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Local-density self-consistent energy-band structure of cubic CdS Alex Zunger* and A. J. Freeman

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of the orthogonalized-plane-wave (OPW) model, "'
independent theoretical studies on compounds made
of first-row atoms (diamond, ' boron nitride~a) and
photoemission studies on the core level. s of com-pounds containing 4d elements,

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have revealed
serious difficulties with the OP% representation.

These include (i) errors of the order of 1-3eV in the calculated P -like valence- and conduction-band
states of compounds made of first-row atoms due to convergence difficulties in the absence of a pseudopo-

tential cancellation for these l = 1 states""""; (ii)
spurious shifts of about 12 eV of the corelike 4d
levels in the course of the self-consistent treat-

ment'; and (iii) errors in excess of 6 eV in the lev-
el ordering of the cation 4dand anion s bands rela-tive to recent photoemission data.

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This paper presents a self-consistent all-elec-tron first-principles electronic-band-structure
study of cubic CdS carried out within the LDF
formalism, using our previously developed LCAO
technique"'" in a numerical-basis-set represen-
tation. Long a favorite II-VI compound for study,
recent interest in the electronic structure of CdS

derives from its use in solar cells" (e.g.,

in CdS-

Cu, S heterojuctions) and the observation of elec-tron-hole complexes for high excitation densities in this material.

'""

Our principal motivation for
undertaking this study wa,s to provide an indepen-
dent rigorous test of the SCOP% method for solv-ing the local-exchange problem" for covalent
solids. Although the recent advent in first-princi-
ples self-consistent LCAO techniques using analyt-ic basis sets [e.g.,

the linear combination of Gaus-

sian orbitals"'" (LCGO)] has permitted an indepen-dent test of the predictions of the discrete varia-tional (nonlinearly optimized) numerical-basis-set approach"'" for some simple crystals,

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such a

comparison with the SCOP% model for transition or fourth-row metal compounds is unavailable at present, primarily due to the practical difficulty in providing sufficient variational flexibility us-ing linear (energy-independent) simple basis sets in the LCGO representation.
For these reasons, as a zpajor part of this work, we present in Sec. II a direct comparison of the results of the SCOPW model with those

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directly to find the optimal configuration ff„„Q™] for Cd and 8 that minimizes b.p(r) in the least-
squares sense, "'"'"it is instructive to follow this
procedure in some detail —as is done in the Appen-dix—so as to gain some insight into the role of
charge transfer and intrasite excitations in this system. This procedure results in an optimal con-figuration Cd'*O5'(5s'855p'") and
81 05 (5sl 955p4 903do 20) M
Clearly, a superposition representation of the ~ charge density of

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(ii} The Cd 4d band appears in the SCOPW calcu-lations to lie 16.6 eV below the valence-band edge, while in the present study it is at only 10 eV below

l „„.Furthermore, this band shifts by as much as 12.4 eV during the SC iterations in the SCOPW study' and lies considerably belo~ the S-derived
Ss band. Empirical adjustments in the SCOPW re-
sults, '

necessary to bring the calculated optical
gaps into agreement with experiment, are found to shift the Cd 4d band by about 11 eV (placing it above the 8 Se band). By contrast, we find in our self-consistent model that the Cd 4d band lies

above the S Ss band and shifts only by a small amount (0.8 eV) during iterations.
We note that in the SCOPW model, the Cd 4d or-

bital is treated as a part of the (frozen) core (i.e., the plane waves are explicitly orthogonalized to the atomic Cd 4d orbital}. Figure 2 shows the Bloch or'bitals

4„(k,r) =g e' '"~}t, (r —R„-d)

FIG. 2. Charge and configuration self-consistent Bloch basis functions at the p point for the CdS system in the exchange and correlation model, along the I:ill] bond di-rection in CdS. Some of the radial nodes near the Cd nucleus are omitted.

of the potential. Several conclusions can be drawn from the comparison of the first-principles results:

(i) Excluding the Cd 4d band and the lowest sul-
phur-Se-like band (1, „-K, „ I, „), the -average
discrepancy for the high-symmetry points shomn (for which SCOPW data are available) is 0.52 eV/level in the valence bands and 0.18 eV/level in the conduction bands, although individual differences can be as large as 0.9 eV. Insufficient conver-gence in the employed basis sets can probably ex-plain only part of this discrepancy; the GPW rep-
resentation is well converged for states of s and p
symmetry around the 8 site (due to the pseudopo-
tential cancellation associated with the presence of f = 0, 1 species in the atomic core) while only states having strong l= 2 character around the S

site (e.g., L, „X,„and I,,) might give rise to
convergence difficulties (due to the absence of an S d core). On the LCAO part, the basis set is well converged for the energy range studied (consis-tent also with the fact that their average discrep-ancy w'ith the SCOPW results, is higher in the va-lence bands than in the conduction bands, while basis set shortcomings in the I CAO representa-tions usually reflect themselves in an opposite trend"").

(where R„and d denote unit-cell and ineguivalent-site vectors, respectively), for Cd 4d and some other representative states. It is clear that the Cd 4d state is intermediate between being a core state and a valence state in that it overlaps non-negligibly with other states but still has some lo-calized features. Furthermore, the energy eigen-value difference between the Cd 4d and the S Ss in

the f usee atoms (2.5 eV)" is of a similar order of
magnitude to the width of the nearby valence bands

in this material, '"'""and d-s hybridization can-
not be excluded. Clearly, inclusion of the Cd 4d as a valence state is hardly practical in the QP%'
formalism due to the severe plane-wave conver-
gence problems associated with its l.ocalized fea-tures in real space. Further, considering this orbital as a part of the core is not only in conflict with its valencelike characteristics (cf. also Fig.

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eV below I'„„and has considerable (1.2-eV) dis-
persion. This discrepancy is directly attributed
to the lack of appropriate Cd 4d-S 3s hybridiza-
tion in the SCOPW method, due to the reasons dis-
cussed in (ii). We find that the S Ss band contains
some admixture of (o-type) Cd 4d character and that it appears belozo the Cd 4d band throughout
the zone. The discrepancy in the location of this
band between the SCOPW and the present result is 0.5 eV at I', 1.7 eV at X, and 1.4 eV at L.
It is interesting to note that the charge transfer between the Cd and S sublattices occurring ip, the
course of the self-consistent treatment tends to

diminish the Cd 4d-S 3s gap even to a larger ex-
tent than is anticipated from a simple point-ion corrected atomic model (cf., Fig. 9 of the Appen-dix), facilitating thereby d -s hybridization in the
solid. Similarly, the small changes in the radial
extension of these orbitals, accompanying charge-
transfer effects (cf.Fig. 7 of the Appendix) results
in a favorable situation for their mixing (i.e.,

the

orbital moments (r ') are rather similar: 1.1 a.u. ' for Cd 4d and 0.85 a.u. '

for S 3s at the ionic limit

@=+1).
Finally, we have examined the effect of increas-ing the number of k points used to sample the crys-

tal density p„,(r). Comparing our results for four points with that obtained with six points (I', X, I, W, 4, and Z) we find that the changes in the rela tive location of the bands do not exceed 0.15 eV, while the absolute position relative to the vacuum changes by 0.60 eV. We have repeated the calcu-lation for the I" point using 10 k points for the BZ sampling (adding the points Z, Z as well as those

halfway between b and I' and I and F). This re-sulted in relative changes of a similar magnitude. The average discrepancies between the present results and the SCOPW results remained roughly
unchanged (i.e.,

increased by about 8%) upon in-
creasing the number of BZ sampling points.
We conclude that the SCOPW model introduces

errors of the order of 0.5-1.0 eV in the valence
and conduction bands and about a few eV in the
lower Cd 4d and S 3s bands.

III. RESULTS OF THE SELFXONSISTENT EXCHANGE
AND CORRELATION MODEL

A fully self-consistent band calculation w ET BT /Xi5 8.94 .L7887L6 268.255160.42 Td (Ae-)Tj ET BT /Xi5 9.0 Tf 19.98 614.18 Td (oeated)

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RESULTS

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EXCH470de. E1T /X increasj ET BT /Xi5 9.96 T94.48 244105 Td (eV)T45 T',

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9 19 Td (ted)081.T BT /Xi5 8.89 Tf 1Tf 229.165 280.22 5ixtures.

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and

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TABLE II. Energy eigenvalues obtained in the SC ex-

change and correlation model for cubic CdS. Lattice O constant a, =5.818 A. Energies are given in eV relative
to the

I, OCAI. -DENSITY SEI, F-CONSISTENT ENERGY-BAND... TABLE III. X-ray photoemission results (Bef. 11) for

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found near the L,,

and X,,

levels (Fig. 5) whi. ch
are located at 2.7 and 2.6 eV, respectively, above
the bottom of the conduction band (i.e., 14.6 and
14.5 eV above the center of gravity of the Cd 4d band). This corresponds to the observed peaks
at 14.4-14.2 eV in the results of Cardona et al. 4'
and Walker and Osantowski. ' The Kramers-
Kronig analys8.81 Tf 253.26 650.29 Tf 73.26 649.77 Td2

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I"» „-X,, gap decreases with pressure. There is no experimental evidence to test this result as

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stabilized by increasing the ionicity, while states
formed predominantly from the Cd sublattice or-
bitals (e.g.,

the Cd 4d band) are stabilized by the
ionicity. Crystal states that are extended over
large portions of the unit

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