FIRST PRINCIPLES STUDY OF AlBi

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Abstract

Using the first principles method of the full potential linear augmented plane waves (FPLAPW), the structural and the electronic properties of AlBi are investigated. It is found that this compound has a small and direct semiconducting gap at Γ. Through the quasi-harmonic Debye model, in which the phononic effects are considered, the dependences of the volume, the bulk modulus, the variation of the thermal expansion α, as well as the Debye temperature θ_D and the heat capacity C_v are successfully obtained in the whole range from 0 to 30 GPa and temperature range from 0 to 1200 K.
1 Introduction

Compared to other III-V materials, less is known about bismuth GaBi, AlBi and InBi binaries. Using first principles FPLAPW methods, Ferhat et al [1] have found that the zinc-blende structure is the most stable for AlBi and GaBi while InBi prefers the tetragonal PbO structure. In the zinc blende (B3) phase, first principle calculations show that GaBi and InBi are conductors, while AlBi is found to be a semiconductor with a small and direct band gap of 0.042 eV at Γ with a linear relation between the bulk modulus and the cell volume for the zinc blende phase [2].

The purpose of this work is to provide some additional information to the existing data on the physical properties of AlBi with state-of-the-art first-principles calculations. Additionally to the structural and electronic properties, the thermodynamic properties have also been investigated. The latter are the basis of solid-state science and industrial applications and their study is of importance to extend our knowledge on their specific behaviour when undergoing severe constraints of high-pressure and high temperature environments. This is particularly true since the coming of modern technologies (geophysics, astrophysics, particle accelerators, fission and fusion reactors, etc.) from which we always expect new advances and innovations in materials science to reach higher performances.

The paper is organized as follows. The utilized method is outlined in section 2, the results are presented in section 3 then a summary is given in section 4.

2 Theoretical framework

We have employed the first principles full potential linear augmented plane wave (FP-LAPW) method [3] as implemented in the WIEN2k code [4]. The exchange and correlation effects are described in the framework of the density functional theory [5, 6] with the parameterization of Perdew et al [7]. The unit cell is divided into non overlapping muffin-tin spheres of radius RMTS and an interstitial region, the Kohn-Sham wave functions being expressed in spherical harmonics within spheres and in plane waves in the interstitial regions. To ensure the correctness of our calculations, we have taken \( l_{\text{max}}=10 \), \( R_{\text{MT}} \) \( K_{\text{MAX}}=8 \), RMTS=2.3 a.u for Al and 2.7 a.u for Bi. The number of the irreductible Brillouin zone special K–points and the total number of plane waves involved in the calculations were 47 and 1088 respectively.

To investigate the thermodynamic properties, we used the quasi-harmonic Debye model [8] in which the non-equilibrium Gibbs function \( G^*(V; P, T) \) is written in the following form:

\[
G^*(V; P, T) = E(V) + PV + A_{\text{vib}}[g(V); T] 
\]  \hspace{1cm} (1)

2
where $E(V)$ is the total energy per unit cell, $PV$ corresponds to the constant hydrostatic pressure condition, $\theta(V)$ is the Debye temperature and $A_{vib}$ is the vibrational term which can be written using the Debye model of the phonon density of states as [9, 10]:

$$A_{vib}(\theta; T) = nkT \left[ \frac{9\theta}{8T} + 3ln(1 - e^{\theta/T}) - D(\frac{\theta}{T}) \right]$$  \hspace{1cm} (2)

where $n$ is the number of atoms per formula unit, $D(\theta/T)$ represents the Debye integral and for an isotropic solid, $\theta$ is expressed as [9]:

$$\theta_n = \frac{\hbar}{k}[6\pi^2 V^{1/3} n]^{1/3} \sqrt{\frac{B}{M}}$$  \hspace{1cm} (3)

$M$ being the molecular mass per unit cell, $B_S$ is the adiabatic bulk modulus, which is approximated given by the static compressibility [8]:

$$B_s = B(V) = V \frac{d^2 E(V)}{dV^2}$$  \hspace{1cm} (4)

Details on $f(\sigma)$ can be found elsewhere [11, 12]. Therefore, the non-equilibrium Gibbs function $G^*(V; P, T)$ as a function of $V, P$ and $T$ can be minimized with respect to volume $V$:

$$\left[ \frac{\partial G^*(V; P, T)}{\partial V} \right]_P = 0$$  \hspace{1cm} (5)

By solving Eq.(5), one can obtain the thermal equation-of-state (EOS) $V(P, T)$. The heat capacity $C_V$ and the thermal expansion coefficient $\alpha$ are given by [13]:

$$C_V = 3nk \left[ 4D(\frac{\theta}{T}) - \frac{3\theta/T}{e^{\theta/T} - 1} \right]$$  \hspace{1cm} (6)

$$\alpha = \frac{\gamma C_V}{B_s V}$$  \hspace{1cm} (7)

where $\gamma$ is the Grüneisen parameter which is defined as

$$\gamma = -\frac{d \ln \theta(V)}{d \ln V}$$  \hspace{1cm} (8)
Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities of any temperatures and pressures of AlBi from the calculated $E-V$ data at $T = 0$ and $P = 0$.

3 Results and discussion

First, we have calculated the total energy of zinc blende AlBi as a function of the volume, then the equilibrium volume, the equilibrium lattice constant, the bulk modulus $B$ and its derivative were obtained by fitting to the Murnaghan equation of state [14]. The results are presented in Table 1. The calculated lattice parameters and bulk modulus are in general in good agreement with literature. The cohesive energy is calculated using the following formula: $E_{\text{coh}} = E_{\text{tot}} - E_{\text{Al}} - E_{\text{Bi}}$, where $E_{\text{tot}}$ is the total energy of AlBi. The elastic constants are also listed and enable us to infer the Young modulus $Y = 33.53$ GPa, the Poisson ratio $\sigma = 0.3556$ and the shear modulus $C = 12.124$. It is clear that AlBi is elastically stable in the zinc blende (B3) phase since $C_{12} < B < C_{11}$ and all the following quantities are positive: $C_{11} - C_{12}$, $2C_{12} + C_{11}$ and $C_{44}$. Unfortunately, there are no experimental data to check our results.

Fig. 1 shows the band structure of AlBi for the equilibrium volume. We remark an almost zero $\Gamma - \Gamma$ direct fundamental gap. Its magnitude is found to be about $\sim 0.02$ eV which is underestimated by LDA so that AlBi is probably a semiconductor. Density of states calculation (Fig. 2) shows that the top of the valence band (VB) is highly due to $p$-orbital since the major contributions come from the $6p$-Bi orbital followed by the $3p$-Al. On the other hand, the conduction band (CB) is due to both $s$- and $p$- orbitals of the two atomic species.

The thermal properties are determined in the temperature range from 0 to 1200 K, where the quasi-harmonic model remains fully valid. The pressure effect is studied in the 0-30 GPa range. The relationship between the volume and temperature at different pressures are shown in Fig. 3. The volume increases with increasing temperature but the rate of increase is very moderate. The relationship between the bulk modulus $B$ and temperature at different pressures are shown in Fig. 4. These results indicate that $B$ decreases with $T$ at a given pressure and increases with $P$ at a given temperature. It shows the fact that the effect of increasing pressure on AlBi is the same as decreasing its temperature.

From Fig. 5, we remark that the effect of the temperature on the Debye temperature $\theta_D$ is not as important as the pressure on $\theta_D$. The heat capacity has also been plotted at pressures of 0, 10, 20, and 30 GPa (Fig. 6). It is found that when $T < 400$ K, the heat capacity $C_V$ is dependent on both temperature and pressure. This is due to the anharmonic approximations. However, at higher temperatures and higher pressures, the anharmonic effect on heat capacity is suppressed, and $C_V$ is close to the Dulong-Petit limit $3k_B$ ($\sim 49.90$ J.mol$^{-1}$K$^{-1}$), which is
common to all solids at high temperatures. The variation of the thermal expansion $\alpha$ with temperature and pressure are shown in Fig. 7. We note that the temperature dependence of $\alpha$ is slightly greater at higher temperatures and higher pressures.
4 Conclusion

In summary, we have applied the FPLAPW method and the quasi-harmonic Debye model to investigate the structural, elastic, electronic and thermal properties of AlBi. In particular, we confirm the semiconducting nature of AlBi with a small and direct bandgap which makes it a good candidate for opto electronic applications. Various useful data have been calculated and may be checked in further works.

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References

Table 1. Lattice constant \(a\), bulk modulus \(B\), pressure derivative of bulk modulus \(B'\) and elastic constants parameters of \(\text{AlBi}\) at zero pressure and zero temperature, compared with the experimental data and other theoretical works.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Present work</th>
<th>Other theoretical works</th>
</tr>
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<tbody>
<tr>
<td>(E_{\text{coh}}) (eV)</td>
<td>4.004</td>
<td>6.31 (^a) 6.266 (^b)</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>6.448</td>
<td>6.31 (^a) 6.266 (^b)</td>
</tr>
<tr>
<td>(B) (GPa)</td>
<td>38.750</td>
<td>45.58 (^a) 48.2 (^b)</td>
</tr>
<tr>
<td>(B')</td>
<td>4.576</td>
<td>4.23 (^a) 5.237 (^b)</td>
</tr>
<tr>
<td>(C_{11}) (GPa)</td>
<td>48.498</td>
<td>[^a]-Ref. [1] [^b]-Ref. [2]</td>
</tr>
<tr>
<td>(C_{12}) (GPa)</td>
<td>29.001</td>
<td>[^a]-Ref. [1] [^b]-Ref. [2]</td>
</tr>
<tr>
<td>(C_{44}) (GPa)</td>
<td>14.5</td>
<td>[^a]-Ref. [1] [^b]-Ref. [2]</td>
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Fig. 1. Band structure calculated along high-symmetry directions of AlBi. The energy zero is taken at \(E_F\).
Fig. 2. Calculated partial density of states and total density of states of AlBi.

Fig. 3. Calculated $P$-$V$-$T$ relationship of the compound AlBi, (a) variation with temperature and (b) variation with pressure.
Fig. 4. The relationships between bulk modulus $B$ and temperature at pressures of 0, 10, 20, and 30 GPa, respectively.

Fig. 5. Variation of the Debye temperature $\theta$ with the temperature at different pressures of 0, 10, 20, and 30 GPa, respectively.
Fig. 6. The heat capacity versus temperature at pressures of 0, 10, 20, and 30 GPa, respectively.

Fig. 7. The thermal expansion versus temperature at pressures of 0, 10, 20, and 30 GPa, respectively.