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Full Paper

Superconductivity in Group III-V Semiconductor *AlN* Under High Pressure

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Abstract: The electronic properties of cubic zinc blende type group III-V semiconductor AlN under pressure is studied using full potential linear muffin-tin orbital (FP-LMTO) method. At normal pressure, AlN is an indirect bandgap semiconductor with band gap value 4.56 eV. 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 indirect closing of the band gaps in AlN (metallization). On further increase of pressure, AlN becomes a superconductor and AlN comes under the class of electron-phonon-mediated high pressure superconductors. The superconducting transition temperatures (Tc) of AlN are obtained as a function of pressure for the CsCl structure. It is also confirmed that the metallization, structural phase transition and onset of superconductivity do not occur simultaneously in this compound.

Keywords: band structure; density of states; phase transition; metallization; superconductivity; high pressure

1. INTRODUCTION

Group III-V semiconductors have been extensively studied because it is considered as an important technological material in electronic and opto-electronic applications [1]. Generally aluminum compounds (*AlN*, *AlAs*) crystallize in zinc blende (ZnS) structure [2]. The effect of pressure on the electronic properties of group III-V compounds can be investigated in many ways [3, 4]. The technological applications of *AlN* compound require significant progress in the fundamental understanding of their behavior at normal and high pressures [5]. Subjecting *AlN* to high pressure leads to pressure-induced metallization, structural phase transition, and superconducting transition [2]. Wang *et al.* [6] presented the mechanical and electrical properties of twelve III-V semiconductors, under pressure, using Plane wave Pseudopotential method. Edgar [7] presented the properties of group III nitrides using experimental observations. Wagner *et al.* [8] reported the electronic and phonon deformation potentials of GaN and AlN using Ab initio calculations *versus* experimental values. There are no high pressure-involving studies related to metallization and superconductivity in *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 [9]. We have analyzed the phenomena of metallization (*NaCl* structure) and superconductivity for high pressure (*CsCl*) structure of AlN [1, 2]. It is hoped that this analysis will enable us to make some general statement regarding the path to high *Tc* superconductivity in covalent compounds.

2. MATERIAL AND METHODS

2.1. Band structure and density of states

2.1.1. Calculative 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 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*, and $2s^2$ $2p^3$ for *N*. There are 8 valence electrons

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contributing to the valence bands. The final energy convergence is within 10^{-5} Ry. The calculated total energies were fit to Murnaghan's equation of state (EOS), to determine the phase-transition pressure and other ground-state properties [1, 2]. Murnaghan's equation of state is given by the following formula to obtain the equilibrium lattice constant and other ground state properties.

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

In our calculations we have chosen the ZnS structure for *AlN* at ambient pressure. The phase stability of the *ZnS* and *NaCl* structures of *AlN* is analyzed using the enthalpic calculation [1]. The enthalpy *H(P)* is defined by:

$$H(P) = E_{\mathrm{tot}}(P) + PV(P) \qquad (2)$$

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

$$H_{ZnS}(P) = H_{\mathrm{NaCl}}(P) \qquad (3)$$

where H_{ZnS} and H_{NaCl} are the enthalpies of the *ZnS* and *NaCl* phases, respectively.

2.1.2. The Band structure of AlN under pressure

The band structures of *AlN* 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 *AlN* along the symmetry directions *Γ-X-W-L-Γ-K* and the corresponding density of states of *AlN* (Figs.1 to 4). The volume compressions corresponding to V/V_o=1.0 and V/V_o=0.756 for *AlN* is given. A single band nearer to the bottom arises from $2s^2$ electrons of *N* (Fig. 1). The three bands appearing below the Fermi level are due to the $3s^2$, $3p^1$ electrons of *Al* and $2p^3$ electrons of *N* (Fig. 1). The empty conduction bands above the Fermi level are due to 3p, 3d states of *Al* and 3d, 2p states of *N* (Fig. 1). At normal pressure, the band gap of *AlN* is indirect with valence band maximum at *Γ* 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) [7]. 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).

Table 1. Equilibrium lattice constant (a_o), bulk modulus (B_o) and its pressure derivative (B_o^1) of *AlN* in *ZnS* structure

Ground State Properties	***AlN***		
	Present work	**Experimental work [7]**	**Previous theoretical work [6]**
a_o a.u.	8.2603	8.3	8.1273
B_o Mbar	2.03	2	1.84
B_o^1	4.152	4.2	3.98
E_g eV	4.56	4.503	3.92

2.1.3. The 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 *AlN* 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 $2s^2$, $2p^3$ electrons of *N* 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, 2p states of *N*. The general features of the band structure and density of states (figures 1-4) are similar to that of the other group III-V compounds [1, 2].

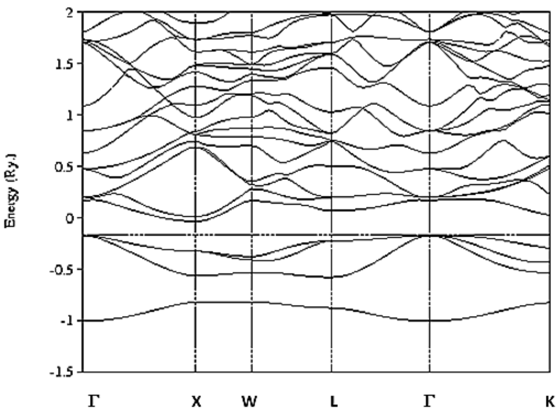

Figure 1. Band Structure of AlN at V/Vo = 1 (normal pressure).

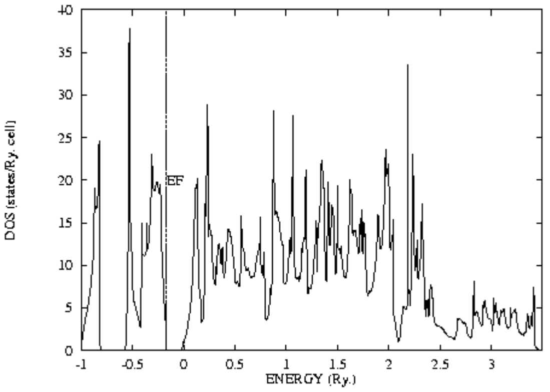

Figure 2. Density of states of AlN at V/Vo = 1 (normal pressure).

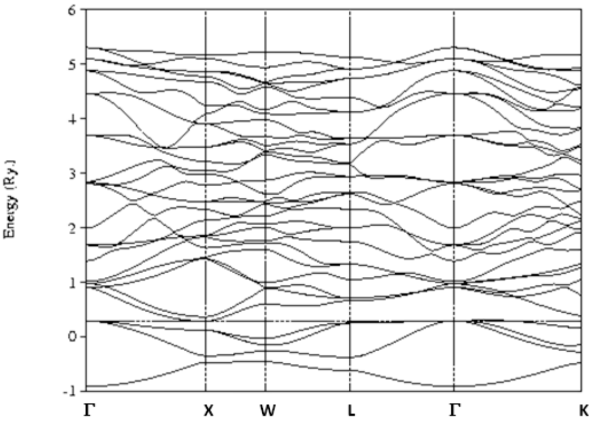

Figure 3. Band Structure of AlN at V/Vo = 0. 756 (metallization pressure =1Mbar).

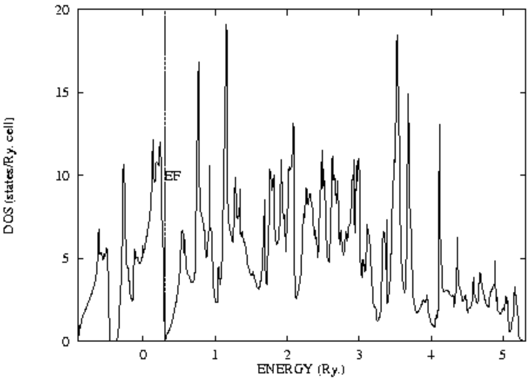

Figure 4. Density of states of AlN at V/Vo = 0. 756 (metallization pressure=1Mbar).

3. RESULTS AND DISCUSSION

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_o) for *ZnS, NaCl,* and *CsCl* phases of *AlN* [1]. Here, V_o is the experimental equilibrium volume corresponding to the experimental equilibrium lattice constant. In Table 1, the equilibrium lattice constant (a_o), band gap (E_g), bulk modulus (B_o) and its pressure derivative (B_o^1) values are compared with experimental [7] and previous theoretical works [6]. The values of reduced volume, pressure, and lattice constant are given in Table 2. The calculated total energies were fit to Murnaghan's equation of state to obtain the equilibrium lattice constant and other ground state properties.

Table 2. Reduced volumes, Lattice constant and Presssure values of *AlN*.

V/V0	Lattice constant(au)	Pressure(Mbar)
1	8.2608	0
0.9	7.9759	0.2642
0.8	7.6692	0.7101
0.756	7.5255	1.0005
0.7	7.3356	1.4879
0.6	6.9686	2.9161
0.5	6.5581	5.7428
0.4	6.0884	12.0035
0.3	5.532	28.5828

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 analyzed using the enthalpic calculation [1]. The phase transition pressure (P_T) and the corresponding reduced volume $(V/V_o)_T$ estimated in our calculation are given in Table 3. For *AlN*, our calculated phase transition pressure is in good agreement with the experimental and previous theoretical results [4, 5]. 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 [1, 2].

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 the metallization of *AlN* are shown in figures 3 and 4, respectively. In *AlN*, the metallization occurs through indirect closing of the band gap between valence band maximum at Γ point and conduction band minimum at *X* point. The metallization volume of *AlN* is V/V_o=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_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. However, there are no experimental nor theoretical studies available for comparison at these pressures [1, 2].

Table 3. Structural phase transition pressure for AlN.

Compound	**Structural phase transition**	**Present study**		**Experiment [4]**		**Previous theory [5]**	
		$(V/V_o)_T$	P_T (Mbar)	$(V/V_o)_T$	P_T (Mbar)	$(V/V_o)_T$	P_T (Mbar)
AlN	ZnS to NaCl	0.9	0.264	0.91	0.25	0.832	0.358
	NaCl to CsCl	0.7	1.5	0.72	1.42	0.65	1.851

3.4. Superconductivity in *AlN* under pressure

The promotion of an *s* electron to the *d* shell in solids is one of the factors, which will induce superconductivity. Under very high pressures, aluminum compounds are not only metals but also superconductors. The theory of Gaspari and Gyorffy in conjunction with McMillan's formula is used to calculate *Tc* [1].

The electron –phonon mass enhancement factor, λ is:

$$\lambda = \frac{N(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle} \quad (4)$$

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.

$\langle I^2\rangle$ (in Rydbergs) can be written as:

$$\langle I^2\rangle = 2\sum_l \frac{(l+1)}{(2l+1)(2l+3)} M_{l,l+1}^2 \frac{N_l(E_F)N_{l+1}(E_F)}{N(E_F)N(E_F)} \quad (5)$$

where $M_{l,l+1} = -\phi_l\ \phi_{l+1}\ [(D_l(E_F)-1)(D_{l+1}(E_F)+l+2) + (E_F-V(S))S^2]$ and in this, ϕ_l is the radial wave function at the muffin-tin sphere radius corresponding to the Fermi energy, D_l is the logarithmic derivative of the radial wave function at the sphere boundary, *V(S)* is the muffin-tin potential at the sphere boundary, and *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:

$$\langle\omega^2\rangle = \frac{1}{2}\theta_D^2 \quad (6)$$

The variation of Debye temperature with pressure $\theta_D(P)$ is given by:

$$\theta_D(P) = \frac{\sqrt{E_F}}{\sqrt{E_F^o}}\frac{a_o}{a}\theta_D^o \quad (7)$$

where θ_D^o, a_o and E_F^o are normal pressure quantities.

The McMillan's formula used for *Tc* calculation [2],

$$Tc = \frac{\theta_D}{1.45}\exp\left[\frac{-1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right] \quad (8)$$

gives a good estimate of the *Tc* value. Here μ^* is the electron-electron interaction parameter which is estimated using the relation,

$$\mu^* = \frac{0.26N(E_F)}{1+N(E_F)} \tag{9}$$

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 θ_D, λ, μ^* and Tc as a function of pressure using Eqs. (4 - 9) .

The onset of superconductivity occurs at V/Vo=0.5, with Tc= 0.024K. On further increase of pressure, *Tc* begins to increase. Our results indicate that *AlN* is a one-band rather than a one-electron material. The electron-phonon interaction parameter (λ) and its variation under pressure shows that *AlN* is an electron-phonon mediated superconductor. In this material, the *Tc* increases with pressure. It is found that the *Tc(P)* follow the variation in $N(E_F)$ with pressure. The increase of *Tc(P)* depends mainly on the rate of increase of s/p electron numbers with pressure for *AlN*. At low pressures the rate of increase of these electron numbers are increasing with pressure resulting in the increase of *Tc*. The calculated values at high pressure (*CsCl*) structure are given in Table 4 for *AlN*. As pressure increases our computed value of *Tc* increases and reaches a maximum value. In our calculation, the highest *Tc* obtained in *AlN* is 8.864K at 7.0 Mbar (Table 4). This reflects the fact that the structural and band gap configurations play an important role in the superconducting (high *Tc-max*) behavior of these compounds under high pressure [1, 2].

Table 4. Variation of *Tc* as a function of pressure for *AlN in CsCl* structure.

Pressure P Mbar	λ	θ_D K	μ^*	**Tc K**
5.74	0.165	284.3	0.022	0.024
6.0	0.387	308.7	0.034	3.247
7.0	0.542	368.5	0.048	8.864

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 and superconductivity under high pressure for the first time. When the pressure is increased there is enhanced overlapping between the wave functions of the adjacent 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 (metallization). On further increase of pressure, *AlN* becomes a superconductor, and this material comes under the class of electron-phonon-mediated high pressure superconductor. It is also confirmed that the metallization, structural phase transition, and onset of superconductivity do not occur simultaneously in aluminum compounds [2].

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