

*Ab initio* energy bands for CdO\*J. C. Boettger<sup>†</sup> and A. B. Kunz*Department of Physics, University of Illinois at Urbana-Champaign,  
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*Ab initio* energy bands have been obtained for CdO via the self-consistent Hartree-Fock method. Correlation has been included in the form of polarization and relaxation corrections. The calculated band structure is compared to experiment and previous theoretical calculations. The density of valence states for CdO has been calculated for the theoretical band structure.

## I. INTRODUCTION

CdO is the only IIb-VI semiconductor which crystallizes into the rocksalt structure at standard pressure ( $a = 4.689 \text{ \AA}$ ). In spite of structural differences, the electronic properties of CdO are closely related to the properties of the other IIb-VI semiconductors. All of these compounds have occupied  $d$  bands which lie between the valence  $s$  and  $p$  bands. In CdO, the  $d$  bands are positioned about 12.4 eV,<sup>1</sup> below the center of the band gap. It has also been found that the absorption spectrum of CdO (Ref. 2) is similar to the absorption spectra of the other IIb-VI semiconductors, with one important exception. Unlike the tetrahedrally coordinated IIb-VI compounds, CdO is known to have at least two indirect optical transitions<sup>3,4</sup> with energies below the direct absorption edge, which is at 2.3 eV.<sup>4</sup> The energies of these indirect transitions are 0.8 and 1.1 eV.<sup>4</sup> In the absence of further experimental data, the absorption spectrum can only be interpreted by comparison with theoretical-band-structure calculations.

Three theoretical band structures have been published for CdO to date. The first of these was obtained in 1968 by Maschke and Rössler<sup>5</sup> (MR) with an empirically adjusted augmented-plane-wave (APW) calculation. A second APW calculation was published by Tewari<sup>6</sup> in 1973. The third theoretical result is an empirically adjusted linear combination of atomic orbitals (LCAO) structure obtained in 1973 by Breeze and Perkins<sup>7</sup> (BP). All three of these calculations indicate that the two indirect gaps are associated with valence-band maxima that lie away from the center of the Brillouin zone, on the  $\Sigma$  and  $\Lambda$  axes. The final state for these transitions is located at the center of the zone, as is the first direct gap. In all cases, the theoretical energies for the two indirect gaps and the lowest direct gap are in good agreement with experiment. However, there is disagreement as to which of the two indirect transitions has the lower energy. Where MR find that the lowest transition is  $L-\Gamma$ , both BP and Tewari associate the lower energy with the  $\Sigma-\Gamma$  transition. The calculations disagree

substantially as to the total number of indirect transitions below the direct absorption edge: Tewari's calculation suggests that there are, in fact, five. The three additional gaps result from valence-band maxima on the  $\Delta$ ,  $Z$ , and  $Q$  axes. The latter two gaps are particularly interesting because MR and BP did not obtain bands along those axes. Even above the direct absorption edge, there is disagreement as to what the correct ordering is for the optical transitions. Both of the APW calculations associate the first peak in the absorption spectrum above the direct edge with the  $L_3-L_2$  transition, while the LCAO results attribute the peak to the  $X_{3/2}-X_1$  transition.

It can be seen that there are significant discrepancies between the various theoretical calculations. It is difficult to resolve these discrepancies because none of the theoretical structures was obtained self-consistently, and all were empirically adjusted. Tewari<sup>6</sup> has suggested that more reliable results could be obtained by a self-consistent calculation. In this paper, the first self-consistent, *ab initio* energy bands for CdO are presented.

## II. METHOD OF CALCULATION

This investigation employed the Hartree-Fock (HF) plus correlation method, in the nonrelativistic limit. The methodology used has been described in detail by Kunz<sup>8</sup> and will only be briefly discussed here.

Self-consistent solutions for the HF equations were generated by use of the Adams-Gilbert local orbitals theory,<sup>9,10</sup> with the particular form of the local orbitals equation employed being the multicentered localization one developed by Kunz.<sup>8</sup> The local orbitals were expanded in an STO (Slater-type orbital) basis, and may be written as

$$\phi_{nlm} = Y_{lm}(\theta, \phi) \sum_j C_j^n N_{lj} r^{(n_{lj}-1)} e^{-Z_{lj}r},$$

where the  $n_{lj}$  and  $Z_{lj}$  are STO parameters, the  $N_{lj}$  are single STO normalization constants, and the  $C_j^n$  are

TABLE I. STO parameters and local orbital coefficients for Cd<sup>2+</sup>, in CdO.

$j$	$s$ basis		$p$ basis		$d$ basis	
	$n_{0j}$	$Z_{0j}$	$n_{1j}$	$Z_{1j}$	$n_{2j}$	$Z_{2j}$
1	1	49.177	2	22.222	3	16.809
2	2	38.000	3	11.172	3	9.606
3	2	20.710	3	9.024	4	5.700
4	3	18.450	4	6.167	4	2.700
5	3	10.473	4	4.139		
6	4	5.310				
$j$	$C_j^{10}$	$C_j^{20}$	$C_j^{30}$	$C_j^{40}$	$C_j^{21}$	
1	-0.995 97	-0.233 44	0.095 47	0.041 57	-0.967 75	
2	-0.078 42	-0.205 69	0.113 82	0.054 05	-0.195 92	
3	0.037 28	0.949 76	-0.499 05	-0.232 27	0.154 50	
4	-0.021 66	-0.027 06	-0.058 88	-0.034 12	-0.032 84	
5	0.004 98	0.020 24	0.851 63	0.491 43	0.011 01	
6	-0.000 89	-0.003 55	0.011 84	-0.835 91		
$j$	$C_j^{31}$	$C_j^{41}$	$C_j^{32}$	$C_j^{42}$		
1	0.508 69	0.196 65	0.290 57	-0.083 96		
2	-0.541 93	-0.210 06	0.955 30	-0.325 88		
3	-0.667 10	-0.399 27	0.054 20	0.611 20		
4	0.044 05	0.596 07	-0.006 23	0.716 37		
5	-0.024 36	0.634 42				

the expansion coefficients. The STO parameters and expansion coefficients obtained for CdO are given in Tables I and II. These local orbitals were then used as input for a tight-binding calculation of the occupied energy bands in the crystal. The conduction energy bands were calculated with a basis consisting of 27 plane waves that were orthogonalized to the occu-

TABLE II. STO parameters and local orbital coefficients for O<sup>2-</sup>, in CdO.

$j$	$s$ basis		$p$ basis	
	$n_{0j}$	$Z_{0j}$	$n_{1j}$	$Z_{1j}$
1	1	12.405	2	8.497
2	1	7.611	2	3.748
3	3	8.656	2	2.000
4	2	2.919	2	1.600
5	2	1.821		
$j$	$C_j^{10}$	$C_j^{20}$	$C_j^{21}$	
1	0.045 63	0.025 56	-0.005 48	
2	0.998 50	-0.316 81	0.214 26	
3	0.028 56	-0.026 12	-0.466 64	
4	0.009 70	0.481 62	0.858 08	
5	-0.002 75	0.816 30		

ried crystal eigenfunctions. Having thus obtained the HF solution to the band problem, correlation was included in the limit of polarization and relaxation corrections as discussed by Pantelides *et al.*<sup>11</sup> Finally, the density of valence states (DOVS) was calculated for the correlated energy bands as described by Mickish *et al.*<sup>12</sup>

Over the last year, this methodology has been applied to a wide range of compounds. Kunz has performed calculations for the alkali halides,<sup>8</sup> silver halides,<sup>13</sup> and transition-metal oxides.<sup>14</sup> Weidman and Kunz<sup>15</sup> have applied this methodology to the alkaline-earth oxides, sulfides, and selenides. In addition, the present authors have obtained energy bands for the tetrahedrally coordinated IIb-VI compounds, which will be published at a later date. In all cases where reliable HF bands already had been calculated, the present method has given good agreement with those prior results.

### III. RESULTS

The correlated energy bands for CdO are shown in Fig. 1. The symmetry notation employed is consistent with Bouckaert *et al.*,<sup>16</sup> and assumes that the origin is on the cation site. In Table III, the Hartree-Fock and correlated energies obtained are compared at the high-symmetry points in the Brill-

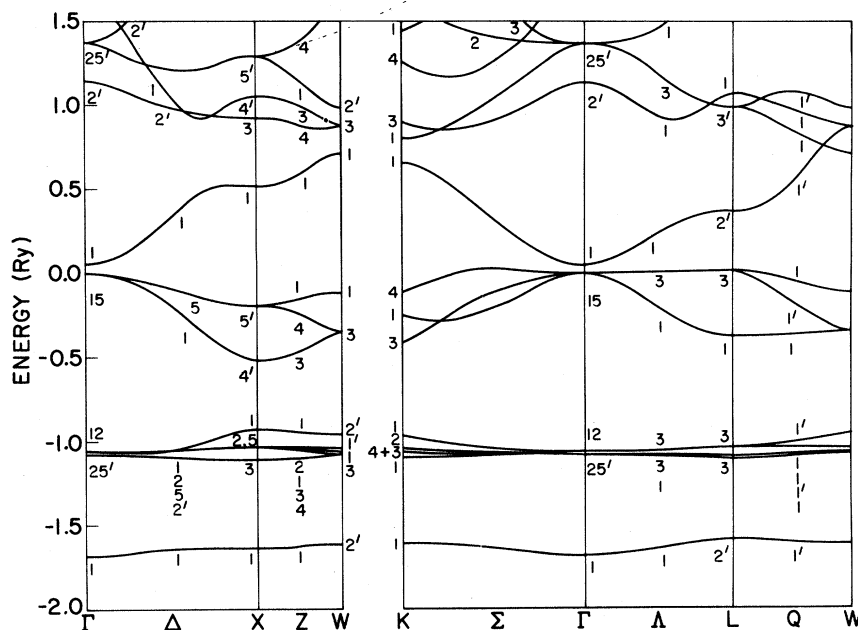


FIG. 1. Correlated energy bands are shown for CdO. All energies are in rydbergs.

loun zone. Contrary to Tewari's results,<sup>6</sup> we find only two indirect optical transitions below the first direct transition. The smallest gap is  $\Sigma_4-\Gamma_1$  with an energy of 0.4 eV. The second indirect transition is  $L_3-\Gamma_1$  with an energy of 0.5 eV. The direct gap at the center of the zone is 0.8 eV. All of these gaps are much smaller than the experimental gaps, with the largest error being 1.5 eV for the direct gap. The size of the error in the direct gap is not unreasonable, since the correlation correction to the band gap was about 10 eV. However, the fact that the error in the indirect gaps is not the same as the error in the direct gap makes it impossible to attribute any significance

to the ordering of the indirect gaps.

Other than the ordering of the two indirect gaps, the topology of the energy bands found in this investigation is in agreement with the results obtained by MR.<sup>5</sup> In particular, it is clear that the second and third direct transitions will be the  $L_3-L_2'$  and  $X_3'-X_1$  transitions with energies of 4.8 and 9.7 eV, respectively. These transitions are associated with peaks in the absorption spectrum at 5.8 and 8.0 eV.<sup>2</sup> Some of the difference between the theoretical transition energies and the experimental positions of the peaks may be due to relativistic effects which have not been included. In addition, it is unlikely that the peaks in

TABLE III. The Hartree-Fock and correlated energies in CdO are compared at the high-symmetry points in the Brillouin zone. All energies are in eV.

Symmetry point	HF energy	Correlated energy	Symmetry point	HF energy	Correlated energy
$\Gamma_1$	4.2	0.8	$K_1$	12.3	8.9
$\Gamma_{15}$	-6.8	0.0	$K_4$	-8.2	-1.5
$\Gamma_{12}$	-19.9	-14.4	$K_1$	-9.7	-3.4
$\Gamma_1$	-30.5	-22.9	$K_3$	-11.8	-5.7
$X_1$	10.5	7.1	$L_2'$	8.5	5.1
$X_{5'}$	-9.0	-2.6	$L_3$	-6.7	0.3
$X_{4'}$	-13.0	-7.1	$L_1$	-11.1	-5.1

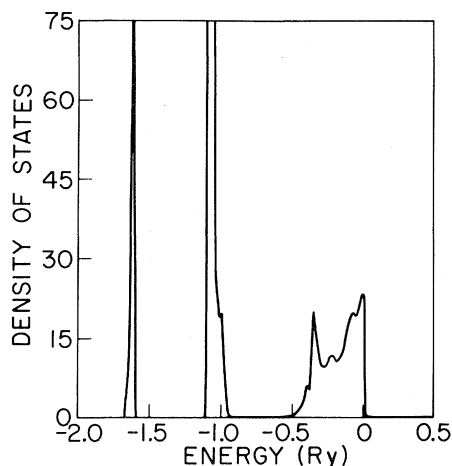


FIG. 2. Theoretical density of valence states is shown for CdO. All energies are in rydbergs.

the absorption spectrum occur precisely at the critical transition energies. Overall, the identification of the transitions should be correct although the energies do not exactly match.

The DOVS for CdO is shown in Fig. 2. Unfortunately, there are few experimental data available for the valence bands in CdO. The  $d$  bands are located about 15.2 eV below the center of the band gap. This compares to an experimental value of 12.4 eV,<sup>1</sup> i.e., the  $d$  bands are roughly 3 eV too low. All of the previous calculations place the  $d$  bands about 5 eV

too high. Not surprisingly, the valence-band widths found in this investigation are also larger than those found in the previous investigations by several eV. It is to be hoped that more experimental information will become available in the near future.

#### IV. CONCLUSION

It has been found that CdO is an indirect-gap semiconductor with only two indirect gaps below the direct absorption edge. Unfortunately, this calculation was not sufficiently accurate to resolve the dispute as to the correct ordering of the two indirect gaps. However, it is clear that the second and third direct transitions will be  $L_3-L_2'$  and  $X_5'-X_1$ . Thus it has been possible to resolve two of the three major discrepancies among the three prior calculations. To obtain the accuracy needed to determine the correct ordering of the indirect gaps via the HF plus correlation method, it would be necessary to include relativistic effects and treat correlation in a more rigorous fashion. Hopefully, the methodology needed to perform such a calculation will be forthcoming.

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<sup>1</sup>C. J. Vesely and D. W. Langer, Phys. Rev. B **4**, 451 (1971).

<sup>2</sup>J. L. Freeouf, Phys. Rev. B **7**, 3810 (1972).

<sup>3</sup>H. Köhler, Solid State Commun. **11**, 1687 (1972).

<sup>4</sup>F. P. Koffyberg, Phys. Rev. B **13**, 4470 (1976).

<sup>5</sup>K. Maschke and U. Rössler, Phys. Status Solidi **28**, 577 (1968).

<sup>6</sup>S. Tewari, Solid State Commun. **12**, 437 (1973).

<sup>7</sup>A. Breeze and P. G. Perkins, Solid State Commun. **13**, 1031 (1973).

<sup>8</sup>A. B. Kunz, Phys. Rev. B **26**, 2056 (1982).

<sup>9</sup>W. H. Adams, J. Chem. Phys. **34**, 89 (1961).

<sup>10</sup>T. L. Gilbert, in *Molecular Orbitals in Chemistry, Physics, and Biology*, edited by P. O. Lowdin and B. Pullman (Academic, New York, 1964).

<sup>11</sup>S. T. Pantelides, D. J. Mickish, and A. B. Kunz, Phys. Rev. B **10**, 2602 (1974).

<sup>12</sup>D. J. Mickish, A. B. Kunz, and S. T. Pantelides, Phys. Rev. B **10**, 1369 (1974).

<sup>13</sup>A. B. Kunz, Phys. Rev. B **26**, 2070 (1982).

<sup>14</sup>A. B. Kunz (unpublished).

<sup>15</sup>R. S. Weidman and A. B. Kunz (unpublished).

<sup>16</sup>L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 57 (1936).