G. Yalcin, S. Bagci, M. Ustundag, M. Aslan, Comput.Mater. Sci. **98**, 136 (2015).
[9] W. Gouasmi, D. Boudjaadar, F. Oumelaz, *et al.*, Eur. Phys. J. B 98, (2025)85.
[10] Wissem Gouasmia *et al.,*International Journal of Modern Physics B,40 (2026) 7.
[11] Netram Kaurav, *Phys. Scr.* 88 (2013) 015604.
[12] J. C. Slater and J. G. Kirkwood,
[13] F. D. Murnaghan, Proc. Natl. Acad. Sci. U. S. A. 3 (1994) 244.