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Electronic structure of Cue[

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The electronic band structure of zinc-blende CuCl is computed using a self-consistent, first-principles, all-electron approach. The calculated energy levels agree with

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p,„,(r) =X X„i(r

—R»

—7). Here R» and

r

denote the translationally equivalent and inequivalent
position vectors, respectively. This charge-and-configuration self-consistency (CCSC) yields the ef-

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-9.5- L,{f)

-I I.O-

-I l,5-
~-t2.0-
LtJ

LL1 -2l—

-22-

I I I I

'(o)
Xi(i)

I,(I)
r, (l}

-I.O—
-2.0'=
~ -2.&-

&- -2.8-

- 5.0—

-6.0—=

L,(4.:

-6.5— -23 -0.4 0 04 -04
LATTI CE DEFORMATION (a. u.)

FKJ. 2. Variation of the band states at high-symmetry
points in the zone with the lattice parameter shift ha. Full dots indicate calculated points. (a) VB1, (b) VB2, (c) VB3, (d) CB1.

predominantly (90%) of Cl-3s character, has a small
(0.5 eV) width and is separated by 10 eV (at L) to 12 eV (at I') from the CI-3p-derived (7S%) band VB2. The two Cl-based bands VB1 and VB2 are separated by a 3.5-eV gap from the main Cu-3d-based VB3 band. The latter has a nearly dispersionless subband L3(2) - I t2 - X~(2) and a wider (1.5 eV) subband at higher energies which contain 24% of Cl-3p and 76% Cu-3d character at the zone center. This gives rise to a two-peak structure in the VB3 density of states with a 0.95 eV separation. The magnitude of these orbital
hybridizations (determined here from the Mulliken
population analysis of the bands) agrees well with the
experimentally deduced values based on exciton
spin-orbit splitting8 (25% Cl 3p), exciton g factor'6 (23 +2% Cl 3p) and x-ray" and uv~ photoelectron spectra (24% Cl 3p). At the zone center the lowest conduction band (CB1, with an electron effective
mass of 0.42 m,) is composed of Cu 4s (with some
Cl-3s admixture), with increasing proportions of Cu 4p and Cl 3d towards the zone boundaries [e.g., 2S% at Li(4)].
We find that the charge density at I"~(2) has a large amplitude on the Cl site, due to the enhanced range of
the somewhat depopulated Cu 4s orbital. This sug-
gests that the polarity of the cryr

0.has

Cl

(CB1, with

the (24% gests

values to

24% conduction the VB3 on-me(0.)Tj e TfT /Xi2T /Xi23.81 Td621 T8 191.7eTrahedr9.78 Td (values)Tj ET 2 8.6389.4 gests the VB1, that polarity VvaluT BT //Xi23 Xi5 59783 81.43 T78 Td38 Td (valu /X8T /Xi39 364.59769.26 243hat)38 Td (valuTj ET BT /Xi2 7.89 Tf 15355onic3litude)Tj gTj ETjTi/Xi2 432.64689 Tf t.32 T3Td (to)Tjj ET 81 Tf32 /752 6.9608 Tdd (3)38 Td (valuT /Xi2 82 Tf 8412 82 43 T708 Tde1 6brET BT /Xi2 funET BTtermined)Tj ET BT /X6 Td (44Td (oectron)Tj ap 47.19 Td (bands)Tj ET82 8.2497.93262122 Td (4dis(d2c (polarity)Tj ET Bi22 8.425.32262122 Td (4me.37nism4 Td (This)Tj ET B i2 8.4865 Tf62122 Td (45.54 Td (by)T (24%

d Td s

t997.f 3sts

determined

74VB4 BT /Xrelax

24% gaedr9.78 Tdone-ss 9.38 Tdedr9.78 TdBTT T BT /3 Tfj 1556354 22517.98 T0d ET BT /Xi247 8.697 46 T8.89.11 Td4h11020ity w20h w20h cente20hf

en3d bET BT /Xni2 8.54 Tf 190.02 5 375.4ET 29T BT /Xi2ergan2 8.as43646765382446.89 .06 T299c2 ET BTdi BTr BT /Xi2 7.62 Tf 8949..9 Tf 7 BT /299c4 Td ((a))Tj T

1. We of

1Td76975Tominant=/Xi2 7.9.17139711569 Tf .2Tddd 33. ET BT /Xi2 8.55 Tf 191.6.fj 169.160.2.7as

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TABLE I. Calculated and observed interband transition energies in CuC1. The experimental no-tation is given in parenthesis. Results are given in eV.

States

Calc.

Energy Experimental.

1) r»(2) —r, (2)
tX,(2) -r, (3)

L (3)-L (4)),()-,()

4) L,{3)—L,(S)
)

',(3)-,'{}

6) x$(2), x2 x5(3)

7) r»(1) 1,(2)
8) x,(1)-x,(3)
9) L,(2)—L)

(4)):,(1)-,(5)

11) L,(2) -L,(4)
12) X,(1)-X,(3)

2.0

6.1
5.7
7.0
8.0
9.9
13.9

6.8
10.0
11.1
11.9
1S.9
17.5

3 4a, b

6.3'(E,)

6.8, 6.S'{E,')
83'83~(E,)
10 ' 99~(E)
14.2'

6.8,', 6.5~(EO')
10, 9.9~(E»)
19c

16.0' '
17 5'

13) I](1)' I](2)
14) L', (1)-L', (4)
1s) x) {1) x3(3)

18.8
21.2
21 ~ 3

19-21'

'Reference 8, ~Reference 18. 'Reference 19.

large range of assumed electronic populations
n and m. Hence, although a one-electron band struc-ture with e = 1 or with an assumed non-self-consistent atomic configuration of Cu 3d9 produces in CuCl a large gap (3.2 and 3.4 eV, respectively, with the present method) due to the stabilization of the localized VB3 band with respect to the more diffused CB1 band, the agreement with the experimental gap (3.4 eV) might be fortuitous. The consistent choice of a Kohn and Sham exchange (a = 3

=2) plus the
homogeneous correlation term'" used here yields in turn a smaller one-electron gap (2.0 eV) plus an es-timated nonlocality correction of 1.0—1.

Sham

31.86 ET BT /Xi3 7.96 Tf 156.22 63.3 Td (t7)Tj7lations