Electronic structure of the rocksalt-structure semiconductors ZnO and CdO

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ZnO, which normally occurs in the hexagonal wurtzite structure, can be transformed to the cubic rocksalt (NaCl) structure by the application of high pressure; this cubic phase has been reported to be metastable at atmospheric pressure. The band structure of this phase is calculated by the *ab initio* correlated Hartree-Fock method. Not surprisingly, the band structure of rocksalt ZnO is very similar to that of CdO, which has the same crystal structure; we present a band-structure calculation for CdO, which we believe is more accurate than any in the literature. A hallmark of these band structures is that the valence-band maximum is not at the center of the Brillouin zone, in contrast to the situation in tetrahedrally coordinated II-VI semiconductors. We confirm by direct calculation that this peculiarity of the band structure is a consequence of the hybridization of oxygen $2p$-derived orbitals with Zn $3d$ or Cd $4d$ states, combined with octahedral point symmetry.

The IIB-VIA binary compound semiconductors are an important group of technological materials. Most of them crystallize in either the cubic zinc-blende or the hexagonal wurtzite structure (or both) where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa. This tetrahedral coordination is typical of sp^3 covalent bonding, but these materials also have a substantial ionic character, as indicated by the Phillips ionicities[1] shown in Table I. The most ionic IIB-VIA compound, CdO, forms only in the rocksalt (NaCl) structure which is more typical of ionic insulators. It is well known that tetrahedrally coordinated materials tend to transform under pressure to higher (usually octahedral) coordination, with the transition pressure decreasing as ionicity increases.[2] These transition pressures can be predicted from a common-tangent construction based on theoretically calculated total-energy curves for the structures of interest (for example, zinc blende and rocksalt). Such *ab initio* total-energy studies have been carried out quite extensively for GaAs (Ref. 3) and MgO,[4] and to some extent for IIB-VIA compounds[5] also. However, the actual band structures of these high-pressure phases have received little attention, especially for the IIB-VIA compounds.

More than 20 years ago it was reported[6] that ZnO transforms to the rocksalt structure at a pressure in the neighborhood of 95 kbar (9.5 GPa). The high-pressure phase was found to be metastable at lower pressure, persisting for long periods of time even at ambient pressure as long as the temperature was not too high. Although this metastability makes the phase readily accessible to experiment, very little data on it are available. We therefore undertake a theoretical study to learn more about rocksalt ZnO. The present work will concentrate on calculation of the band structure, determination of the origins of its salient features, and comparison to the band structure of CdO. In future work we plan to study the energetics of the phase transformation under pressure and to extend our study to other compounds in the same group.

We will calculate the band structure of rocksalt ZnO by the all-electron local-orbitals Hartree-Fock method,[7] with long-range correlation effects included by means of the virtual-polaron approximation[8] and short-range

TABLE I. Ionicities of IIB-VIA semiconductors, after Phillips (Ref. 1). Equilibrium ambient-pressure crystal structures are indicated by Z for zinc blende, W for wurtzite, and R for rocksalt. Experimental pressures for the transition from the wurtzite or zinc-blende phase to the rocksalt phase are tabulated in Ref. 2.

Compound	Ionicity	Structure	Transition pressure (kbar)
ZnO	0.616	W	95
ZnS	0.623	Z, W	180
ZnSe	0.676	Z, W	125
ZnTe	0.546	Z	110
CdO	0.785	R	<0
CdS	0.685	Z, W	25
CdSe	0.699	W	32
CdTe	0.675	Z	28

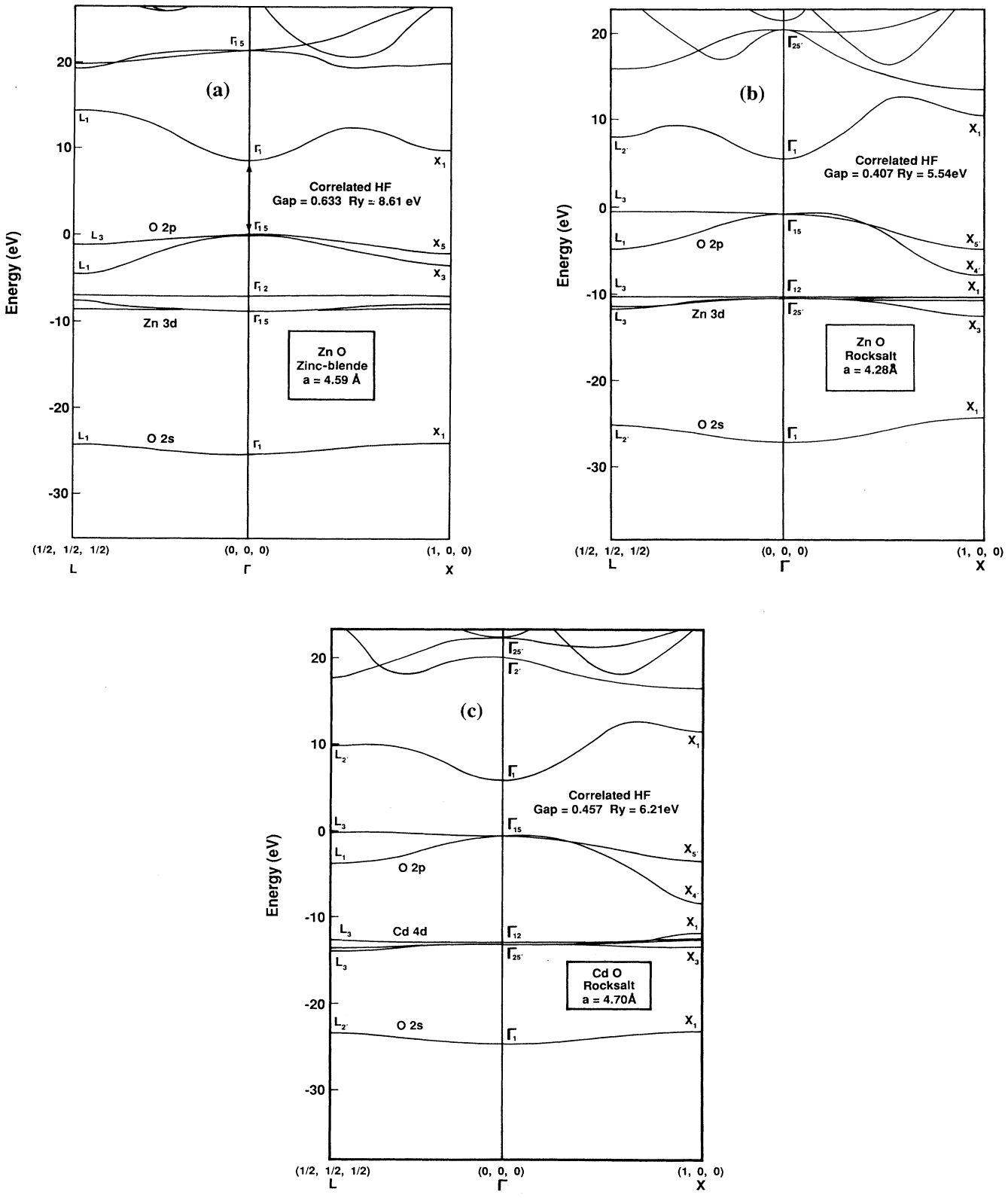

FIG. 1. Correlation-corrected Hartree-Fock band structure of (a) ZnO in the zinc-blende structure, (b) ZnO in the rocksalt structure, (c) CdO in the rocksalt structure. The symmetry classifications in (a) differ from those in (b) and (c) because of the different point symmetry of the two crystal structures.

correlation corrections obtained by a cluster orbital relaxation approximation.[9] This approach has previously been found to yield very accurate valence bands (including those derived from cation d orbitals) for ionic insulators and polar semiconductors.[10] The inclusion of correlation effects also largely corrects the well-known tendency of Hartree-Fock theory to produce band gaps much larger than experiment, though for semiconductors the principal gap remains a few eV too large. The latter error tends to remain constant across groups of similar compounds, much like the familiar band-gap error (of the opposite sign) that occurs in local-density theory (which also seriously underestimates the binding energy of cation d orbitals.)

The virtual-polaron approximation uses the optical dielectric constant ϵ_∞ as an input. In principle this quantity could be calculated self-consistently from the joint density of states of conduction and valence bands, but in practice we take its value from experiment; it is not, however, in any way adjusted to produce a particular value for the band gap or other results, so our procedure is still essentially *ab initio*. No experimental results are available for ϵ_∞ in compressed or rocksalt-structure ZnO, so we estimate its value from the Clausius-Mossotti relation[11] taking into account the change in density from the usual equilibrium low-pressure phase. In ZnO the latter actually has the wurtzite structure, but we will make the approximation of treating it in the zinc-blende structure. This facilitates comparison between the bands corresponding to the fourfold- and sixfold-coordinated structures, since the zinc-blende and rocksalt structures share the same Bravais lattice (fcc) and hence the same Brillouin zone. It also ensures similarity of convergence parameters since the number of atoms per primitive cell is kept the same (though the cell volume of course changes.) A large number of both experiments and calculations indicate that major features like band gaps and bandwidths typically differ by only a few hundredths of an eV between zinc-blende and wurtzite modifications of the same semiconductor, so this is not a severe approximation.

The reported lattice constant[6] a of rocksalt ZnO at a pressure of 105 kbar is 4.116 Å, while at ambient pressure its lattice constant has expanded to 4.280 Å. The equivalent zinc-blende lattice constant of the wurtzite phase at ambient pressure is 4.593 Å. The correlated band structures of the ambient-pressure zince-blende[10] and rocksalt phases are shown in Fig. 1, along with the band structure of CdO which we will discuss below. For reasons of space we include only the ΓL (Δ) and ΓX (Σ) high-symmetry lines in Fig. 1, with some additional points of the rocksalt ZnO band structure shown in Fig. 2. Numerical values for the main features of these bands are given in Table II, and densities of states (DOS) are plotted in Fig. 3. A striking feature associated with the change from tetrahedral to octahedral coordination is the shift of the valence-band maximum away from the Γ point, so that the gap becomes indirect. Broad maxima appear along the ΓL and ΓK lines, with a very slight maximum also appearing along ΓX near Γ. The valence-band maximum is located near the point $(4\pi/a)(0.30,0.30,0)$. Another significant difference between the rocksalt and zinc-blende band structures is in the form of the d-electron bands, which are very narrow near Γ and wider elsewhere in the rocksalt case, but of approximately constant width in zinc blende.

For purposes of comparison we have also calculated the band structure of CdO, which occurs experimentally

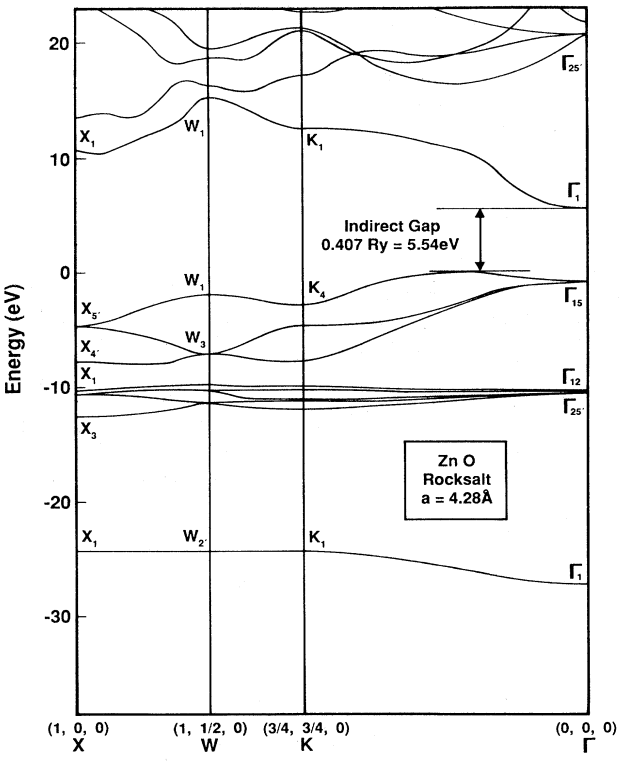

FIG. 2. Correlation-corrected Hartree-Fock band structure of ZnO in the rocksalt structure for some additional directions in reciprocal space.

TABLE II. Principal features of the electronic structure of rocksalt ZnO in our correlated Hartree-Fock calculation.

Feature	Symmetry	Energy (eV)
Direct gap	Γ_{1c}-Γ_{15v}	6.54
Indirect gap	Γ_{1c}-$\Sigma 4v$	5.54
Upper valence-band width	Σ_{4v}-Z_{3v}	8.08
Position of Zn 3d	Γ_{15v}-Γ_{12d}	9.49
Maximum width of Zn 3d	X_{1d}-X_{3d}	2.35
Minimum width of Zn 3d	Γ_{12d}-$\Gamma_{25'd}$	0.15
Total valence-band width	Σ_{4v}-Γ_{1v}	26.24
O 2s bandwidth	X_{1v}-Γ_{1v}	2.39

only in the rocksalt structure. Our results for the O-derived valence bands are very similar to those of Boettger and Kunz,[12] who used essentially the same methods for everything except the long-range correlation correction, which they estimated phenomenologically. However, even at the uncorrelated level our results for the direct band gap and Cd $4d-O2p$ valence-band separation disagree with theirs. We believe this may be due to

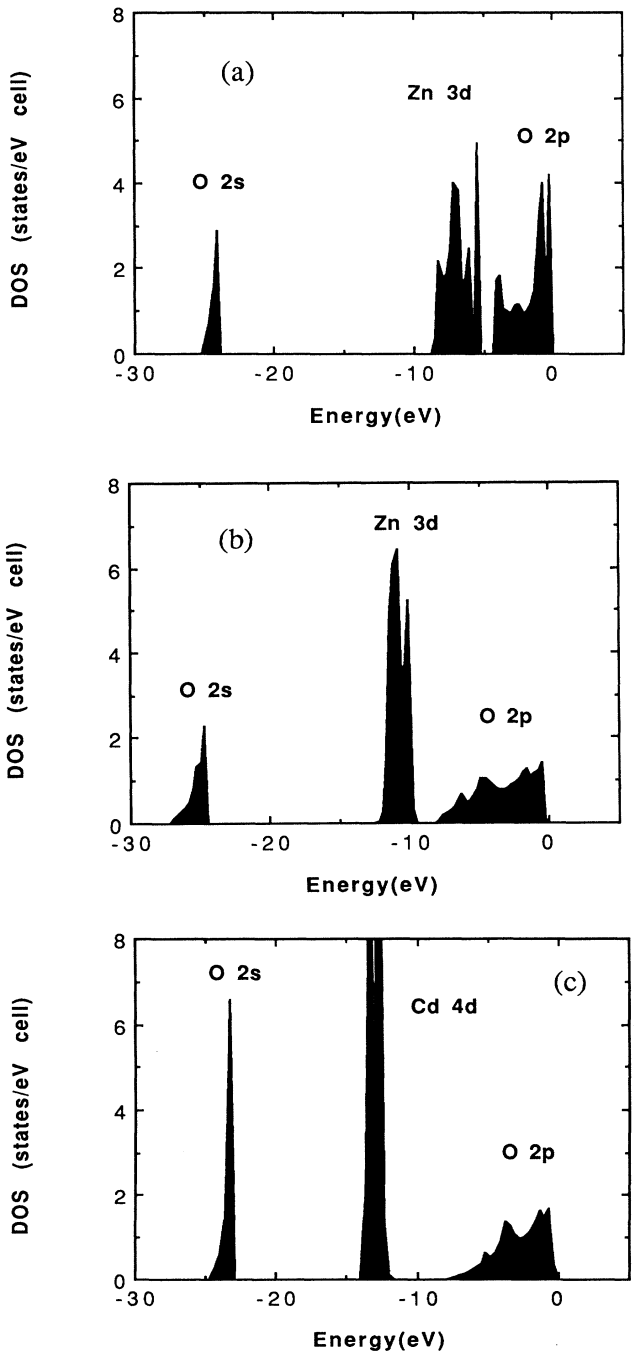

FIG. 3. Total density of states for (a) zinc-blende ZnO, (b) rocksalt ZnO, (c) rocksalt CdO.

an incorrect Coulomb potential term (the so-called residual Madelung depth) in the earlier work. Table III contains a comparison of our results for CdO with earlier theoretical work[13–15] and with experiment.[16,17] Our band structures for rocksalt ZnO and CdO are extremely similar, as Fig. 1 shows.

This similarity, and the differences from the zinc-blende case, can be understood in terms of the effect of the point symmetry of the ion sites on the interband hybridization of electron states. If allowed by symmetry, the Zn $3d$ or Cd $4d$ levels will hybridize with the O $2p$-like states at the top of the valence band. This hybridization produces a repulsion[18] between the two types of state, so that the top of the valence band is raised in energy. In zinc-blende-structure materials this hybridization is possible throughout the Brillouin zone, while the higher (octahedral) point symmetry in rocksalt-structure crystals does not allow p-d mixing at the Γ point, but does allow it elsewhere in the zone. As a result, away from Γ the upper valence bands are repelled upward, but at Γ they are not, so that valence-band maxima move away from Γ, an effect first discussed in connection with an early semiempirical calculation[15] on CdO. The behavior of the Zn $3d$ bands is also a consequence of p-d hybridization, the width of the d-band manifold being approximately proportional to the strength of the band interaction. It should be noted that our results for the Cd $4d$ binding energy in CdO agree well with experimental data;[16] the underestimate of this energy in Refs. 13–15 is probably due to the use of charge densities and potentials which were not calculated self-consistently in the crystalline environment.

We have undertaken further calculations to separate the effects of the changes in coordination and density associated with the transition from zinc blende to rocksalt, and to directly evaluate the effects of p-d hybridization. To see the effect of a change in density alone, we have calculated the band structure of zinc-blende ZnO with the same lattice constant (hence the same density) as rocksalt ZnO at ambient pressure. The resulting bands are much more similar to those of uncompressed zinc-blende ZnO than to those of the rocksalt phase. In particular the valence-band maxima along the ΓL and ΓK lines disappear. We have also attempted to directly determine the effects of p-d hybridization in rocksalt ZnO by "freezing out" the interaction of the bands through the use of an artificially large Slater exponent in the basis wave functions used to represent the Zn $3d$ orbitals. This procedure leads to an O $2p$-derived upper valence band for rocksalt ZnO that is similar to the usual upper valence band of zinc-blende-structure materials in that the valence-band maximum returns to its familiar location at the Γ point, confirming that p-d repulsion is the source of the anomalous valence-band structure in rocksalt IIB-VIA compounds. (Indeed, in IIA-VIA compounds, which almost always have the rocksalt structure but lack d orbitals near the upper valence band, the valence-band maximum is always at Γ.)

Since our Hartree-Fock (HF) method tends to overestimate band gaps, it is desirable to make some estimates of what the gap of rocksalt-structure ZnO would be in an

TABLE III. Present results for the electronic structure of CdO, compared with earlier theoretical results and experimental data.

Feature (eV)	Present	Ref. 12	Ref. 15	Ref. 13	Ref. 14	Expt.
Direct gap	6.56	0.8	2.4	1.8	2.4	2.3[a]
Indirect gap	6.07	0.4	0.8	1.3	1.2	0.8[a]
Upper valence-band width	8.20	7.5	4.1	1.9	4.8	
Position of Cd 4*d*	12.12	14.4	4.3	3.7	4.4	12.4[b]
Maximum width of Cd 4*d*	1.62	2.5	1.6	1.6	3.1	
Minimum width of Cd 4*d*	0.26	0.4	0.2	0.5	0.2	
Total valence-band width	24.41	23.3		16.0	18.4	
O 2*s* bandwidth	1.36	1.4		0.2	3.0	

[a]Reference 17.
[b]Reference 16.

exact calculation. The direct gap at Γ in CdO is known experimentally to be approximately 2.38 eV, while in our calculation it has the value 6.56 eV. Our calculated value of the same gap in rocksalt ZnO is 6.54 eV, just 0.02 eV lower. This suggests that the actual value of this direct gap in rocksalt ZnO should be 2.36 eV. The smallest indirect gap should still be about 1.0 eV lower, or 1.36 eV.

Metastable rocksalt-structure IIB-VIA compounds may be interesting for a number of reasons. The very flat valence-band maxima imply large hole effective masses and therefore unusual transport properties for *p*-type samples. The change in symmetry from the usual low-pressure structures may lead to altered selection rules which, together with the altered density and band hybridization, may lead to unusual optical properties. CdO has not proven to be technologically useful as a semiconductor due to difficulties in controlling stoichiometry and carrier density, but it is possible that rocksalt ZnO may behave better in this regard. It should also be noted that conditions analogous to high pressure (positive or negative) may arise in strained-layer epitaxy, so high-pressure phases may possibly be stabilized more easily than might otherwise be expected.

In summary, we have calculated the band structure of the metastable rocksalt-structure phase of ZnO, compared it to that of CdO, and accounted for its unusual characteristics. These are mainly a result of the hybridization of the Zn $3d-$ and O $2p-$derived bands in the presence of octahedral point symmetry, and provide one more illustration of the importance[18] of including such effects in calculations on IIB-VIA compounds.

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