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Band Structure, Metallization and Superconducting Transition of Group III-V Semiconductors AlP and AlAs under High Pressure

V. Benaline Sheeba¹, C. Nirmala Louis²*

¹Udaya School of Engineering, Vellamodi, Kanyakumari District, Tamil Nadu, India
²Research Center in Physics, Holy Cross College, Nagercoil, Tamil Nadu, India
*Corresponding Author: nirmala_louis@yahoo.co.in

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Abstract The results of a full potential linear muffin-tin orbital (FP-LMTO) study on the electronic properties of cubic zinc blende type group III-V semiconductors AlP and AlAs under pressure are presented. The equilibrium lattice constant, bulk modulus, pressure derivative of bulk modulus and the phase transition pressure at which the compounds undergo structural phase transition from ZnS to NaCl and NaCl to CsCl are predicted from the total energy calculations. The ground state properties and band gap values are compared with the experimental results. At normal pressure AlP and AlAs are indirect bandgap semiconductors. When the pressure is increased there is enhanced overlapping between the wave functions of the neighbouring atoms. As a result the widths of the valence and empty conduction bands increase. These changes lead to the narrowing and indirect closing of band gaps in AlP and AlAs (metallization). On further increase of pressure, AlP and AlAs become superconductors, and these materials come under the class of electron-phonon-mediated high pressure superconductors. The superconducting transition temperatures (Tc) of AlP and AlAs were experimentally measured by Hellwege et al[12]. There is no high pressure studies related to metallization and superconductivity in both AlP and AlAs. This motivated us to take up the present investigation of these compounds under high pressure. In this work self consistent full potential linear muffin tin orbital method (FP-LMTO) is employed to study...
the effect of pressure on the band structure of these compounds.[13] We have analyzed the phenomena of metallization and superconductivity for high pressure (CsCl) structure of these materials. It is hoped that this analysis will enable us to make some general statement regarding the path to high \( T_c \) superconductivity in covalent compounds. In Section 2, we give the details of the calculational procedure, electronic band structure and density of states corresponding to various pressures. The ground-state properties, structural phase transition, metallization and superconducting transition temperature \( T_c \) and its variation under pressure are discussed in Section 3. Concluding remarks are given in Section 4.

2. Band Structure and Density of States

2.1. Calculational Procedure

The electronic band structure calculations were performed for AlP and AlAs corresponding to different reduced volumes in ZnS, NaCl and CsCl structures, by the first-principle FP-LMTO method with in generalized gradient approximation (GGA) [14]. We have used the exchange-correlation potential of Ceperley and Alder as parametrized by Perdew and Zunger [15]. Similar to our earlier studies on ZnSe and CdSe the details of the FP-LMTO method are well described in the literature[13] and we give here only the calculational details. The electronic configurations of \( Al \) and \( P \) are [Ne] 3s\(^2\) 3p\(^1\) 3d\(^{10}\) (\( Z = 13 \)) and [Ne] 3s\(^2\) 3p\(^3\) (\( Z = 15 \)) respectively, and for \( As \) it is [Ar] 4s\(^2\) 4p\(^3\) (\( Z = 33 \)). The valence electronic configurations chosen in our calculations are 3s\(^2\) 3p\(^1\) for \( Al \), 3s\(^2\) 3p\(^3\) for \( P \) and 4s\(^2\) 4p\(^3\) for \( As \). There are 8 valence electrons contributing to the valence bands[13]. The final energy convergence is within 10\(^{-5}\) Ry. The calculated total energies were fitted to Murnaghan’s equation of state (EOS)[16], to determine the phase-transition pressure and other ground-state properties.

2.2. Band Structure of AlP and AlAs under Pressure

The band structures of AlP and AlAs were computed for various reduced volumes ranging from \( V/V_o=1.0 \) to 0.3 in steps of 0.05. Even though we have obtained the band structure for \( V/V_o \) values from 1.0 to 0.3, we have presented here the band structures of AlP and AlAs along the symmetry directions \( \Gamma-X-W-L-\Gamma-K \) and the corresponding density of states of AlP and AlAs (Figs.1 to 8). The volume compressions corresponding to \( V/V_o=1.0 \) and \( V/V_o=0.52 \) for AlP, and \( V/V_o=1.0 \) and \( V/V_o=0.5 \) for AlAs only. The overall topology of the band structure of AlP and AlAs at \( V/V_o=1.0 \) (Figs.1 and 3) is same as that of previous calculations[9]. A single band nearer to origin arises from 3s\(^2\) electrons of \( P \) (Fig.1) and 4s\(^2\) electrons of As (Fig.3). The three bands appearing below the Fermi level are due to the 3s\(^2\), 3p\(^1\) electrons of \( Al \) and 3p\(^3\) electrons of \( P \) (Fig.1). Similarly in Fig.3, the three bands positioned below the Fermi level are due to 3s\(^2\), 3p\(^1\) electrons of \( Al \) and 4p\(^3\) electrons of \( As \). The empty conduction bands above the Fermi level are due to 3p, 3d states of \( Al \) and 3d, 3p states of \( P \) (Fig.1) and 4d, 4p states of \( As \) (Fig.3).
At normal pressure, the band gap of AlP is indirect with valence band maximum at $\Gamma$ point and conduction band minimum at $X$ point with band gap value 2.1 eV. In the case of AlAs, band gap is indirect with a value of 2.2 eV with valence band maximum at $\Gamma$ point and conduction band minimum at $X$ point. The calculated energy gaps are in agreement with the experimental values[12] for both AlP and AlAs (Table 1). As pressure increases the width of the valence band and the empty conduction band get widened. These changes leads to the narrowing of the band gap under pressure (Figs. 5 and 7).

Table 1. Equilibrium lattice constant ($a_0$), bulk modulus ($B_0$) and its pressure derivative ($B_0'$) of AlP and AlAs in ZnS structure

| Ground State Properties | AlP |          |          | AlAs |          |          |
|-------------------------|-----|----------|----------|------|----------|----------|
|                         | Present work | Experimental works[4,12] | Previous theoretical works[9,10] | Present work | Experimental works[4,12] | Previous theoretical works[9,10] |
| $a_0$ a.u.              | 10.327 | 10.432 | 10.034 | 10.7 | 10.825 | 10.547 |
| $B_0$ bar               | 0.86 | 0.89 | 0.74 | 0.82 | 0.84 | 0.76 |
| $B_0'$                  | 4.037 | 4.143 | 3.954 | 4.182 | 4.423 | 4.142 |
| $E_g$ eV                | 2.1 | 2.4 | 1.92 | 1.95 | 2.2 | 1.84 |

Figure 4. Density of states of AlAs at $V/V_0=1$ in zinc blende structure (normal pressure)

Figure 5. Band structure of AlP at $V/V_0=0.52$ in CsCl structure (pressure = 2.275 Mbar)
Figure 6. Density of states of AlP at V/V₀ = 0.52 in CsCl structure (Pressure = 2.275 Mbar)

Figure 7. Band structure of AlAs at V/V₀ = 0.5 in CsCl structure (Pressure = 2.44 Mbar)

Figure 8. Density of states AlAs at V/V₀ = 0.5 in CsCl structure (Pressure = 2.44 Mbar)
2.3. Density of States under Pressure

The density of states (DOS) (states/Ry.) calculations for all the reduced volumes have been carried out. The density of states (DOS) histogram of AlP corresponding to normal pressure is shown in Fig. 2. At normal pressure the levels arising from 3s^2 electrons of Al give the long spike near the origin. The short spikes near the Fermi energy are due to 3p^3, 3p^2 electrons of P and 3p^1 electron of Al. The short peaks above the Fermi energy E_F are due to the 3p, 3d states of Al and 3d, 3p states of P. The density of states (DOS) histogram of AlAs corresponding to normal pressure is shown in Fig. 4. At normal pressure the levels arising from 3s^2 electrons of Al give the long spike near the origin. The short spikes near the Fermi energy are due to 4s^2, 4p^3 electrons of As and 3p^1 electron of Al. The short peaks above the Fermi energy E_F are due to the 3p, 3d states of Al and 4d, 4p states of As. The general features of the band structure and density of states (Figs 1-8) are similar to that of the alkali halides [17].

This trend is changed under high pressure. The increase of pressure leads to the broadening of bands which results in the decrease of density of states value in most of the energy regions and also increase in the width of the valence band and empty conduction bands. When pressure increases the value of E_F increases whereas no density of states is available at the Fermi level up to metallization pressure. The variation in the total energy as a function of reduced volume for AlP is shown in Fig. 11. From this figure, it is found that, in AlP, up to V/V_o = 0.73, ZnS structure has the lowest energy and on further reduction of volume NaCl structure becomes more stable in energy than the ZnS structure. Also up to V/V_o = 0.62, NaCl structure has the lowest energy and on further reduction of volume CsCl structure becomes more stable in energy than the NaCl structure.

3. Results and Discussion

3.1. Ground State Properties

The ground state properties and structural phase transitions of AlP and AlAs are studied from their total energies obtained from our calculation. The total energy is calculated as a function of reduced volume (V/V_o) for ZnS, NaCl and CsCl phases of AlP and AlAs. Here, V_o is the experimental equilibrium volume corresponding to the experimental equilibrium lattice constant. The calculated total energies were fitted to Murnaghan’s equation of state [16]

\[
P = 1.5B_o \left( (V/V_o)^{7/3} - (V/V_o)^{5/3} \right) \left[ 1 + 0.75 (B_o^{-1} - 4) \left( (V/V_o)^{2/3} - 1 \right) \right]
\]

(1)

to obtain the equilibrium lattice constant and other ground state properties. The relation between reduced volume and lattice constant is shown in Fig. 9. Here lattice constant decreases with decrease of reduced volume. The relation between reduced volume and pressure is shown in Fig. 10. When reduced volume decreases pressure increases. The variation in the total energy as a function of reduced volume for AlP is shown in Fig. 11. From this figure, it is found that, in AlP, up to V/V_o = 0.73, ZnS structure has the lowest energy and on further reduction of volume NaCl structure becomes more stable in energy than the ZnS structure. Also up to V/V_o = 0.62, NaCl structure has the lowest energy and on further reduction of volume CsCl structure becomes more stable in energy than the NaCl structure.

![Figure 9. Relation connecting reduced volume and lattice constant](image-url)
Figure 10. Relation connecting reduced volume and pressure

Figure 11. Relation connecting total energy and reduced volume curve of $\text{AlP}$

Figure 12. Relation connecting total energy and reduced volume curve of $\text{AlAs}$
The variation in the total energy as a function of reduced volume for AlAs is shown in Fig. 12. From this figure, it is found that, in AlAs, up to $V/V_o = 0.76$, ZnS structure has the lowest energy and on further reduction of volume NaCl structure becomes more stable in energy than the ZnS structure. Also up to $V/V_o = 0.625$, NaCl structure has the lowest energy and on further reduction of volume CsCl structure becomes more stable in energy than the NaCl structure. In Table 1, the equilibrium lattice constant ($a_o$), band gap ($E_g$), bulk modulus ($B_o$) and its pressure derivative ($B'_o$) values are compared with experimental and previous theoretical works[1-10]. From Table 1, it is observed that one gets larger lattice constant corresponding to smaller bulk modulus. Our estimated bulk modulus of AlAs is less than that of AlP, as a result compressibility is higher for AlAs than AlP (Fig.10). Thus, it is noted that the compressibility decreases as the size of the anion decreases. This is the general trend in alkali halides[17], which is confirmed now for AlP and AlAs.

3.2. Structural Phase Transition

In our calculation we have chosen the ZnS structure for both AlP and AlAs at ambient pressure. The phase stability of the B3 (ZnS), B1 (NaCl) and B2 (CsCl) structures of AlP and AlAs is analysed using the enthalpy calculation [13]. The enthalpy $H(P)$ is defined by

$$H(P) = E_{tot}(P) + PV(P)$$

and the transition pressure corresponding to the phase transition from B3 to B1 is obtained from the relation

$$H_{B3}(P) = H_{B1}(P)$$

where $H_{B3}$ and $H_{B1}$ are the enthalpies of the B3(ZnS) and B1(NaCl) phases respectively. Similarly $H_{B1}(P) = H_{B2}(P)$ where $H_{B1}$ and $H_{B2}$ are the enthalpies of the B1(NaCl) and B2(CsCl) phases respectively. The phase transition pressure ($P_T$) and the corresponding reduced volume ($V/V_o)_T$ estimated in our calculation are given in Table 2.

For AlP and AlAs, our calculated phase transition pressure is in good agreement with the experimental and previous theoretical results. The mechanism for the phase transition is a geometric effect involving a change in the coordination number from 4 in the ZnS phase to 6 in the NaCl phase and to 8 in the CsCl phase under pressure[17].

3.3. Metallization

At normal pressure AlP and AlAs are wide gap semiconductors. With the increase of the pressure, the band gap decreases and at a particular pressure, there is a closing of the band gap. The band structure and density of states corresponding to metallization of AlP and AlAs are shown in Figs. 5 to 8 respectively. In AlP and AlAs, the metallization occurs through indirect closing of the band gap between valence band maximum at $\Gamma$ point and conduction band minimum at $X$ point. The metallization volume of AlP is $V/V_o=0.52$ (CsCl structure), which corresponds to the pressure $P_M = 2.275$ Mbar. In the case of AlAs the indirect closure of the band gap between $\Gamma$ and $X$ point takes place at the reduced volume $V/V_o=0.50$ (CsCl structure), the corresponding metallization pressure is 2.44 Mbar.

The metallization pressure calculated for AlAs is greater than that of AlP (Table 2). This means, in group III-V compounds, metallization pressure increases with the increasing size of the group - V element. This trend is opposite to the trend observed in alkali halides having NaCl structure at ambient conditions (metallization pressure increases with decreasing size of alkali metal[17]). The reason for this difference is that, prior to metallization, alkali halides undergo structural transition from NaCl to CsCl structure whereas group III-V compounds undergo structural transition from ZnS to NaCl to CsCl structure. At the metallization pressures, the values for density of states at Fermi energy $N(E_F)$ are very small (pseudo gap), which indicate that metallization has just set in AlAs and AlP (Figs.6 and 8). Thereafter $N(E_F)$ increases slowly with pressure and becomes fairly large at a particular value of $V/V_o$. The values of $E_F$ and $N(E_F)$ corresponding to different $V/V_o$ are used in studying the pressure variation of superconducting transition temperature[13]. However, there are no experimental or theoretical study available for comparison at these pressures.

| Aluminum Compound | Metallization | Phase transition ZnS to NaCl and NaCl to CsCl | Onset of superconducting transition |
|-------------------|---------------|-----------------------------------------------|-----------------------------------|
|                   | P (Mbar)      | (V/V_o) M                                     | P (Mbar)                          | (V/V_o) S                        |
| AlP               | 2.275         | 0.52                                          | 0.5116                            | 0.730                            |
|                   |               |                                               | 1.084                            | 0.620                            |
|                   |               |                                               | 3.0                              | 0.532                            |
| AlAs              | 2.44          | 0.50                                          | 0.40                             | 0.760                            |
|                   |               |                                               | 3.0                              | 0.514                            |
3.4. Superconductivity in AlAs and AlP under Pressure

The promotion of \( s \) electron to \( d \) shell in solids is one of the factors which will induce superconductivity. Under very high pressure, aluminum compounds are not only metals but also superconductors. The theory of Gaspari and Gyorffy [18] in conjunction with McMillan’s formula is used to calculate \( T_c \).

The electron -phonon mass enhancement factor, \( \lambda \) is [19]

\[
\lambda = \frac{N(E_F)\langle I^2 \rangle}{M\langle \omega^2 \rangle}
\]

(4)

where \( M \) is the atomic mass, \( \langle \omega^2 \rangle \) is an average of the phonon frequency square and \( \langle I^2 \rangle \) is an average (over the Fermi energy) of the electron – phonon matrix element square [19].

\[
\langle I^2 \rangle = \sum_{l} \frac{(l+1)}{(2l+1)(2l+3)} M_{l} I_{l} \frac{N_I(E_F)N_{l+1}(E_F)}{N(E_F)N(E_F)}
\]

(5)

where \( M_{l} \) is the muffin-tin potential at the sphere boundary.

\( V(S) \) is the muffin-tin potential at the sphere boundary.

\( S \) is the radius of the muffin-tin sphere.

The above quantities are taken from the band structure results. The average of the phonon frequency square is

\[
\langle \omega^2 \rangle = \frac{1}{2} \theta_D^2
\]

(6)

The variation of Debye temperature with pressure \( \theta_D(P) \) is given by [13]

\[
\theta_D(P) = \sqrt{\frac{E_F}{E_F^0}} \frac{a_o \theta_D}{a}
\]

(7)

where \( \theta_D^0, a_o \) and \( E_F^0 \) are normal pressure quantities.

The McMillan’s formula [20] used for \( T_c \) calculation,

\[
T_c = \frac{\theta_D}{1.45} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right]
\]

(8)

gives the good estimate of the \( T_c \) value. Here \( \mu^* \) is the electron-electron interaction parameter which is estimated using the relation [21],

\[
\mu^* = \frac{0.26N(E_F)}{1 + N(E_F)}
\]

(9)

where \( N(E_F) \) is the density of levels per atom per eV at \( E_F \).

With the results obtained from the self-consistent calculation, we have computed \( \theta_D, \lambda, \mu^* \) and \( T_c \) as a function of pressure using Eqs.(4 - 9). The calculated values at high pressure (CsCl) structure is given in Tables 3 and 4 for AlP and AlAs respectively. As pressure increases our computed value of \( T_c \) increases and reaches a maximum value. In our calculation the highest \( T_c \) obtained in AlP is 5.911 K at 4.5 Mbar (Table. 3), whereas in AlAs the highest \( T_c \) obtained is 14.54 K at 4.5 Mbar (Table. 4). The calculated \( T_c \) values depend more sensitively on changes in \( \lambda \) than \( \mu^* \), indicating that these compounds are electron-phonon-mediated superconductors. Similar to alkali halides and group II-VI compounds, group III-V compounds come under the class of pressure induced superconductors [13,17]. When pressure is increased \( T_c \) increases and reaches the maximum value in both the AlP and AlAs. This reflects the fact that the structural and band gap configurations play an important role in the superconducting (high \( T_c\)-max) behaviour of these compounds under high pressure. [13]

### Table 3. Variation of \( T_c \) as a function of pressure for AlP in CsCl structure

| Pressure (Mbar) | \( \lambda \) | \( \theta_D \) (K) | \( \mu^* \) | \( T_c \) (K) |
|----------------|-------------|----------------|-----------|-----------|
| 3              | 0.286       | 528            | 0.101     | 0.122     |
| 3.5            | 0.343       | 671            | 0.112     | 0.546     |
| 4              | 0.431       | 732            | 0.124     | 2.203     |
| 4.5            | 0.527       | 868            | 0.138     | 5.911     |

### Table 4. Variation of \( T_c \) as a function of pressure for AlAs in CsCl structure

| Pressure (Mbar) | \( \lambda \) | \( \theta_D \) (K) | \( \mu^* \) | \( T_c \) (K) |
|----------------|-------------|----------------|-----------|-----------|
| 3              | 0.327       | 573            | 0.113     | 0.289     |
| 3.5            | 0.418       | 698            | 0.124     | 1.725     |
| 4              | 0.522       | 786            | 0.132     | 5.683     |
| 4.5            | 0.653       | 912            | 0.140     | 14.54     |

### 4. Conclusion

In the present investigation, the pressure dependent band structures and density of states of AlP and AlAs are computed and the results are used to study the metallization and superconductivity under high pressure for the first time. When the pressure is increased there is enhanced overlapping between the wave functions of the neighbouring atoms. As a result the widths of the valence and empty conduction bands increase. These changes lead to the narrowing and closing of band gaps in AlP and AlAs (metallization). On further increase of pressure, AlP and AlAs become superconductors, and these materials come under the class of electron-phonon-mediated high pressure superconductors. It is also confirmed that the metallization, structural phase transition and onset of superconductivity do not occur simultaneously in aluminum compounds.
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