

First principles calculations of the ground-state properties and structural phase transformation in CdO

Roberto J. Guerrero-Moreno and Noboru Takeuchi

Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Apartado Postal 2681, Ensenada, Baja California, 22800, México

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We have studied the structural properties of CdO in the rock-salt (sodium chloride), cinnabar, orthorhombic *cmcm*, cesium chloride, nickel arsenide, zinc blende, and wurtzite structures using first-principles total energy calculations. Rock-salt is the calculated ground state structure with $a=4.77$ Å, $B_0=130$ GPa. The experimental lattice constant is $a=4.704$ Å. There is an additional local minimum in the wurtzite structure. Within the precision of the calculations, its total energy is the same as the energy of the rock-salt structure. At high pressure (~ 89 GPa), our calculations predict a phase transformation from the NaCl to a CsCl structure.

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I. INTRODUCTION

Group IIB–group VIA semiconductors have been extensively studied^{1–10} because they are considered important technological materials. Similar to the case of group IIIA–group VA semiconductors,^{12–18} they crystallize in either the zinc blende or the wurtzite structure. The difference in total energy between these two phases is very small and sometimes both of them can be obtained experimentally. Wurtzite and zincblende are structurally similar [they differ only by the stacking in the (111) direction, and atomic coordination in either zinc blende or wurtzite is exactly the same through the second neighbor]. These tetrahedrally coordinated materials present several high pressure structures. Recent experiments and first principles calculations have shown that the transition sequence for CdTe is zinc blende→cinnabar→rocksalt→orthorhombic *cmcm* phase.^{4–6} In the case of CdSe, the cinnabar phase transforms directly in to the *cmcm* phase, skipping the rock-salt structure. For ZnTe the cinnabar structure is not obtained, and the experimentally observed transition sequence is zinc blende→cinnabar→*cmcm*.⁷ For ZnSe, calculations found a sequence similar to the one for CdTe,⁶ but experiments have not observed neither the cinnabar structure, nor the *cmcm* phase.

Less is known about the high pressure behavior of group IIB oxides. First principles calculations have shown that ZnO also presents several high pressure structures: from the zinc blende structure it transforms to the rock salt and then to an eightfold-coordinated CsCl structure.¹⁰ To our knowledge, there are no studies of the high pressure behavior of CdO. At ambient pressure CdO differs from the other II-VI semiconductors: its ground state structure is neither wurtzite nor zinc blende, but it crystallizes in the rock salt (NaCl) phase.⁹ We have performed first principles total energy calculations to study the properties of CdO. In particular we wanted to see if some of the high pressure phases obtained in CdTe and/or CdSe were possible for CdO. We were also interested in checking the stability of CdO in rock salt with respect to the zinc blende and wurtzite structures. It was found that rock salt is indeed the ground state structure of CdO. There is an additional local minimum in the wurtzite configuration with

almost the same total energy. The existence of a metastable wurtzite phase is important in the fabrication of ternary compounds with Cd, O, and S, since the ground state configuration of CdS is wurtzite, and in the fabrication of multilayers of CdO and CdS. Very recently the formation of a CdO layer on CdS has been achieved experimentally. However in this case, the overlayer of CdO seems to have rock-salt structure.¹¹ At ~ 89 GPa, our calculations predict a high pressure phase transformation to a CsCl structure, similar to the predicted transition in ZnO. We have also found that the cinnabar structure is not stable for CdO, and the *cmcm* phase is less stable than the NaCl phase in the pressure region of interest.

II. METHOD

The calculations were performed in the framework of density functional theory. We have employed the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN97 code.²¹ The exchange and correlation effects were treated using the generalized gradient approximation (GGA).^{22,23} It should be noted that some of the calculated phases can be metallic. Therefore, a large number of integrating points over the irreducible Brillouin zone (BZ) was used: 72 k points for the rock salt, 84 for the CsCl structure, 76 for the NiAs phase, 70 for the wurtzite, 73 for the zinc blende, 67 for the cinnabar, and 84 for the orthorhombic *cmcm* phase. We have used muffin-tin radii of $R_O=1.5$ and $R_{Cd}=1.75$ a.u. for the O and Cd atoms, respectively, angular momenta inside the muffin-tin sphere up to $l=10$, and RKMAX=9. All these values were carefully tested as shown in Fig. 1, where we plot the energy as function of RKMAX,²⁴ number of k points, and number of angular momenta components inside the muffin-tin sphere. Differences in energy cannot be observed for the different ranges of k -point sampling and maximum number of angular momenta. With the choice of RKMAX=9, the relative stability of the different phases does not change. To compare the total energy of the NaCl and orthorhombic *cmcm* phase, we have used the same orthorhombic cell with the same k -point sampling for both calculations.

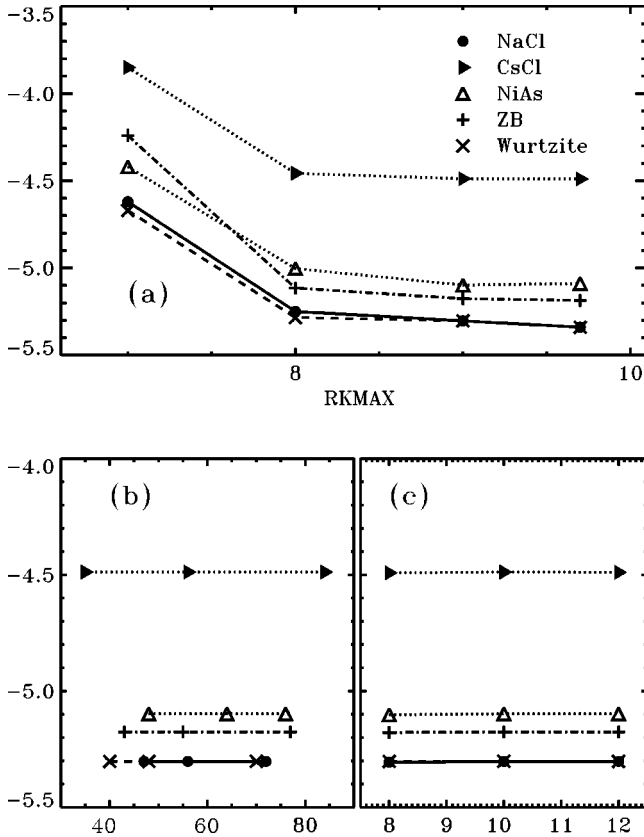


FIG. 1. Test of convergence of the total energy for the different phases. (a) RKMAX, (b) k -point sampling, (c) maximum l value for partial waves used inside atomic spheres.

III. STRUCTURAL PROPERTIES

Total energy versus volume data for the rock-salt, cinnabar, CsCl, NiAs, zinc blende, and wurtzite phases of CdO are shown in Fig. 2. Energies and volumes are per single CdO formula unit: there are two in a wurtzite and NiAs cell, three in the cinnabar cell and one in all the other cases. We have taken as the zero the sum of the energies of isolated neutral

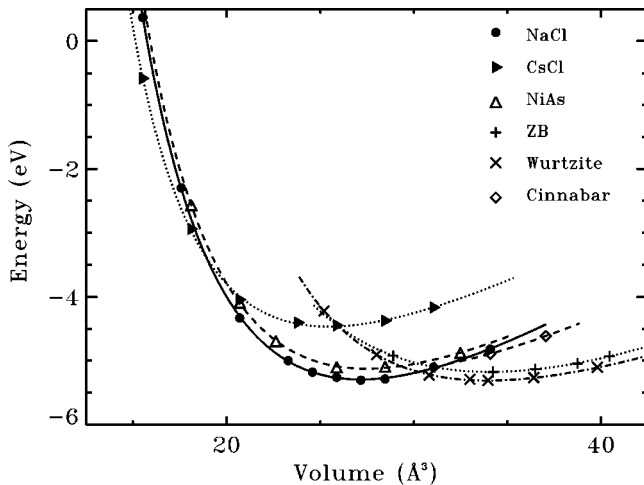


FIG. 2. Total energy (in eV per formula unit) versus the atomic volume (in \AA^3) for several structures of CdO.

TABLE I. Calculated structural properties of CdO in the rock-salt, cesium chloride, nickel arsenide, zinc blende, and wurtzite structures.

Structure	NaCl	CsCl	NiAs	zinc blende	wurtzite
a (\AA)	4.77	2.94	3.34	5.15	3.66
c/a			1.7		1.6
u					0.35
V (\AA^3)	27.15	25.41	27.46	34.07	34.10
B_0 (GPa)	130	114	116	82	86
B'_0	4.13	4.66	4.30	3.0	4.52
E_0 (eV)	-5.30	-4.47	-5.13	-5.18	-5.30

Cd and O atoms. Therefore, the absolute value of the energy at the minimum of each curve gives the cohesive energy of the corresponding CdO phase. The data is fitted to the Murnaghan equation of state for each phase. In this way, we can obtain the equilibrium lattice constant, the bulk modulus and other structural parameters (see Table I). In all cases, the fit is very good. To determine the most stable structure at finite pressure and temperature, the free energy $G = E + pV - TS$ should be used. Since the phase transformations reported for CdTe and CdSe do not depend on the temperature, we neglect the last term and work with the enthalpy $H = E + pV$. We employ seven crystal structures, and we cannot exclude the possible existence of other stable or metastable structures.

The rock salt is the calculated ground state with $a = 4.77 \text{ \AA}$, $B_0 = 130 \text{ GPa}$, and cohesive energy $E_0 \sim 5.3 \text{ eV}$. The experimental lattice constant is $a = 4.704 \text{ \AA}$, indicating a good agreement between theory and experiment. This result shows the usual trend of GGA: with respect to LDA, it over-corrects the lattice constant.

There is an additional local minimum in the wurtzite structure with almost the same total energy. The existence of a metastable wurtzite phase is important in the fabrication of ternary compounds with Cd, O, and S, since the ground state configuration of CdS is wurtzite, and in the fabrication of multilayers of CdO and CdS. This is similar to the case of MnTe: its ground state has a NiAs structure, but a metastable zinc blende structure can be stabilized during growth.²⁵

From Table I, we can observe that there is a large structure dependent variation of the bulk modulus from 82 up to 130 GPa. Bulk moduli of zinc blende and wurtzite phases are similar. As mentioned in the introduction, both phases are structurally similar, with individual atoms tetrahedrally coordinated, and very similar equilibrium volume. The bulk modulus in the rock-salt structure is larger than in the wurtzite and zinc blende phases, indicating a harder material. In this phase, atoms are six-fold coordinated and also the bonding is more ionic. A larger bulk modulus in the rock-salt phase than in wurtzite and zinc blende structures have been experimentally obtained and theoretically predicted in many semiconductors such as GaN,^{26,27} AlN,²⁸ InN, ScN,²⁹ ZnO,¹⁰ MgSe,³⁰ MgTe,³⁰ and others. Bulk modulus in the CsCl structure is smaller than in the NaCl phase. Although in the

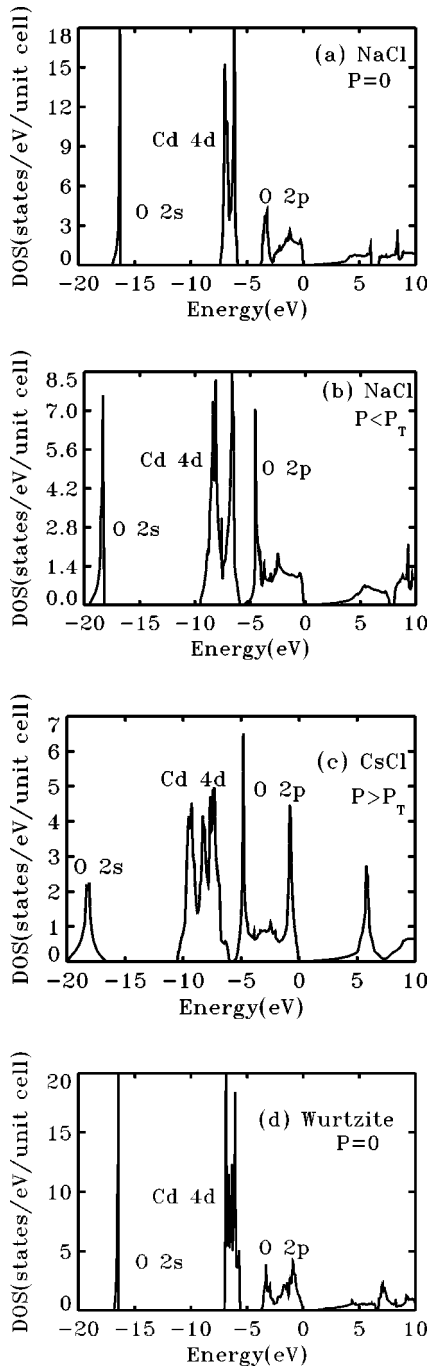


FIG. 3. Total density of states for CdO in (a) the rock-salt structure at $p=0$, (b) the rock-salt structure before the transition ($p < P_T$), (c) the cesium chloride phase after the transition ($p > P_T$), and (d) the wurtzite structure at $p=0$.

CsCl phase individual atoms are eight-fold coordinated, there is a reduction in the nearest neighbor distance. This kind of behavior, has also been obtained in ZnO,¹⁰ ScN,²⁹ MgSe,³⁰ MgTe,³⁰ and other semiconductors.

In Fig. 3 we can see that the curve corresponding to the NaCl crosses the curve of the CsCl structure, indicating a high pressure phase transition from the NaCl to the CsCl structure. The common tangent between the NaCl and CsCl curves determines the transition path between the two

structures. Because it is difficult to calculate accurate slopes from the common-tangent line, we have calculated $p(V) = -dE/dV$ to obtain the enthalpy $H = E + pV$ for each phase. The transition pressure is obtained from the enthalpy curve crossings. We have then inverted the expression

$p(V) = -dE/dV$ to obtain the respective volumes. We can predict the transition pressure to be ~ 89 GPa.³¹ At this pressure the enthalpies of both structures are equal. Across the transition, there is a volume reduction of about 6% from 19.5 to 18.3 \AA^3 . Similar transitions, from NaCl to CsCl structures have been observed experimentally and predicted theoretically in other compounds.^{10,19,20}

We have also checked the stability of the cinnabar and orthorhombic *cmcm* structures, two phases that have been recently observed in CdTe. The cinnabar phase is a hexagonal lattice composed of two concentric helices of cations and anions running along the *c* axis. Two internal parameters *u* and *v* determine the helix radii for cations and anions, respectively. Though hexagonal rather than cubic in symmetry it can be considered as a distortion of the NaCl arrangement. For $u=v=2/3$ and $c/a=\sqrt{6}$, the cinnabar phase coincides with the rock-salt structure. From Fig. 1 we can observe that for volumes larger than $\sim 32 \text{\AA}^3$, the cinnabar phase is indeed more stable than the rock-salt structure. However, for these volumes, the wurtzite structure has lower energy. The ground state of CdTe and CdSe is wurtzite and the cinnabar structure is an intermediate phase between the wurtzite and the NaCl phase. In the case of CdO, the ground state is rock-salt and the total energy of the wurtzite structure is very similar. Therefore, it is not surprising that the cinnabar structure is not energetically favorable for CdO.

The *cmcm* phase can also be considered as a deformation of the rock-salt structure in to an orthorhombic unit cell. Atomic positions are also displaced with respect to those of the rock-salt structure. For a given (001) plane of atoms, the cations and anions are shifted along the same (010) direction but by a different amount. Atoms in the adjacent planes are shifted in opposite direction. We have also optimized the atomic positions and the lattice parameters of orthorhombic *cmcm* structures for volumes 17, 19, and 20.7 \AA^3 . The unit cell of the orthorhombic *cmcm* structure has five parameters, *a*, *b*, *c*, and two internal parameters *y*(Cd) and *y*(O) describing the displacements of cations and anions. In our calculations the total energy is minimized with respect to all these parameters for a given volume. We have started with the experimental values of ZnTe,⁷ rescaled for the case of CdO. We first optimized the *c/b* ratio, keeping *a* fixed. Once the *c/b* ratio was optimized, we have proceeded to optimized the *a/b* ratio, keeping the *c/b* ratio fixed. After that we again check the *c/b* ratio to confirm that we are at the minimum. For each calculation in the optimization, we have fully relaxed the *y*(Cd) and *y*(O) atomic positions. For volumes $V = 19$ and $V = 20.7 \text{\AA}^3$, we ended up in the rock-salt structure. For $V = 17 \text{\AA}^3$ we found that the *cmcm* structure is ~ 0.06 eV more stable than the rocksalt. Structural parameters are slightly different from those of the rock-salt phase: $b/a = 1.016$, $c/a = 0.984$, $y(\text{Cd}) = 0.692$, and $y(\text{O}) = 0.190$. Although at this volume the *cmcm* structure has a lower energy

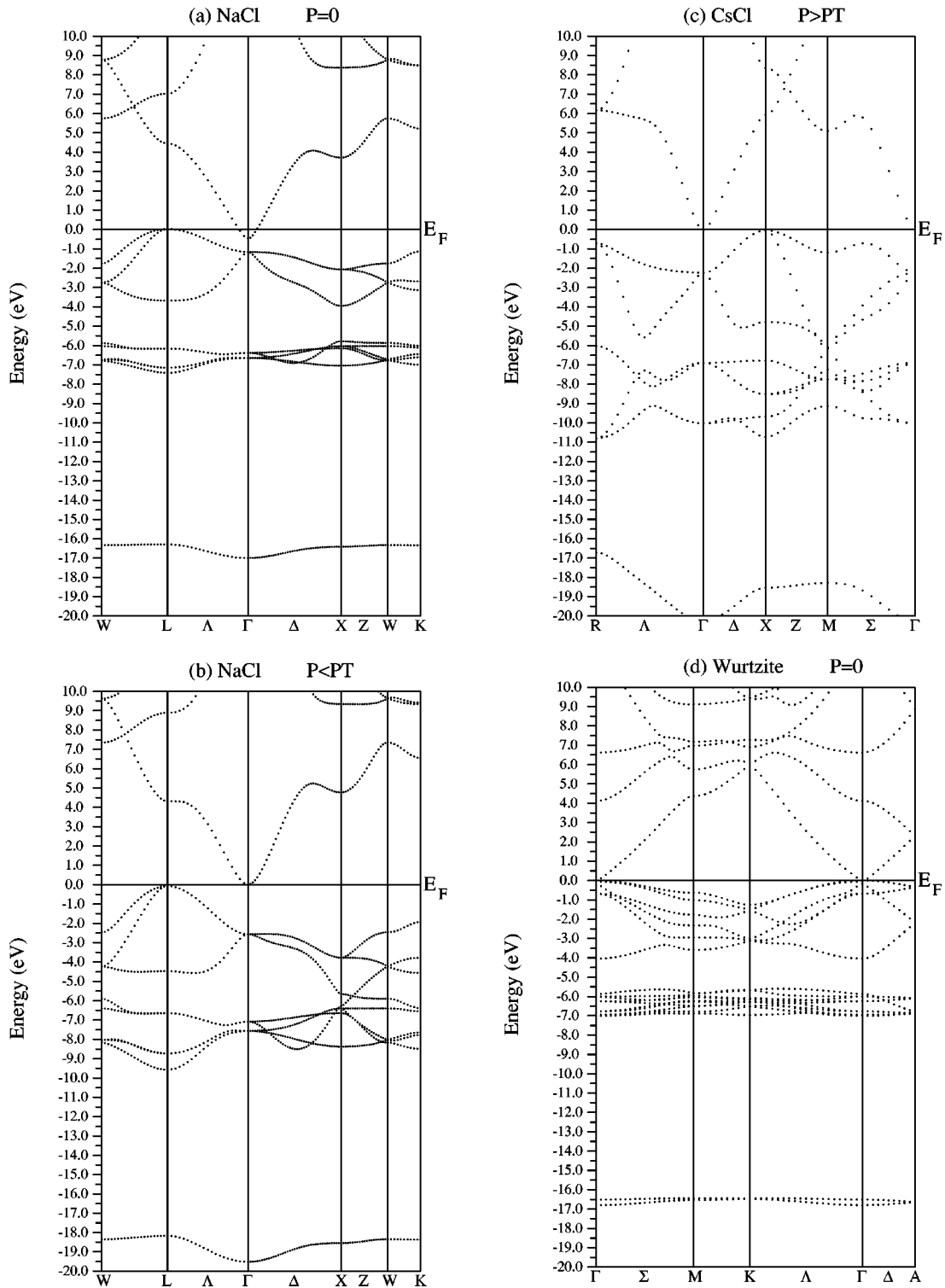


FIG. 4. Band structure for CdO in (a) the rock-salt structure at $p=0$, (b) the rock-salt structure before the transition ($p < P_T$), (c) the cesium chloride phase after the transition ($p > P_T$), and (d) the wurtzite structure at $p=0$.

than the rock salt, the *cmm* phase is not stable, since at this pressure the transformation to the CsCl phase has already occurred. The transition pressure from NaCl to orthogonal *cmm* phase has been predicted to be 12.0 GPa for CdTe and 36.5 GPa for CdSe.⁶ Therefore, it is understandable that this transition pressure is higher for the case of CdO.

IV. ELECTRONIC PROPERTIES

The knowledge of the electronic properties is crucial to the understanding of the stability of the different structures at different volumes. Two different factors determine the response of CdO to pressure: (a) changes in nearest-neighbor

distances and (b) changes in symmetry. At the phase transition from NaCl to CsCl phases, although the transition occurs to a structure of higher coordination, the nearest-neighbor distance lengthen even though the density is increased. These two factors are related to the band structure: the changes in nearest-neighbor bond lengths affect the overlaps and bandwidths of the bands, while the changes in symmetry affect the p - d hybridization and band repulsion. To see how these two factors affect the electronic properties, we present in Fig. 3 the total density of states (DOS) and in Fig. 4 the band structure for CdO at four different structures or densities: (a) the rock-salt phase at zero pressure, (b) the rock-salt structure just before the phase transition (P_T), (c) the CsCl phase after the transition, and (d) the wurtzite phase at zero pressure. Figure 3(a) shows the total DOS of CdO in the rock-salt structure at zero pressure. We can clearly observe the peaks corresponding to the O $2s$, O $2p$, and Cd $4d$ bands. Upon compression of the rock-salt phase of CdO [Fig. 3(b)], the upper valence bands broaden greatly, there is an increase in the splitting of the Cd $4d$ peak, and the O $2s$ band moves down in energy and broadens too. There is also some mixing of the Cd $4d$ and O $2p$ states. With the rock salt \rightarrow CsCl transition, a peak corresponding to the O $2p$ states appear near the valence band maximum. The structure of the Cd $4d$ states heavily hybridized with O $2p$ states and the O $2s$ states broaden further and shift up in energy. In Fig. 3(d), we show the total DOS of the wurtzite phase at zero pressure. As in the rock-salt structure at zero pressure, the O $2s$, O $2p$, and Cd $4d$ peak are clearly resolved, but they are narrower and shifted up in energy.

The band structures provide more information of the electronic properties. Figure 4(a) shows the band structure of CdO in the rock-salt structure at zero pressure. There is a small overlap between the conduction and valence bands of ~ 0.5 eV, and a direct bandgap of ~ 0.7 eV at Γ . Experimentally, it has been reported indirect bandgaps at 0.8 and 1.09 eV (Ref. 32) and a direct bandgap of ~ 2.3 eV. These values indicate that our conduction band minimum is too low by ~ 1.5 eV. Our calculations were performed using the density functional theory (DFT) and it is well known that calculations done with DFT give excited states too low in energy. Figure 4(b) shows the band structure of CdO in the rock-salt structure before the phase transition. As in the total DOS, there is a broadening of the upper Cd $4d$ and O $2p$ bands, with some intermixing between them. The conduction band minimum (CBM) is shifted up in energy, resulting in an almost zero indirect bandgap. Considering that at zero pressure, the CBM is ~ 1.5 eV too low in energy, and using the same shift for the high pressure structure, we expect an indirect bandgap of ~ 1.5 eV. With the rock-salt \rightarrow CsCl phase transition, the bandgap remains almost unchanged [see Fig. 4(c)] but the Cd $4d$ and O $2p$ states are completely hybridized and can not be disentangled. With increasing pressure (not shown), the band gap increases even more. Figure 4(d) shows the band structure of CdO in the wurtzite structure at zero pressure. We observe a zero bandgap, but

this time the valence band maximum (VBM) and the CBM are both at the Γ point, indicating a direct band gap. Assuming that the correction of the CBM is approximately independent of structure we estimate the gap to be ~ 1.5 eV. In the wurtzite structure, we observe that the valence band is very wide at the Γ point. In the rock-salt structure, the valence band is very narrow at the Γ point. As mentioned before, the response of the CdO band structure to compression and changed atomic coordination depends on the change in nearest-neighbor distances and changes in symmetry. As the neighboring atoms get closer together due to the compression, the wave functions overlap more strongly, producing an increase in the dispersion of the bands in k space and therefore an increased in the bandwidths along the energy axis. When there is a phase transition to a structure with higher coordination, the nearest-neighbor distance is increased even though there is an increase in density. The behavior of the bandwidths of the rock salt and CsCl phase reflects these considerations. Differences in the bandwidths of rock salt and wurtzite structures at the Γ point can be understood by band repulsion between Cd $4d$ and O $2p$ states. When the symmetry permits hybridization of the Cd $4d$ and O $2p$ bands, there is a repulsion between them, which pushes the anion $2p$ states upwards. In the tetrahedrally coordinated wurtzite phase this repulsion is present throughout the Brillouin zone, but in the cubic rock-salt structure it is suppressed near the Γ point as a result of the inversion symmetry. As a consequence, the O $2p$ bands are repealed upwards near the zone boundaries but not at the zone center. This is also the reason why in the rock-salt and CsCl phases, the VBM occurs at the zone boundary

V. SUMMARY

In summary, we have performed first principles total energy calculations of CdO in the rock-salt, cesium chloride, nickel arsenide, zinc-blende, orthorhombic $cmcm$, cinnabar, and wurtzite structures. The rock salt is the ground state configuration, but a second local minimum in a wurtzite structure is found. Within the precision of our calculations, both structures have the same total energy. The calculated lattice constant is in very good agreement with experimental results. Different from CdTe and CdSe, our calculations do not support the existence of stable orthorhombic $cmcm$ or cinnabar structures. Instead, they show the possibility of a phase transformation to a cesium chloride structure at ~ 89 GPa. Although the predicted transition pressure is high, we hope this calculations stimulate experimental work of CdO at high pressures.

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