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# Structural, Electronic and Elastic Properties of ZnO and CdO: A First-Principles Study

A. JemmyCinthia<sup>a</sup>, G. Sudhapriyanga<sup>a</sup>, R.Rajeswarapalanichamy<sup>a\*</sup>, M.Santhosh<sup>a</sup><sup>a</sup>*Department of Physics, N.M.S.S.V.N college, Madurai, Tamilnadu-625019, India*

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## Abstract

A theoretical investigation of the structural, electronic and elastic properties of the transition metal monoxides Zinc monoxide (ZnO) and Cadmium monoxide (CdO) in the cubic B1 (rock-salt) B2 (CsCl) and B3 (zinc blende) phases are performed using the first-principles calculations. The optimized lattice parameters and their bulk modulus values are found to be in accord with the available experimental and other theoretical values. To understand the electronic properties of ZnO and CdO, their electronic band structures are analyzed. A pressure induced structural phase transition occurs from B3 to B1 at a pressure of 11.2 GPa and from B1 to B2 at even higher pressure of 243.3 GPa occurs in ZnO; whereas the transition is from B1 to B2 phase at a pressure of 88.5 GPa in CdO. The elastic constants are computed to investigate the mechanical stability at normal and elevated pressures. The pressure dependence of the various moduli, Poisson's ratio, anisotropy and the hardness of ZnO and CdO are also analyzed.

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*Keywords:* "Ab-initio calculations, Electronic structure, Structural phase transition , Elastic properties."

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## 1. Introduction

Recently the transition metal monoxides zinc monoxide (ZnO) and cadmium monoxide (CdO) have received much attention, owing to their potential application in various technologically important areas such

\* Corresponding author. Tel.: 0452-2459187; fax: 0452-2458358.

*E-mail address:* [rpalanichamy@gmail.com](mailto:rpalanichamy@gmail.com)

as solar cells, gas sensors, flat panel displays, anti-reflection coatings, etc.(Champness et al.(1995); Lokhande (2004); Nomura et al.(2003); Lee et al.(1987)). First principles calculation is a powerful tool to calculate the structural, electronic and elastic properties of these transition metal monoxides. ZnO crystallizes in the hexagonal wurtzite (B4) or cubic zinc blende (B3) or both at ambient conditions. Jaffe et al.(2000) have predicted several high pressure structures for ZnO. It transforms from the zinc blende (B3) structure to the NaCl (B1) structure and then to the CsCl (B2) structure at high pressures. Hummer (1973) has determined the band gap of ZnO as 3.44 eV; while Zhou et al.(2007) have calculated the band gap value to be 1.8 eV by the LDA+U method. Unlike ZnO and other II-IV semiconductors which crystallize in either wurtzite (B4) or zinc blende (B3), CdO crystallizes in the NaCl (B1) structure with Fm-3m space group at ambient pressure. Roberto et al. (2002) have predicted a high pressure phase transition from B1 to B2 (CsCl) structure at 89 GPa, while this transition pressure was calculated as 90.6 GPa by Liu et al.(2004). Most high pressure studies are limited to phase transition only and not much work has been studied on the elastic properties. In this paper we report the ground state electronic, elastic properties and phase transitions of ZnO and CdO in detail. The computational method is described in section 2. In section 3, the results are discussed and finally the conclusion is presented in section 4.

## 2. Computational details

The density functional theory (DFT) calculations are carried out using the Vienna ab initio simulation package (VASP) (Perdew et al.(2004), Blöchl (1994)). The generalized gradient approximation (GGA), introduced by Perdew, Burke, and Ernzerhof (Kresse et al. (1999)) is used for the exchange correlation functional. The electronic wave functions expanded in a plane wave basis set with an energy cut off of 400 eV is used in the computation (Kresse et al.(1996), Perdew et al.(1997)). Brillouin zone integrations are performed using the Monkhorst-Pack procedure (Monkhorst and Pack (1976)). Both internal atomic coordinates and lattice parameters are fully relaxed, so that the convergence of Hellmann-Feynman forces was better than  $1\text{meV}\text{\AA}^{-1}$ . The self consistent total energy calculations are converged with energy difference less than 0.1meV. The zinc  $3d^{10}4s^2$ ; cadmium  $4d^{10}5s^2$  and oxygen  $2s^2 2p^4$  orbitals were included as valence electrons. The crystal structures of these transition metal monoxides MO (M=Zn, Cd) in the B1 (NaCl) B2(CsCl) and B3(ZB) phases are shown in Fig 1. In the B1 (NaCl) and B2 (CsCl) structures the metal and the oxygen atoms are positioned at (0,0,0) and (1/2,1/2,1/2) respectively; while in the B3 phase the metal atom is at (0,0,0) and the oxygen atom is at (1/4,1/4,1/4).

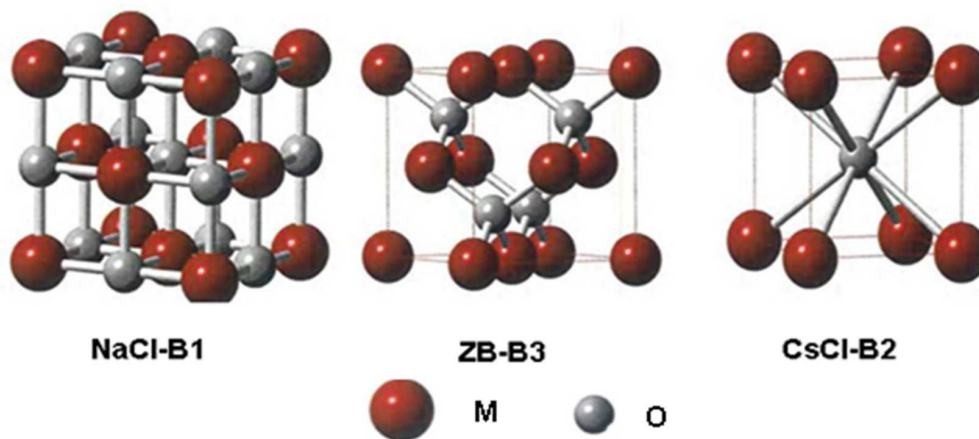


Fig 1. Unit cell of different phases of MO

## 3. Results and discussion

### 3.1. Structural and electronic properties

A full geometry optimization is initially carried out for the three cubic phases of the metal monoxides ZnO and CdO. The total energies for the various volumes are first computed. From the volume corresponding to the minimum energy, the optimized lattice parameters are calculated (Fig2a, Fig.2b).

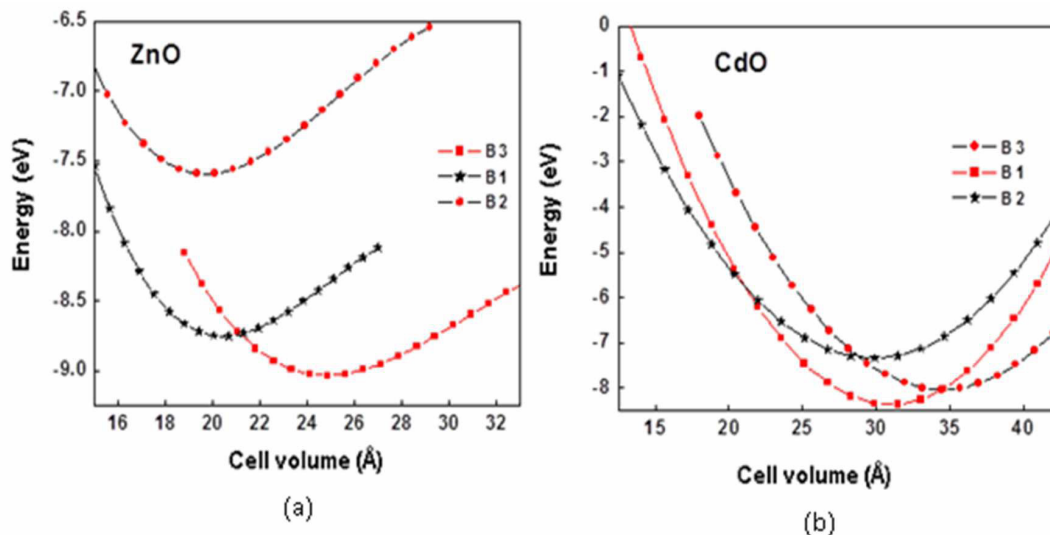


Fig.2 The total energies as a function of cell volume: (a) ZnO (b) CdO

These data are then fitted to the universal Birch-Murnaghan equation of state (Murnaghan(1994)) in order to find the bulk modulus  $B_0$  and its pressure derivative  $B_0'$ . In table 1, all these parameters are summarized together with the available experimental and other theoretical works. Obviously, the calculated values of the lattice parameters and the bulk modulus are in good agreement with the experimental and other theoretical values. The B3 phase of ZnO and the B1 phase of CdO are found to be the most stable phases at ambient conditions. The calculated cohesive energies also confirm B3 phase of ZnO and the B1 phase of CdO as most stable phases at ambient conditions.

Table 1. Calculated lattice parameters  $a$  (Å), equilibrium volume  $V_0$  (Å<sup>3</sup>), valence electron density  $\rho$  (electrons/ Å<sup>3</sup>), bulk modulus  $B_0$  (GPa) and its first derivative  $B_0'$  for the ZnO and CdO for three different structures.

	Phase	Approach	$a_0$	$V_0$	$\rho$	$B_0$	$B_0'$	$E_{coh}$
ZnO	B1	Present	4.33	20.3	0.88	222	4.0	6.2
		Exp <sup>a</sup> .	4.271			228	4.0	
		Others <sup>b</sup>	4.223			209	4.46	
	B2	Present	2.69	19.4	0.92	158	4.1	5.1
	B3	Present	4.61	24.6	0.73	116	4.3	6.5
		Exp <sup>c</sup> .	4.62			-	-	
Others <sup>b</sup>		4.52			168	4.6		
CdO	B1	Present	4.779	27.2	0.65	141	4.0	5.5
		Exp <sup>d</sup> .	4.770			147	4.2	
		Others <sup>e</sup>	4.771			130	4.13	
	B2	Present	2.94	25.4	0.70	123	4.2	4.7
		Exp <sup>d</sup>	2.936			128	4.6	
		Others <sup>e</sup>	2.939			114	4.66	
	B3	Present	5.149	34.1	0.52	103	4.1	5.4

<sup>a</sup>Karzel et al. (1996); <sup>b</sup>Amrani et al. (2006); <sup>c</sup>Oshikiri et al. (1999); <sup>d</sup>Liu et al. (2004); <sup>e</sup>Roberto et al. (2002).

Structural changes in the form of phase transition are studied for ZnO and CdO. The Gibb's free energy  $G = U(V) + PV - TS$  is the thermodynamic relation that governs the crystal stability at a given pressure and temperature. The first principles calculations are generally performed at zero Kelvin; hence the Gibb's free energy relation reduces to the enthalpy relation  $H = E(V) + PV$ , with the internal energy  $U(V) = E(V)$ . Fig.3a and Fig.3b, represents the enthalpy versus pressure plots for ZnO and CdO. For a given pressure, the phase with the lowest enthalpy is the most stable phase and the crossing of the curves indicates a first order pressure induced phase transition. The enthalpies of the two phases are equal at the transition pressure. From Fig.3a; we find that ZnO undergoes a phase transition from B3 to B1 at 11.2 GPa and From B1 to B2 at much higher pressure of 243.3 GPa. As for CdO, the phase transition occurs from B1 to B2 (Fig. 3b) at a pressure of 88.5, which is very close to the experimental value of 90.6 GPa reported by Liu et al. (2004).

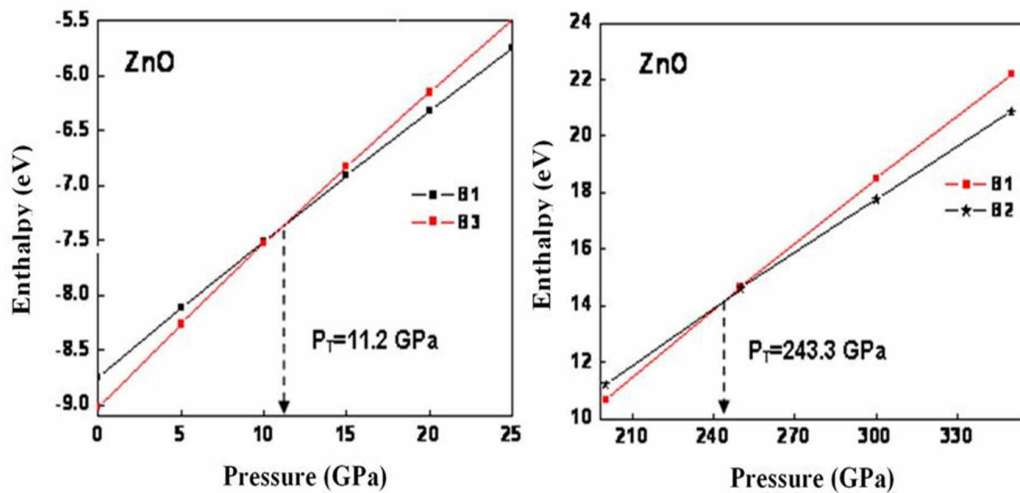


Fig.3 (a) The enthalpy as a function of pressure of ZnO

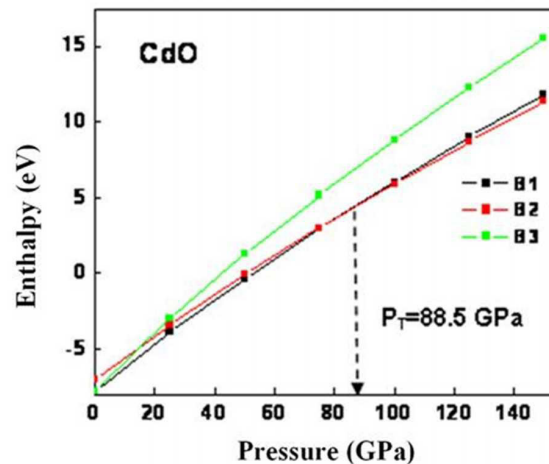


Fig.3 (b) The enthalpy as a function of pressure of CdO

The electronic band structure is an important property, providing information about the type of material – metal, semi-conductor or insulator. The electronic band structure changes if the composition or atomic arrangements are changed. As the B3 phase of ZnO and the B1 phase of CdO are the most stable phases at

ambient condition, the electronic band structures of ZnO (Fig 4a) and of CdO (Fig.4b) in these phases are analysed. The Fermi level is indicated by dotted horizontal line. The oxygen 2s states give rise to weakly dispersed bands below -15 eV in both the metal oxides. The Zn 3d states are located in the energy interval 4-5 eV below the valence band maximum and is separated by a large gap of around 12eV from the oxygen 2s states. The uppermost are mainly due to the hybridization of O 2p with Zn 3p states. The band structure (Fig.4a), further reveals that ZnO is a direct band gap semi-conductor, with a band gap of 0.47 eV. As for CdO, the deep low lying bands around -7 eV are due to the Cd 4d states. The bands just below the Fermi level are due to the hybridization of O 2p with Cd 4p states. From fig. 4, we find that CdO has an indirect band gap of -0.664 eV, and it is a semimetal, as its conduction energy band crosses the Fermi level at the  $\Gamma$ -point.

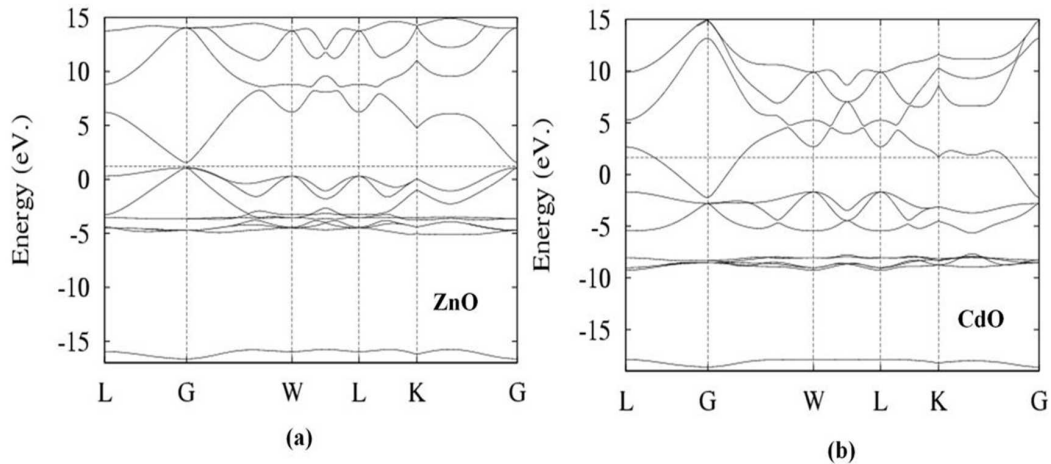


Fig.4 Electronic band structure at normal pressure: (a) ZnO (b) CdO.

### 3.2. Elastic Properties

The elastic constants are essential for applications related to mechanical properties of solids. The high pressure study of these constants is important to predict and understand the material response, strength and its mechanical stability. In order to obtain the mechanical stability description of these systems, a set of elastic constants is obtained from the resulting change in total energy deformation. The elastic constants  $C_{ij}$  are calculated within the total energy method, where the unit cell is subjected to a number of finite size strains along several strain directions (Nye (1957), Kalay et al. (2009), Xu et al.(1987)). The cubic lattices have three independent elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ). The calculated elastic constants are given in Table 2 for ZnO and CdO. Mechanical stability criteria for cubic crystal (Born and Huang (1956)) at ambient conditions is given by

$$C_{44} > 0, \quad C_{11} > |C_{12}|, \quad C_{11} + 2C_{12} > 0 \quad (1)$$

The mechanical properties such as Young's modulus ( $E$ ), shear modulus ( $G$ ) and Poisson's ratio ( $\nu$ ) are important physical quantities, especially for engineering applications. The Zener anisotropy factor ( $A$ ) measures the degree of anisotropy in the solid structure. The value of  $A=1$ , represents completely elastic isotropy, while values smaller or larger than 1 measure the degree of elastic anisotropy. The hardness of the polycrystalline material can be investigated by computing the Lamé constants ( $\lambda$ ,  $\mu$ ), Kleinman parameter and micro hardness parameter ( $H$ ). Physically, the first Lamé constant ( $\lambda$ ) determines the compressibility of the material, while the second Lamé constant ( $\mu$ ) reflects its shear stiffness. These parameters are calculated using the following eqns [Wu et al. (2007)]

$$\nu = \frac{C_{12}}{C_{11} + C_{12}} \quad (2)$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (3)$$

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)} \quad (4)$$

$$\mu = \frac{E}{2(1+\nu)} \quad (5)$$

$$\zeta = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}} \quad (6)$$

$$H = \frac{(1-2\nu)E}{6(1+\nu)} \quad (7)$$

All the calculated mechanical properties for ZnO and CdO with considered structures are presented in Table 2.

Table 2. Calculated elastic constants  $C_{11}, C_{12}, C_{44}$  (GPa), Young's modulus  $E$  (GPa), Shear modulus  $G$  (GPa), B/G ratio, Poisson's ratio  $\nu$ , Zener isotropy (A), Lamé constants ( $\lambda, \mu$ ), Kleinman parameter ( $\zeta$ ) and micro hardness parameter (H) for ZnO and CdO at ambient pressure.

	ZnO			CdO		
	B1	B2	B3	B1	B2	B3
C11	237.6	419.1	157.1	207.8	313.3	120.4
C12	147.8	38.4	114.7	106.3	58.15	94.3
C44	82.4	-58.7	64	54.9	-	38.5
B	177.73	165.3	128.83	140.13	17.99	103
G	64.58	-	41.14	53.20	143.2	24.97
E	172.81	-	111.55	141.67	-	69.31
B/G	2.75	-	3.13	2.63	-	4.12
A	0.42	-	0.47	0.349	-	0.35
$\nu$	0.33	-	0.35	0.33	-	0.38
$\lambda$	126.11	-	96.4	103.38	-	79.52
$\mu$	64.96	-	41.31	53.25	-	25.11
$\zeta$	0.72	-	0.81	0.63	-	0.84
H	28.80	-	18.59	23.61	-	11.55

Bulk modulus (B) and shear modulus (G) can measure the resistance of a material to volume and shape change respectively. From Table 2, it is found that the bulk modulus values obtained from the EOS fit are close to the values calculated using the elastic constants. The results (Table 2) indicate that both oxides are more inclined to resist the volume change than shape change. Materials with high Band G are likely to be hard materials. Young's modulus is a measure of stiffness of a solid, i.e., larger the value of Young's modulus, stiffer is the material. The computed results indicate that ZnO in B1 phase is the stiffest material than CdO. The Poisson's ratio measures the degree of directionality of the covalent bonds. The value of the Poisson's ratio is small ( $=0.1$ ) for covalent materials, whereas it is greater than or equal to 0.25 (Nye (1957)) for ionic materials. The Poisson's ratio of B1 phase of ZnO and CdO are the lowest, indicating that the M–O bonding is more directional in nature. The ratio of bulk modulus to shear modulus (B/G) is used to estimate the brittle or ductile behaviour of materials. A high B/G value is associated with ductility, while a low B/G value corresponds to the brittle nature. The critical value which separates ductile and brittle materials is about 1.75. The calculated values of B/G predict that ZnO and CdO are ductile in nature in the all phases. Also these

oxides are elastically anisotropic at ambient pressure. The calculated H values indicate that ZnO is the hardest material.

In this work the elastic constants at normal and high pressures are calculated to investigate the mechanical stability of ZnO and CdO in their stable phases. Now, there are three independent elastic constants -  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for the cubic structure. ZnO is stable in the B3 phase and transforms into the B1 at a pressure of 11.2 GPa, while CdO is stable in the B1 phase up to a pressure of 88.5 GPa and it transforms to the B2 phase at high pressures. The high pressure studies of the elastic properties are done only for these phases. The calculated values of elastic constants ( $C_{ij}$ ), Young's modulus, shear modulus, poisson's ratio, B/G ratio, anisotropic factor and hardness for ZnO and CdO at ambient pressure are given in Table.2. The negative value of  $C_{44}$  indicates CdO in the B2 phase is highly unstable at ambient condition. However the elastic constants are found to increase with pressure for its stable phase as expected. The variation of the various moduli for the stable phase of ZnO and CdO is shown in fig 5 (a-b).

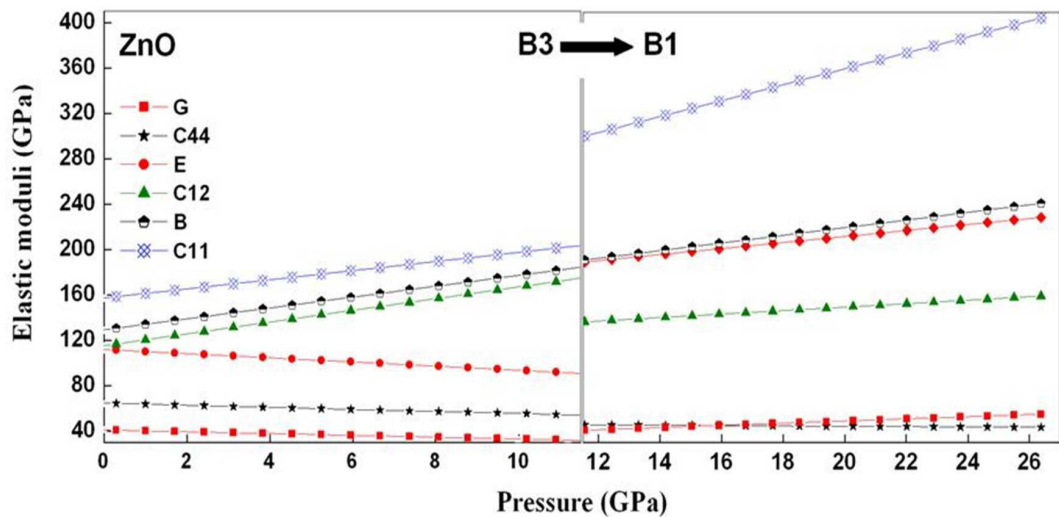


Fig. 5 (a) Pressure dependence of elastic moduli of ZnO.

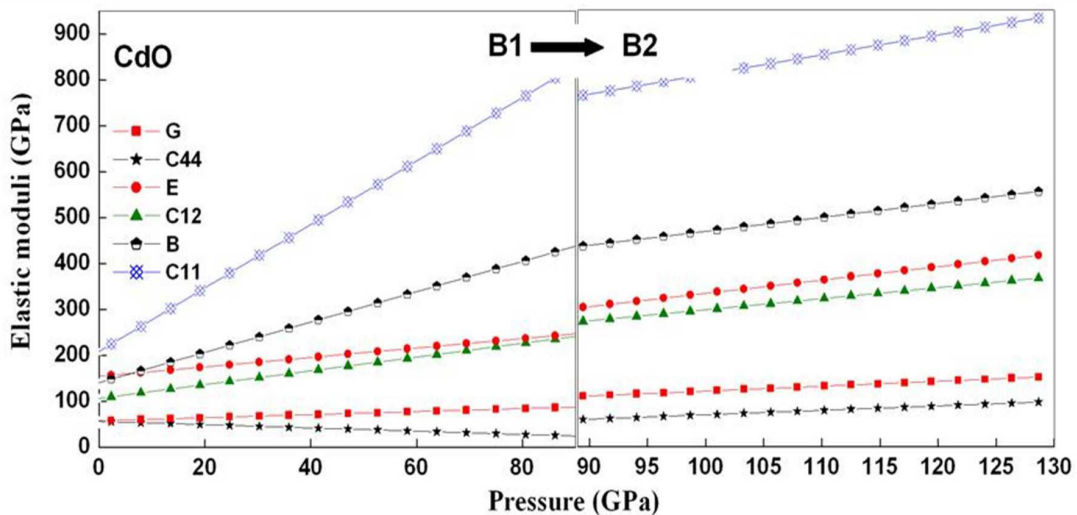


Fig. 5 (b) Pressure dependence of elastic moduli of CdO.



It is worth to notice that  $C_{11}$  increases rapidly with pressure for the B1 phase of both the metal monoxides. The elastic constant  $C_{11}$  represents the elasticity in length. A longitudinal strain produces a change in  $C_{11}$ . The elastic constants  $C_{12}$  and  $C_{44}$  are related to the elasticity in shape, which is a shear constant. A transverse strain causes change in shape without change in volume. Therefore,  $C_{12}$  and  $C_{44}$  are less sensitive to pressure as compared to  $C_{11}$ . The Bulk modulus  $B$ , Young's modulus  $E$  and shear modulus  $G$  increase monotonously with pressure. This indicates that these oxides resist both volume and shape changes. The mechanical stability conditions also depend on the elastic constant values. The elastic stability criteria for cubic crystals under pressure are:  $K = C_{11} + 2C_{12} + P > 0$ ;  $K_1 = C_{44} - P > 0$ ;  $K_2 = C_{11} - C_{12} - 2P > 0$ . The stable phase of CdO obeys elastic stability criteria suggesting its mechanically stable below its transition pressure.

#### 4. Conclusion

The band structure, phase transition and elastic properties of ZnO and CdO were studied in detail using the first principles calculations. The calculated lattice parameters were in accord with the experimental values. Our results indicate that at normal pressure ZnO is stable in the B3 phase; while CdO is stable in the B1 phase. A pressure induced phase transition occurs from B3 to B1 at a pressure of 11.2 GPa and then from B1 to B2 at a higher pressure of 243.3 GPa in ZnO; whereas in CdO it is from B1 to B2 at a pressure of 88.5 GPa, which is in agreement with the experimental value. The ground state band structure calculations reveal that the stable B3 phase of ZnO is a direct band gap semiconductor, while the stable B1 phase of CdO is a semimetal. The pressure dependent study of the elastic constants of ZnO and CdO indicate that they are mechanically stable for the structures studied. Our calculated results indicate that ZnO and CdO are ductile in nature and the ZnO is the hardest material. The first principles study has thus helped us to explore the behavior of ZnO and CdO at extreme conditions.

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