

Band Structure, Density of States, Structural Phase Transition and Metallization in CdO Under High Pressure

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Abstract: The structural phase transition and metallization of the group II-VI compound semiconductor cadmium oxide (CdO) 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 CdO undergoes a first order structural phase transition from the NaCl structure (B1) to the CsCl structure (B2). The band structure, density of states (DOS) and total energy are computed as a function of reduced volume for both NaCl and CsCl 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 NaCl structure (B1) to the CsCl structure (B2) is 0.9 Mbar in CdO. The metallization pressure PM is 1.2 Mbar.

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

1. INTRODUCTION

The physical properties of materials undergo a variety of changes when they are subjected to high pressure [1]. The increase of pressure means the significant decrease in volume, which results in the change of electronic states and crystal structure [2]. 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 [3-7]. In particular, there is a great interest in the pressure induced structural phase transition and metallization of the group II-VI compound cadmium oxide (CdO). Among all the Group II-VI compounds, CdO is more ionic and it is NaCl structure at normal pressure. CdO 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 [8, 9]. Hence, to gain a fundamental understanding of the structural phase transition and metallization of CdO, the electronic band structure studies of this material is essential and this motivated the present investigation.

2. MATERIAL AND METHODS

2.1. Band structure and density of states

2.1.1. Calculative procedure

The electronic configuration of Cd and O are [Kr] $4d^4 5s^2 5p^6$ ($Z = 48$) and [He] $2s^2 2p^4$ ($Z = 8$) respectively. The valence electronic configurations chosen in our calculation are $4d^4 5s^2 5p^6$ for Cd and $2s^2 2p^4$ for O. There are 18 valence electrons contributing to the valence band. The band structures of CdO corresponding to various pressures are obtained in NaCl and CsCl structures using the full potential linear muffin-tin orbital (FP-LMTO) method with in generalized gradient approximation (GGA) [10]. The final energy convergence is within 10^{-5} Ry. The calculated total energies were fitted to the Murnaghan's equation of state (EOS) [2], to determine the phase transition pressure and other ground state properties. Murnaghan's equation of state is given by:

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

to obtain the equilibrium lattice constant and other

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ground state properties. In our calculation, we have chosen the NaCl structure for CdO at ambient pressure. The phase stability of the NaCl and CsCl structures of CdO is analysed using the enthalpy calculation [2]. The enthalpy $H(P)$ is defined by:

$$H(P) = E_{\text{tot}}(P) + PV(P) \quad (2)$$

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

$$H_{\text{NaCl}}(P) = H_{\text{CsCl}}(P) \quad (3)$$

where H_{NaCl} and H_{CsCl} are the enthalpies of the NaCl and CsCl phases respectively.

2.1.2 The Band structure and Density of states of CdO under pressure

The band structures and density of states of CdO 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 [20]. But here we have presented the band structures along the symmetry directions Γ -X-W-L- Γ -K (Figs. 1 and 3) corresponding to volume compressions $V/V_o=1.0$ and $V/V_o=0.63$ for CdO. 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 $5p^6$ electrons of Cd and $2p^4$ electrons of O (Fig. 1). The three bands appearing below the Fermi level are due to the $5s^2 4d^4$ electrons of Cd (Fig.1). The empty conduction bands above the Fermi level are due to $4p, 4d$ states of Cd and O. The characteristic features of CdO band structure are similar to the previous calculations [3]. The fundamental energy gap is between the half-filled p like valence band due to oxygen and empty p like conduction band due to cadmium. At normal pressure, the band gap of CdO is direct (2.25 eV) with top of the valence band in Γ point and the bottom of the conduction band in a Γ 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 CdO corresponding to normal pressure (Fig.2) and metallization pressure (Figure 4). At normal pressure (Fig. 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 $5p^6$

$5s^2 4d^4$ electrons of Cd and $2p^4$ electrons of O. The short peaks above the Fermi energy E_F are due to the $4p, 4d$ states of Cd and $2p, 3d$ states of O. As the pressure increases the width of the valence band and the empty conduction band get widened [11, 12]. These changes lead to the closing of the band gap under pressure (Figure 3) [13].

3. RESULTS AND DISCUSSION

3.1 Ground state properties

The ground state properties of CdO are studied from their total energies obtained from our calculation. The total energy is calculated as a function of reduced volume for both B1 (NaCl) and B2 (CsCl) phases of CdO ($V/V_o=1.0$ to 0.3 in steps of 0.1). Here V_o is the experimental equilibrium volume corresponding to 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 [14] and previous theoretical works [15]. The calculated total energies were fitted to Murnaghan's equation of state to obtain the equilibrium lattice constant and other ground state properties. In CdO, at normal pressure NaCl structure has minimum energy and at high pressure CsCl structure has minimum energy [16].

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

Ground State Properties	CdO		
	Present work	Experimental work [14]	Previous theoretical work [15]
a_o a.u.	8.778	8.876	8.553
B_o Mbar	0.583	0.6	0.523
B_o^1	4.734	4.8	4.687
E_g eV	2.25	2.3	2.16

3.2 Structural phase transition

Under high pressure CdO undergo a structural phase transition from the NaCl structure (B1) to CsCl structure (B2). The phase stability of B1 and B2 structures of CdO is analyzed using the enthalpy calculation. The phase transition pressure (P_T) and the corresponding reduced volume (V_T) estimated in our calculation are $P_T = 0.9$ Mbar and $V_T = 0.72$ respectively. Our calculated phase transition pressure is in good agreement with the experimental value of

0.897 Mbar [14]. The charge transfer causes the phase transition but the mechanism for the phase transition is geometric effort involving a change in coordination number from 6 in the B1 phase to 8 in the B2 phase [17].

3.3 Metallization

At normal pressure, CdO is a direct bandgap semiconductor (Figures 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 and at particular pressure, there is a closing of band gap [1]. CdO becomes metal under pressure but before that it undergoes structural phase transition from B1 phase to B2 phase. The band structure and density of state corresponding to metallization of CdO is shown in Figures 3 and 4. In CdO, metallization takes place by the direct closure (Figure 3) of band gap between valence band maximum and conduction band minimum in between Γ point and H point. The metallization volume of CdO is $V/V_0=0.63$ which corresponds to the pressure $P_M=1.2$ Mbar (Table 2). The metallization occurs because of the closure of band gap between Cd-4p 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. 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 $V/V_0=0.63$ (Figure 4) indicating metallization in CdO.

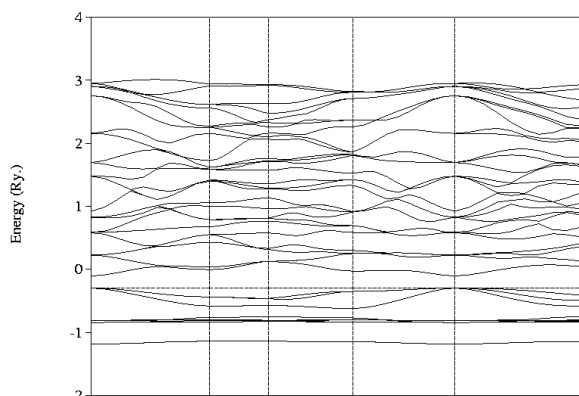


Figure 1. Band Structure of CdO at $V/V_0=1$ (normal pressure).

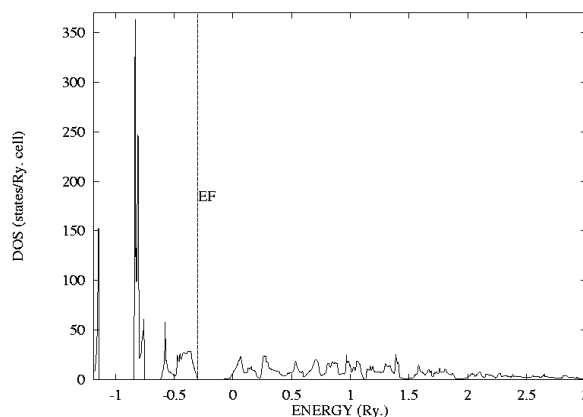


Figure 2. Density of states of CdO at $V/V_0=1$ (normal pressure).

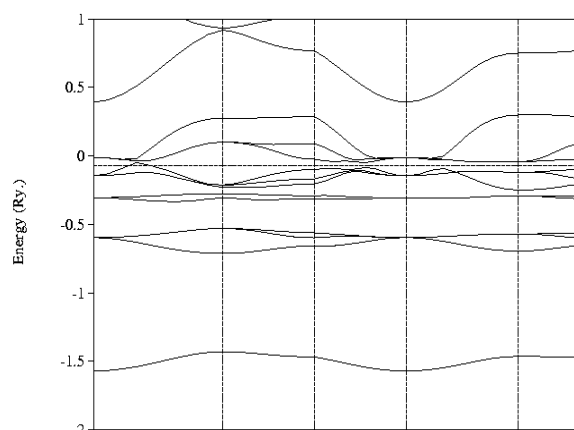


Figure 3. Band Structure of CdO at $V/V_0=0.63$ (metallization pressure = 1.2 Mbar).

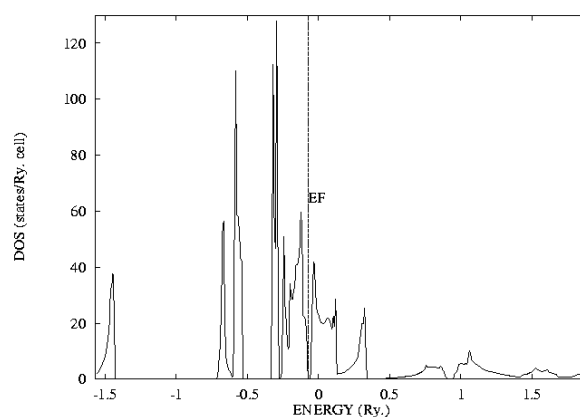


Figure 4. Density of states of CdO at $V/V_0=0.63$ (metallization pressure = 1.2 Mbar).

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 CdO (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 are no experimental or theoretical study available for comparison at these pressures.

Table 2. Structural phase transition and metallization pressure for CdO.

Group II-VI compound	Structural Phase Transition NaCl \rightarrow CsCl		Metallization	
	$(V/V_0)_T$	P_T (Mbar)	$(V/V_0)_M$	P_M (GPa)
	CdO	0.72	0.9	0.63

4. CONCLUSION

The high pressure band structure, density of states, structural phase transition and metallization of CdO is investigated. 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 (metallization). The metallization reduced volume is $V/V_0=0.63$ (CsCl structure), and the corresponding pressure P_M is 1.2 Mbar. In our calculation NaCl phase to CsCl phase transition occurs at 0.9 Mbar. This value is good agreement with the experimental value of 0.897 Mbar. It is also confirmed that the metallization and structural phase transition do not occur simultaneously in cadmium compounds [3].

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