Electronic Band Structure and Metallization of Aluminium Nitride (AlN) under High Pressure

V. Benaline Sheeba1, G. Selva Dancy1, C. Nirmala Louis1*, A. Amal Raj2

1Research Center and Department of Physics, Holy Cross College, Nagercoil, Tamil Nadu, India
2Professor in Chemistry, St. Jerome’s College, Anandhanadarkudy, KK District, Tamil Nadu, India
*Corresponding Author; e-mail: nirmala_louis@yahoo.co.in

Abstract. One basic problem in solid state physics, material chemistry, geosciences and even in planetology, is the precise electronic properties of the materials present in objects. The uniqueness of aluminium nitride (AlN) and its special role in human society is closely related to its structural stability at extreme pressures. In this paper, 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 semiconductor aluminium nitride (AlN) under pressure are presented. The equilibrium lattice constant, bulk modulus, pressure derivative of bulk modulus and the phase transition pressure from ZnS to NaCl is predicted from the total energy calculations. The ground state properties and band gap values are compared with the experimental results. At normal pressure AlN is indirect bandgap semiconductor with bandgap value 4.56eV. 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 AlN (metallization). In AlN, the metallization (at \( V/V_c = 0.756 \) and \( P_H = 1 \text{ Mbar} \)) occurs through indirect closing of the band gap between valence band maximum at \( \Gamma \) point and conduction band minimum at \( X \) point. It is also confirmed that the metallization and structural phase transition do not occur simultaneously in this compound.

Subject classification: 71, 71.15Fv, 61.50.Ks, 64.70.Kb, 74.62.Fj;

Keywords: Band structure, Density of states, Phase transition, Metallization.

1. INTRODUCTION

The enormous properties like ductility, light weight and high strength of aluminium compounds makes it the best choice for many areas of constructive as well as other important engineering applications (Davydov, 2002). The study of materials at high pressure is gaining importance because of recent refinements of the diamond anvil technique and the observation that materials often exhibit new crystal phases and novel behaviour under high pressure (Vladimir et al., 2007). Group III-V semiconductor AlN is extensively studied because it is considered important technological material in electronic and opto electronic applications (Wagner and Wang, 2002). The effect of pressure on the electronic properties of group III-V compounds can be investigated experimentally in many ways (Edgar, 1994). The technological applications of above compounds require significant progress in the fundamental understanding of their behaviour at normal and high pressures (Benaline Sheeba et al., 2013).

Generally these compounds (AlN, GaN and InN) crystallize either in zinc blende (ZnS) or in wurtzite structure because the difference in total energies between these two phases is very small (Nirmala Louis et al., 2012). At ambient conditions AlN, GaN and InN crystallize in the wurtzite structure. Experimentally zinc blende AlN, GaN, InN are also often observed as meta-stable phases by adopting certain growth conditions. Since the ZnS structure has larger optical gain and lower threshold current density, it possesses distinct advantages over wurtzite structure (Benaline Sheeba et al., 2013). In the present investigation, we have chosen zinc blende structure as the normal pressure structure of AlN. Subjecting AlN to high pressure leads to pressure induced metallization, structural phase transition and superconducting transition (Christensen et al., 1999).

The mechanical and electrical properties of twelve III-V semiconductors under pressure using Plane wave Pseudopotential method are given (Wang et al., 2002). There is no high pressure studies related to metallization AlN. This motivated us to take up the
present investigation. 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 this compound (Andersen et al., 1987). The phenomena of mettallization under high pressure (NaCl) structure of this material have been analyzed. 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 and mettallization are discussed in Section 3. Concluding remarks are given in Section 4.

Table 1: Equilibrium lattice constant, bulk modulus and band gap values

<table>
<thead>
<tr>
<th>Compound</th>
<th>Present work</th>
<th>Experiment (Edgar, 1994)</th>
<th>Previous theory (Wang, 2002)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>a$_0$ au</td>
<td>B$_0$ Mbar</td>
<td>E$_g$ ev</td>
</tr>
<tr>
<td></td>
<td>8.2608</td>
<td>2.03</td>
<td>4.50</td>
</tr>
</tbody>
</table>

Table 2: Reduced volumes, Lattice constant and Pressure values of AlN

<table>
<thead>
<tr>
<th>V/V$_0$</th>
<th>Lattice constant(au)</th>
<th>Pressure(Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.2608</td>
<td>0</td>
</tr>
<tr>
<td>0.9</td>
<td>7.9759</td>
<td>0.2642</td>
</tr>
<tr>
<td>0.8</td>
<td>7.6692</td>
<td>0.7101</td>
</tr>
<tr>
<td>0.756</td>
<td>7.5255</td>
<td>1.0005</td>
</tr>
<tr>
<td>0.7</td>
<td>7.3356</td>
<td>1.4879</td>
</tr>
<tr>
<td>0.6</td>
<td>6.9686</td>
<td>2.9161</td>
</tr>
<tr>
<td>0.5</td>
<td>6.5581</td>
<td>5.7428</td>
</tr>
<tr>
<td>0.4</td>
<td>6.0884</td>
<td>12.0035</td>
</tr>
<tr>
<td>0.3</td>
<td>5.532</td>
<td>28.5828</td>
</tr>
</tbody>
</table>

Table 3: Structural phase transition pressure for AlN (ZnS to NaCl)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice constant a.u</th>
<th>Present study</th>
<th>Experiment (Edgar,1994)</th>
<th>Previous theory (Wang,2002)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V/V$_0$)$_T$</td>
<td>P$_T$ (Mbar)</td>
<td>(V/V$_0$)$_T$</td>
<td>P$_T$ (Mbar)</td>
</tr>
<tr>
<td>AlN</td>
<td>8.2608</td>
<td>0.9</td>
<td>0.2642</td>
<td>0.91</td>
</tr>
</tbody>
</table>

2. BAND STRUCTURE AND DENSITY OF STATES

2.1. Calculational procedure

The electronic band structure and density of states calculations were performed for AlN corresponding to different reduced volumes in ZnS, NaCl and CsCl structures, by the first-principle FP-LMTO method with in generalized gradient approximation (GGA). The details of the FP-LMTO method are well described in the literature (Andersen et al. 1987) and we give here only the calculational details (Benaline Sheeba et al. 2013). The electronic configurations of Al and N are [Ne] 3s$^2$ 3p$^1$ 3d$^{10}$ (Z = 13) and [He] 2s$^2$ 2p$^3$ (Z = 7) respectively. The valence electronic configurations chosen in our calculations are 3s$^2$ 3p$^1$ for Al, 2s$^2$ 2p$^3$ for N. There are 8 valence electrons contributing to the valence bands. The final energy convergence is within 10$^{-5}$ Ry. The calculated total energies were fitted to Murnaghan’s equation of state (EOS), to determine the phase-transition pressure and other ground-state properties (Benaline Sheeba et al. 2013). Murnaghan’s equation of state is given by

\[ P = 1.5B_0 \left[ \left( \frac{V}{V_0} \right)^{7/3} - \left( \frac{V}{V_0} \right)^{5/3} \right] + 0.75 \left( B_0^{1/4} - 4 \right) \left( \left( \frac{V}{V_0} \right)^{2/3} - 1 \right) \] (1)

to obtain the equilibrium lattice constant and other ground state properties. In our calculation we have chosen the ZnS structure for AlN at ambient pressure. The phase stability of the ZnS and NaCl structures of AlN is analysed using the enthalpy calculation (Nirmala Louis et al., 2012). The enthalpy $H(P)$ is defined by

\[ H(P) = E_{\text{tot}}(P) + PV(P) \] (2)

and the transition pressure corresponding to the phase transition from ZnS to NaCl is obtained from the relation

\[ H_{\text{ZnS}}(P) = H_{\text{NaCl}}(P) \] (3)

where $H_{\text{ZnS}}$ and $H_{\text{NaCl}}$ are the enthalpies of the ZnS and NaCl phases respectively.
2.2. Band structure of AlN under pressure

The band structures of AlN were computed for various reduced volumes ranging from \( V/V_0 = 1.0 \) to 0.3 in steps of 0.05. Even though we have obtained the band structure for \( V/V_0 \) values from 1.0 to 0.3, we have presented here the band structures of AlN along the symmetry directions \( \Gamma - X - W - L - \Gamma - K \) and the corresponding density of states of AlN (Figs.1 to 4). The volume compressions corresponding to \( V/V_0 = 1.0 \) and \( V/V_0 = 0.756 \) for AlN is given. A single band nearer to the bottom arises from 2\( s^2 \) electrons of N (Fig.1). The three bands appearing below the Fermi level are due to the 3\( s^2 \), 3\( p^1 \) electrons of Al and 2\( p^3 \) electrons of N (Fig.1). The empty conduction bands above the Fermi level are due to 3\( p \), 3\( d \) states of Al and 3\( d \), 2\( p \) states of N (Fig.1). At normal pressure, the band gap of AlN is indirect with valence band maximum at \( \Gamma \) point and conduction band minimum at \( X \) point with band gap value 4.56 eV. The calculated energy gaps are in agreement with the experimental value of 4.8 eV (Table 1) (Edgar, 1994). As pressure increases the width of the valence band and the empty conduction band get widened. These changes lead to the narrowing of the band gap under pressure (Fig. 3).

2.3. Density of states under pressure

The densities of states (DOS) (states/Ry.) calculations for all the reduced volumes have been carried out. The density of states (DOS) histogram of AlN corresponding to normal pressure is shown in Fig.2. At normal pressure the levels arising from 3\( s^2 \) electrons of Al give the long spike near the origin. The short spikes near the Fermi energy are due to 2\( s^2 \), 2\( p^3 \) electrons of N and 3\( p^1 \) electron of Al. The short peaks above the Fermi energy \( E_F \) are due to the 3\( p \), 3\( d \) states of Al and 3\( d \), 2\( p \) states of N. The general features of the band structure and density of states (Figs 1-4) are similar to that of the other group III-V compounds (Nirmala Louis et al., 2012).

3. RESULTS AND DISCUSSIONS

3.1. Ground state properties

The ground state properties and structural phase transitions are studied from the total energies obtained from our calculation. The total energy is calculated as a function of reduced volume \( (V/V_0) \) for ZnS, NaCl and CsCl phases of AlN (Benaline Sheeba et al., 2013). Here, \( V_0 \) is the experimental equilibrium volume corresponding to the experimental equilibrium lattice constant. In Table 1, the equilibrium lattice constant \( (a_0) \), band gap \( (E_g) \), bulk modulus \( (B_o) \) and its pressure derivative \( (B_o') \) values are compared with experimental (Edgar,1994) and previous theoretical works (Wang et al., 2002). The calculated total energies were fitted to Murnaghan’s equation of state to obtain the equilibrium lattice constant and other ground state properties (Table.2). The values of reduced volume, pressure and lattice constant are given in Table.2.
Fig. 2: Density of states of AlN at V/V₀=1 (normal pressure)

Table 4: Metallization Pressure for AlN in NaCl structure

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice constant (a.u)</th>
<th>Present study (V/V₀₉)</th>
<th>P₉ (Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>8.2608</td>
<td>0.756</td>
<td>1.0005</td>
</tr>
</tbody>
</table>

Fig. 3: Band Structure of AlN at V/V₀=0. 756 (metallization pressure =1Mbar)

3.2. Structural phase transition

In our calculation we have chosen the ZnS structure as the ground state structure for AlN. The phase stability of the B3 (ZnS), B1 (NaCl) and B2 (CsCl) structures of AlN is analysed using the enthalpy calculation (Nirmala Louis et al., 2012). The phase transition pressure (P₉) and the corresponding reduced volume (V/V₀₉) estimated in our calculation are given in Table.3. For AlN, our calculated phase transition pressure is in good agreement with the experimental (Edgar, 1994) and previous theoretical works (Wang et al., 2002). 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 (Benaline Sheeba et al., 2013).

3.3. Metallization

At normal pressure AlN is a semiconductor. 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 AlN are shown in Figs. 3 and 4 respectively. In AlN, 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 AlN is \( V/V_0=0.756 \) (\( NaCl \) structure), which corresponds to the pressure \( P_M = 1 \) Mbar. At the metallization pressure, 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 AlN (Fig.4). Thereafter \( N(E_F) \) increases slowly with pressure and becomes fairly large at a particular value of \( V/V_0 \). The values of \( E_F \) and \( N(E_F) \) corresponding to different \( V/V_0 \) are used in studying the pressure variation of superconducting transition temperature. However, there is no experimental or theoretical study available for comparison at these pressures.

Fig. 4: Density of states of AlN at \( V/V_0=0.756 \) (metallization pressure=1Mbar)

4. CONCLUSION

In the present investigation, the pressure dependent band structures and density of states of AlN is computed and the results are used to study the metallization under high pressure for the first time. When the pressure is increased there is enhanced overlapping between the wave functions of the neighboring 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 AlN (metallization). It is also confirmed that the metallization and structural phase transition do not occur simultaneously in aluminum compounds.

REFERENCES


Mrs. V. Benaline Sheeba is a Ph. D research scholar doing research in Research Center & Department of Physics, Holy Cross College, Nagercoil, Tamil Nadu, India. She has published a research paper in an International Journal.

Miss. G. Selva Dancy is a pre doctoral research scholar doing research in Research Center & Department of Physics, Holy Cross College, Nagercoil, Tamil Nadu.

Dr. C. Nirmala Louis Ph.D is working as Assistant Professor of Physics, Research Center & Department of Physics, Holy Cross College, Nagercoil, Tamil Nadu, India. She received her Ph.D degree from Madurai Kamaraj University, Madurai, India. She has vast experience in Teaching and Research and she has published her research in 18 international Journals.

Dr. A. Amal Raj Ph.D is working as Principal & Professor Of Chemistry, St.Jerome’s College, Anandhanadarkudy, Nagercoil, Tamil Nadu, India. He received his Ph.D degree from University of Madras, Madras, India. He had worked as a postdoctoral fellow at Carmanos cancer Institute, Wayne State University School of Medicine, Detroit, USA and at Department of Chemistry, National Taiwan University, Taipei, Taiwan. He has vast experience in Teaching and Research in the fields of Theoretical & Computational Chemistry, Environmental Chemistry, and Organic Synthesis. He has published his research in 19 International Journals. He has attended and organized many Seminars & Conferences.