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# High pressure structural phase transition and metallization in zinc oxide

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**Abstract :** The structural phase transition and metallization of the group II-VI compound zinc oxide (ZnO) is investigated through its band structure obtained using the full potential linear muffin-tin orbital (FP-LMTO) method. The ground state properties and band gap values are compared with the experimental results. Under high pressure ZnO undergoes a first order structural phase transition from the ZnS structure (B3) to the NaCl structure (B1). The band structure, density of states (DOS) and total energy are computed as a function of reduced

volume for both ZnS and NaCl phases. The values of pressure under reduced volume are calculated using Birch-Murnaghan's equation of state. The pressure corresponding to structural phase transition from ZnS structure (B3) to the NaCl structure (B1) is 9 Gpa in ZnO. The metallization pressure  $P_M$  is 95.3 GPa. © Global Scientific Inc.

**Keywords :** Band structure; Density of states; Phase transition; Metallization; ZnO; High pressure.

## INTRODUCTION

The physical properties of materials undergo a variety of changes when they are subjected to high pressure<sup>[1]</sup>. The increase of pressure means the significant decrease in volume, which results in the change of electronic states and crystal structure<sup>[2]</sup>. With the development of high pressure experimental techniques, investigations on pressure-induced structural phase transition, semiconductor-metal transition and superconducting transition are getting the attention of all<sup>[3-7]</sup>. In particular, there is a great in-

terest in the pressure induced structural phase transition and metallization of the group II-VI compound zinc oxide (ZnO). Group II-VI compound ZnO is a wide band gap semiconductor with a range of technological applications including electronic and electro-optic devices, catalysis, chemical sensors and conductive solar cell window layers<sup>[8-17]</sup>. Hence, to gain a fundamental understanding of the structural phase transition and metallization of ZnO, the electronic band structure studies of this material is essential and this motivated the present investigation. The electronic configuration of Zn and O are [Ar]

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$3d^{10}4s^2$  ( $Z = 30$ ) and  $[\text{He}] 2s^2 2p^4$  ( $Z = 8$ ) respectively. The valence electronic configurations chosen in our calculation are  $3d^{10}4s^2$  for Zn and  $2s^2 2p^4$  for O. The band structures of ZnO corresponding to various pressures are obtained using the full potential linear muffin-tin orbital (FP-LMTO) method<sup>[18]</sup>. The calculated total energies were fitted to the Murnaghan's equation of state (EOS)<sup>[19]</sup>, to determine the phase transition pressure and other ground state properties.

## BAND STRUCTURE AND DENSITY OF STATES AT NORMAL PRESSURE

The band structures and density of states of ZnO is computed (Figures.1 to 4) for various reduced volumes ranging from  $V/V_o=1.0$  to 0.3 in steps of 0.05. Fermi level is indicated by dotted horizontal line<sup>[20]</sup>. But here we have presented the band structures along the symmetry directions  $\Gamma$ -X-W-L- $\Gamma$ -K (Figures.1 and 3) corresponding to volume compressions  $V/V_o=1.0$  and  $V/V_o=0.73$  for ZnO. At normal pressure, the single valence band, which is positioned at the bottom of the valence band arise from  $2s^2$  electrons of O. The five bands nearer to the single band arises from  $4p^6$  electrons of Zn and  $2p^4$  electrons of O (Figure 1). The three bands appearing below the Fermi level are due to the  $4s^2 3d^4$  electrons of Zn (Figure 1). The empty conduction bands above the Fermi level are due to  $3p, 3d$  states of Zn and O. The characteristic features of ZnO band structure are similar to the previous calculations<sup>[2]</sup>. The fundamental energy gap is between the half filled  $p$

like valence band due to oxygen and empty  $p$  like conduction band due to zinc. At normal pressure, the band gap of ZnO is direct (3.526 eV) with top of the valence band in  $\Gamma$  point and the bottom of the conduction band in a  $\Gamma$  point (Figure 1). The calculated band gap is in agreement with the experimental value than previous theoretical value (TABLE 1).

The density of states (DOS) (states/Ry.) calculations for all the reduced volumes has been carried out but here we have given the DOS histograms of ZnO corresponding to normal pressure (Figure 2) and metallization pressure (Figure 4). At normal pressure (Figure 2) the levels arising from  $2s^2$  electrons of O give the short spike near the origin. The long spike near the Fermi energy are due to  $4p^6 4s^2 3d^4$  electrons of Zn and  $2p^4$  electrons of O. The short peaks above the Fermi energy  $E_f$  are due to the  $3p, 3d$  states of Zn and O. As the pressure increases the width of the valence band and the empty conduction band get widened<sup>[21,22]</sup>. These changes lead to the closing of the band gap under pressure (Figure 3)<sup>[23]</sup>.

## BAND STRUCTURE AND DENSITY OF STATES AT 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 increase in the width of the valence band and empty conduction band<sup>[24,25]</sup>. When pressure increases the value of  $E_f$  increases whereas no density of states is

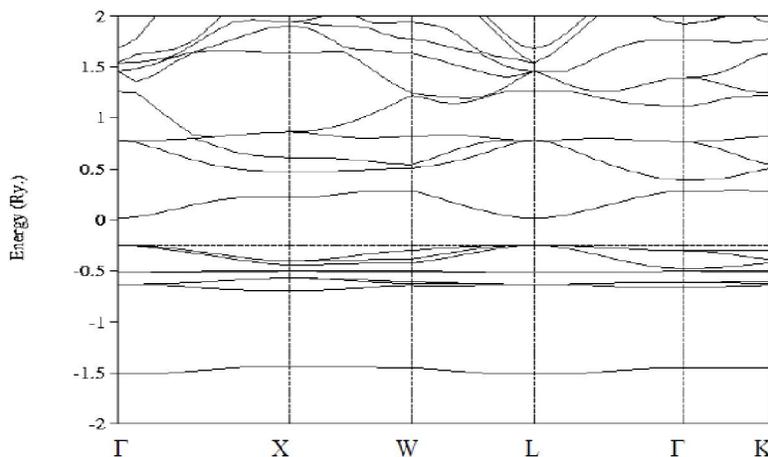


Figure 1 : Band structure of ZnO at normal pressure

TABLE 1 : Equilibrium lattice constant ( $a_o$ ), bulk modulus ( $B_o$ ) and its pressure derivative ( $B_o'$ ), Energy gap ( $E_g$ ) of ZnO

Ground State Properties	ZnO		
	Present study	Experiment <sup>[2]</sup>	Previous theory <sup>[3,30]</sup>
$a_o$ Å	4.534	4.569	4.365
$B_o$ GPa	161.7	158.5	165.5
$B_o'$	3.95	3.97	3.59
$E_g$ eV (direct)	3.526	3.6	3.25

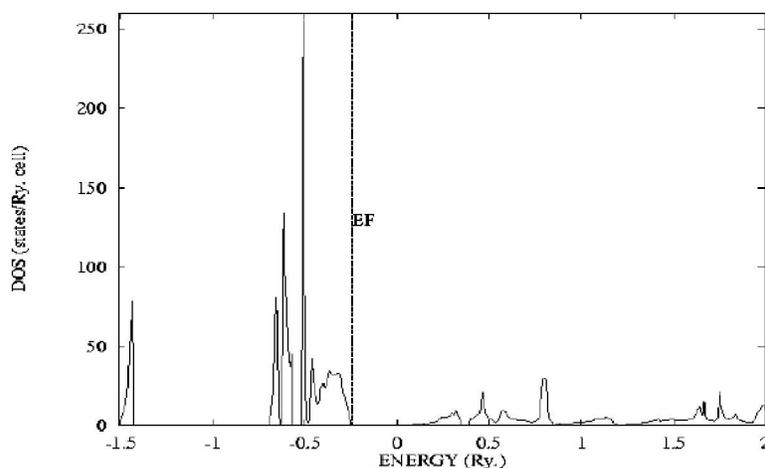


Figure 2 : Density of states of ZnO at normal pressure

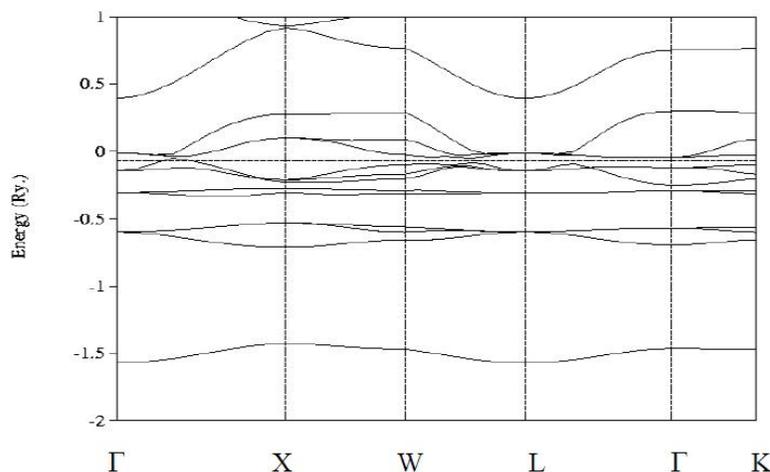


Figure 3 : Band structure of ZnO at metallization pressure

available at the Fermi level up to metallization pressure<sup>[1]</sup>. In Figure 4, there are appreciable values of  $N(E_F)$  for ZnO ( $V/V_o=0.73$ ) in ZnS structure, which indicate the occurrence of metallization in ZnO. Further increase in pressure leads to enhanced density of states at the Fermi level which induces superconductivity. In ZnO, metallization takes place by the indirect closure (Figure 3) of band gap between valence band and conduction band. The metallization volume of ZnO is  $V/V_o=0.73$ , which corresponds to

the pressure  $P_M=95.3$  GPa. The general features of high pressure band structure is similar to previous calculations<sup>[26,27]</sup>. From our calculation, in ZnO an indirect closure of band gap occurs. The density of states histograms of ZnO at high pressure is given in Figure 4. At this pressure ZnO is in NaCl structure. From the histogram, it is seen that the heights of the spikes are considerably reduced when compared to Figure 2. Reason is when pressure increased  $E_F$  increases whereas no density of states is available at

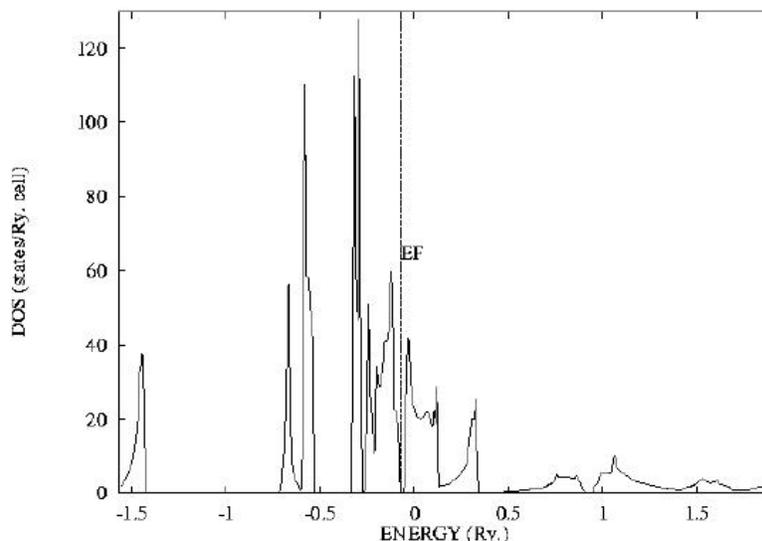


Figure 4 : Density of states of ZnO at metallization pressure

the Fermi level up to metallization pressure. There are appreciable values for DOS at  $V/V_0 = 0.73$  (Figure 4) indicating metallization in ZnO<sup>[1]</sup>. When pressure increases (reduced volume decreases) the value of the DOS at Fermi energy,  $E_F(N(E_F))$  increases<sup>[28,29]</sup>.

## GROUND STATE PROPERTIES

The ground state properties of ZnO are studied from their total energies obtained from our calculation. The total energy is calculated as a function of reduced volume for both B3 and B1 phases of ZnO ( $V/V_0 = 1.0$  to  $0.3$  in steps of  $0.1$ ). Here  $V_0$  is the experimental equilibrium volume corresponding to experimental equilibrium lattice constant. The calculated total energies were fitted to Murnaghan's equation of state<sup>[19]</sup> to obtain the equilibrium lattice constant and other ground state properties.

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

The values of pressure under reduced volume are calculated and given in TABLE.2. In ZnO, at normal pressure ZnS structure has minimum energy and at high pressure NaCl structure has minimum energy<sup>[30]</sup>.

## STRUCTURAL PHASE TRANSITION

Under high pressure ZnO undergo a structural phase transition from the ZnS structure (B3) to NaCl structure (B1). The phase stability of B3 and B1 structures of ZnO is analyzed using the enthalpy cal-

ulation.

The enthalpy 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<sup>[1]</sup>,  $H_{B3}(P) = H_{B1}(P)$

Where  $H_{B3}$  and  $H_{B1}$  are the enthalpies of the B3(ZnS) and B1 (NaCl) phases respectively. The phase transition pressure ( $P_T$ ) and the corresponding reduced volume ( $V_T$ ) estimated in our calculation are  $P_T = 9$  GPa and  $V_T = 0.925$  respectively. Our calculated phase transition pressure is in good agreement with the experimental value of  $9.5$  GPa<sup>[2]</sup>. The charge transfer causes the phase transition but the mechanism for the phase transition is geometric effort involving a change in coordination number from 4 in the B3 phase to 6 in the B1 phase<sup>[1,20]</sup>.

## METALLIZATION

At normal pressure, ZnO is a wide gap semiconductor (Figure 1 and 2). As pressure is increased, there is a charge transfer from s, p to d state, this causes the increase in the width of the valence band and also the empty conduction bands. These changes lead to the narrowing of the band gap and at particular pressure, there is a closing of band gap<sup>[1]</sup>. ZnO becomes metal under pressure but before that it undergoes structural phase transition from B3 phase to B1 phase. The band structure and density of state corresponding to metallization of ZnO is shown in Figure 3 and 4. In ZnO, metallization takes place by

TABLE 2 : Lattice constant( $a$ ), Pressure( $P$ ) and band gap ( $E_g$ ) for different reduced volumes

$V/V_0$	$a$ (a.u)	$P$ (Mbar)	$E_g(P)$
1	4.569	0	3.526
0.9	4.4112	20.97	2.52
0.8	4.2414	56.08	1.27
0.6	4.0568	116.76	0
0.5	3.8536	227.01	0
0.4	3.6264	442.37	0

TABLE 3 : Structural phase transition and metallization pressures

Group II-VI COMPOUND	Structural Phase Transition ZnS→NaCl		Metallization	
	$(V/V_0)_T$	$P_T$ (GPa)	$(V/V_0)_M$	$P_M$ (GPa)
ZnO	0.925	9.0	0.73	95.3

the direct closure (Figure 3) of band gap between valence band and conduction band. The metallization volume of ZnO is  $V/V_0=0.73$  which corresponds to the pressure  $P_M=95.3$  GPa (TABLE: 3). The metallization occurs because of the closure of band gap between Zn-3p- like valence band and O-3s-like conduction band (Figure 3). The increase of pressure causes the broadening of bands which results in the decrease of density of states value in most of the energy regions of DOS histograms. Thus in Figure 4, the heights of the spikes are considerably reduced. When pressure is increased  $E_F$  increases whereas no density of states is available at the Fermi level up to metallization pressure. There are appreciable values for DOS at  $V/V_0=0.73$  (Figure 4) indicating metallization in ZnO.

## CONCLUSION

The high pressure band structure, density of states, structural phase transition and metallization of ZnO is investigated. The metallization reduced volume is  $V/V_0=0.73$  (NaCl structure), and the corresponding pressure  $P_M$  is 95.3 GPa. In our calculation zinc blende phase to rocksalt phase transition occurs at 9 Gpa. This value is good agreement with the experimental value of 9.5 Gpa [2].

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