PHYSICAL REVIEW B VOLUME 35, NUMBER 5 15 FEBRUARY 1987-I

Total-energy and band-structure calculations for the semimagnetic
Cd& „Mn„Te semiconductor alloy and its binary constituents

Su-Huai Wei and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401 (Received 24 June 1986)

Spin-polarized, self-consistent local-spin density total-energy and band-structure calculations have been performed for CdTe, antiferromagnetic (AF) MnTe in its NiAs structure, ferromagnetic (F) CdMnTe2, and the hypothetical zinc-blende phase of MnTe in the F and AF spin arrangements. We find the following: (i) The alloy environment stabilizes a zinc-blende form of MnTe, hitherto un-known to exist in the phase diagram of pure Mn Te. Its calculated Mn—Te bond length (2.70+0.02 A) is very close to that observed in the alloy (2.73 A), but is substantially

35 TOTAL-ENERGY AND BAND-STRUCTURE CALCULATIONS FOR... 2341

and the nature of the low-energy electronic transitions.
Reported results regarding the Mn 3d energy levels are
rather controversial. Photoemission measurement of

Cd~ „Mn Te by Webb et al. '

found the Mn 3d states
3.5 eV below the valence band (v) maximum E„, whereas similar experiment by Orlowski place the same states at E„—6 eV and photoluminescence measurement by Vecchi et al. '

infer these states at E,—0.8 eV. Although

2342 SU-HUAI WEI AND ALEX ZUNGER 35

the stable crystal form at the temperature range

I TI (in-
stead, another phase, i.e., P, is stable there), but the a
phase does exist in the phase diagram of the constituents
at some different temperature range. In

2344 SU-HUAI WEI AND ALEX ZUNGER 35

culations for F MnTe both in its two-atom ZB unit cell
and in the four-atom CuAu-I unit cell and find the two
energies

35 TOTAL-ENERGY AND BAND-STRUCTURE CALCULATIONS FOR... 2345

)( )l 4L)l 4L av ef I~ &&~iF

(AF)

)l ++ --)l

)l)( )(
Jv-ir %N

~ 0
Mn Te

~ 0
Te

7.2— Ol
7.3
Q)

7.4

LLl) 7.5

th

0
U

Req

2346 SU-HUAI WEI AND ALEX ZUNGER 35

50% alloy in extended x-ray-absorption fine-structure
(EXAFS) measurements. ' The nonideal anion displace-
ment (u& ~) in the F CdMnTe~ structure (i.e., the Te
anion moves away from the center of its tetrahedron to-
ward the pair of Mn atoms and away from the pair of Cd
atoms) leads to the formation of Mn

—Te and Cd

—Te
bond lengths similar to what is found in the respective binary systems [R (Mn

—Te) =2.71

A and

R (Cd-
Te)=2.80 A, calculated for pure F MnTe and CdTe,
respectively (Table I)], but considerably different from
what

a virtual-lattice approximation (VLA) would
have predicted [i.e.

,

u

= —, and

R ' I(Mn-
Te)=R' " '(Cd—Te)=W3/4a =2.758 A]. The fact that
our calculated equilibrium bond lengths are close to those
of the pure end-point compounds indicates that the sys-
tem has used its internal degree of freedom u to achieve
nearly ideal tetrahedral bond lengths (at the expense of somewhat distorting the bond angles), thereby lowering its
strain energy. The same effect was observed to occur in
all 3'B"'C2' chalcopyrite crystals as well as in the
50%-50% alloy system CxaP-InP.
(v) We evaluate the enthalpy of formation (per four atoms) bH'"' for the ferromagnetic phases relative to the equilibrium ZB forms of CdT and

F MnTe as

b,H'"'=E[F CdMnTe2]

—E[CdTe] E[F Mn—Te]

. (4)

For the AF phase we have the formation enthalpy

bHI "'=E[AF CdMnTe2]

—E[CdTe] E[AF Mn—Te]

.

(5)

We find

a negative value of bH'"'=

—0.05+0.01 eV (Fig.
4). Hence, the ordered CuAu Iphase of-F CdMnTe2 is
predicted to be stable against disproportionation into its ZB
constituents. Bonding with

35 TOTAL-ENERGY AND BAND-STRUCTURE CALCULATIONS FOR... 2347

TABLE II.

SU-HUAI %'EI AND ALEX ZUNGER

F - CdMn Te2 a = 6.255 A, u = 0.242

Ch
OP

tA

O

~ ~

CAC
4P

80—

40

40-

80-

80-

40—

40-

80-

80—

40—

0-

s

I!
I
/
I

!
!
$'! 1
!
!
!

I!

I!!!
l'~s

Te
Site

Cd

, Site

Mn
Site

':: Px5

:-&.(pd)

px5:.:
I

!!
II

II!'

I

!!

Px !
!

2350 SU-HUAI WEI AND ALEX ZUNGER 35

c5 2

c

cn

C V3

a5

2

Po

m

gE
QQ C/J c Eo

cn

o

~og E ~ C

c7n

c

~op o

II

E2

Q

E-& o o E ~

cda
No

bQ
c5 a5

bQ

o

CQ

o

E

~

c$

bQo
cA

Ctl

a5

gogE
~2o o goo E ~o

cn

o

oo

'M

o

o

35 TOTAL-ENERGY AND BAND-STRUCTURE CALCULATIONS FOR... 2351
o oo O O
CJ o N o o o o o o o o o o
o o o o o o O O o o o o o

o

o

o o
o o o o
o o
VOo

~oo o a o o w o
ooo o
o o o w o o o o o O O o o o ch ~oo
o

I

o o

o

ooo
o o

o o o ~oo o
o

oOO

o o
o o

o

4 4

2352 SU-HUAI WEI AND ALEX ZUNGER 35

6-
L3C

TABLE IV. Comparison of high-symmetry band eigenvalues
(in eV) of CdTe for a=6.480 A of the present study

35 TOTAL-ENERGY AND BAND-STRUCTURE CALCULATIONS FOR.

2354 SU-HUAI WEI AND ALEX ZUNGER 35

are given, unfortunately in Ref. 17), except for an up-
wards shift of their s-like conduction bands, presumably
because of omission of relativistic effects.

ture calculation for the zinc-blende MnTe with the first

kind of AF order, i.e., with successive (001) planes aligned
antiferromagnetically (see the inset to Fig. 13). Figure 13 shows the band structure of AF-ZB-MnTe at a=6.244 A. The density of states of AF-ZB-MnTe is shown in Fig. 14.
Eigenvalues at I points, calculated for the experimental
lattice constant, '

are given in Table III. We find the oc-
cupied "spin up" (i.e.,

first Mn sublattice) Mn d band to
be centered at E,—2.5 eV, whereas the empty, "spin-
down" (i.e., second Mn sublattice) d band is centered at E,+2.2 eV; hence, the exchange splitting is A„(d)=+4.7 eV (smaller than in F MnTe; see Fig. 11). The valence-band maximum is strongly hybridized, having a 2&& 12.6% Te p character and about a 24% Mn d charac-ter on each of the Mn sublattice. The bottom of the con-
duction band is almost dispersionless. The direct band
gap at I is 1.13 eV, which is 0.9 eV larger than the one
we calculate for the NiAs structure of MnTe realized at
point A (see below), confirming our expectation based on Fig. 2(a). Our calculation indicates that AF-ZB-MnTe is
a semiconductor rather than a metal, because the intra-
atomic exchange splitting for the Mn ion is large enough to keep the unoccupied spin states above the top of the Te p bands. The AF ordering increases the band gap. In contrast with the ferromagnetic case, there is no negative

p-d exchange splitting and band overlap of E,'

and E,'
(where U stands for valence band and c for conduction
band) in the AF spin arrangement. This is so because in
the AF phase there is an equal number of Mn atoms with 3d levels below and above the Te p levels (compare, how-ever, the ferromagnetic case in Fig. 7). The latter are re-

D. Comparison of CdTe, Xi14 9.02 Tf 500.679.c

1 Tf 435.59pres /Xi14 8.79 Tf 387.67 46089 Td (shift)Tj ET BT /Xi14 10Xi14 9.50 ET 416.5 Tf 6T BT78.67 382643 Td (she)Tj ET eT /Xi14 9.1 Tf

(0ate

at

(com567h com567h where

inAF(in)Tj ET opj ET T 416.5 Tf 6T BT20.33 402033 Td (be)Tj ET Bow BT /Xi14 8.97 Tf 451522 700411 Td (et)Tj ET /Xi14 8.94 Tf 582.11 532(con-)F(in)Tj ET 50 E

com53AF

the /Xi14 8.26 Tf 475.56 38(AF-ZB51levels)TjT /Xi14 8.46 Tf 3702.58 41678 Td 1sublattic»T /Xi14 13.67 Tf 395267 38 Td (bo1)Tj ETT /Xi14 9.77 Tf 4pre067 3886(com

at pMnTe

3dalmost almost
13 T wiate23up" where217e top AF-ZB-MnTTo BT /Xi14 9.26 Tf 3pre067 405.18 Td1.44f 503TjDOS /Xi14 8.65 Tf 397.33 68106T15(nd?8 TdTj E BT /Xi14 8.98 Tf 503 67 385Thomi6there 001) incre225Tj ETT /Xi14 9.14 Tf 2254.67 606.83 Td21in j E /Xi14 9.12 Tf 345.56 395 Td (U2(atvels)Tj ~ /Xi14 9.26 Tf 4.14.67 47 1are)T19in bBT /Xi14 8.97 Tf 496.44 395981 Td21Mn 13ndtheis theIE,cha1051Tj ET B-8 /Xi14 9.26 Tf 572.78 5698Tj104an

a7is

2356 SU-HUAI WEI AND ALEX ZUNGER 35

= I

eU Et j 2 2.5y0. 5

e+t+ (6c)

The observed Mn d value is at about E,—3.5 eV. In our
calculation E,

'—:E„—(2.0—2.5 eV), hence the relaxation

shift is b, (N, N —1)=-—(1—1.5 eV). The reason that this shift is so much smaller than in the free Mn + ion' '

is

related to the effective screening of the t+ hole in the
solid: similar calculations for 3d impurities in semicon-
ductors' have shown that the hybridized host crystal res-onances respond to the creation of a hole in a localized t orbital by increasing the amplitude of their wave function on the impurity site, thereby returning to it much of its charge lost in the ionization process (the "self-regulating response"' '

). Hence, whereas in occupation number
space we have a d ~d transition, in coordinate space we have a L d ~L 'd transition, where the ligands (L,

figurations for ionization. The two limiting situations'
(in crystal-field language) involve ionizations from
either the t+ or the e+ orbitals. In the former case,
the final state can be denoted formally as

[Mn +,d",e+t+e F', Tz] (where the final-state orbital F a—conduction or vacuum level, is occupied) whereas in
the latter case we have [Mn +,d, e+t+e F', E]. Our
discussion of Sec. VA emphasized the significant differ-
ence between the two cases: whereas the t+ orbital is hy-bridized with the host crystal (p-d mixing being allowed in the tz representation of Td), the e+ orbitals are essen-tially nonbonding (no p-d coupling for the e representa-
tion is allowed in Td symmetry). As we ionize r+ [Fig.
15(b)] to t+ [Fig. 15(a)], the orbital energy drops, as we have relieved part of the Coulomb repulsion (even though
the reduced exchange splitting will move the bands up).
The ionization energy relative to the valence-band max-
imum c, in this donorlike transition is

b,E,(0/+) =E[Mn +]—E[Mn +]

initially with M electrons) have lost approximately one electron and the impurity site remained essentially neutral "charge transfer" excitation. ' This process is not to be confused with ordinary dielectric screening (returning 1—1/e electrons to the ionized site, where e is the

tric rontants)

ccuras wiuch

on

a

lar

caole

(a

not

one

is

n(related)Tj ET BT /Xi16 9.26 Tf 157.11 359.11 Td (to)Tj ET BT /Xi16 8.94 Tf 527.33 639.22 Td (the)Tj ET BT /Xi16 8.61 Tf5442 342.67 Td dey-

of the aials

hybridization.

the

et(rewe)Tj ET BT /Xi16 8.85 Tf3926.44 681.56 Td (limie)Tj ET BT /Xi16 8.34 Tf4315.89 138.44 Td (hven)Tj ET BT /Xi16 8642 Tf 441.22 638.3

electro', is

ionie(d,)Tj ET BT /Xi16 8.23 Tf4197.78T038.11 Td (we)Tj ET B

(6c)

� 5
(ed) the

e+

orbital

is

nonbondin],

the

self-regulating

not ns ordinary

2358 SU-HUAI WEI AND ALEX ZUNGER 35

TABLE V. Eigenvalues c (in eV) and l-decomposed local-charge character (in percentages) of AF MnTe in the NiAs structure at c=6.705 A, a=4. 143 A with RMT(Mn)=1. 48 A and RMT(Te) =1.434 A. The l character is given first

2360 SU-HUAI WEI AND ALEX ZUNGER 35

102

F- CdMnTe„a = 6.255 A,
(a)
10

U= 0.242

1

p-2. 4 (c)

10
1

p-2.4

total

FIG. 18. Calculated charge density [in e/(a. u.)] contours for F CdMnTeq on a plane defined by R(Mn—Te) and R(Cd—Te).
[(0,—1,1) if u=0.25]; (a) spin up, (b) spin down, and (c) total. A logarithmic scale is used, with a step size of 10 '. Shaded regions
highlight the covalent bonding.

the following discussion), the occupied Mn d states cen-
tered at a Mn atom have the symmetry 3+,3+, 1+, but the
empty states centered at the second Mn atom have the

symmetry 2,3,3, and the Te p states at the top of
valence band have the symmetry 3+,3. p- d repulsion
then raises the p states with 3+ symmetry and lowers the p states with 3 symmetry. This explains why the VBM in H-Mn Te occurs at 3 point and why the direct band gap of MnTe is smaller than that of MnTe in ZB struc-
tures. Furthermore, because of the different symmetry,
the electronic transition is more bandlike. This symmetry argument is also supported by the density of state plots for AF-ZB-MnTe [Figs. 14(a)—14(d)] and AF-H-MnTe [Figs. 17(a)—17(d)]. Figures 17(a) and 17(c) show for H MnTe a bandlike DOS near the VBM with little d charac-

ter, whereas Figs. 14(a) and 14(c) show for ZB MnTe a large DOS near the VBM with a pronounced d character.

The bandwidth of the localized unoccupied Mn d band in the ZB structure (1.6 eV) is also smaller than that in the NiAs structure (3.0 eV), suggesting stronger multiplet ef-fects in the former. In addition, because of the smaller band gap of AF-H-MnTe (1.3 eV), any intra-atomic tran-
sition (—2.2 eV) will be obscured by the fundamental
transitions.

IX. CHARGE DISTRIBUTION

Figures 18 and 19 depict the calculated density con-
tours of F CdMnTez and AF-H-MnTe, respectively. In
both cases, we find the partial ionic and partial covalent
bonds connecting Mn—Te and Cd—Te atoms, typical to
most II-VI semiconductors. From Figs. 18(a) and 18(b)
and Fig. 19(a), which show the spin-up and spin-down charge densities, we see that the Mn 3d electron partici-

AF - MnTe],'NiAs, ')

a= 4.143 A, c= 6.705 A

Flax. 19. Calculated charge density [in e/(a. u.)] contours for

point

299ed

atoms,

35 TOTAL-ENERGY AND BAND-STRUCTURE CALCULATIONS FOR ~.. 2361

1200

2362 SU-HUAI WEI AND ALEX ZUNGER 35

TABLE VIII. Calculated exchange interaction coefficients in
comparison with experimental data (see also the text).

System

MnTe (ZB)
CdMnTe2 (CuAu-I)
ASW'
Experiment

'Reference 17.
Reference 15.
'Reference 5.

JNN (K)

—16

—17 —7.5

Noa (eV)

0.48
0.54
0.33
0.22'

NpP ieV)

—1.16 —1.30 —1.05 —0.88'

tively, and (S,) is the average Mn spin. Using the calcu-
lated band structure and (S,) value for F MnTe and F
CdMnTe2, we have calculated Noa and NOP. Results are listed in Table VIII and compared with experimental data
and previous calculations by Hass et al. ' The agreement is satisfactory. We find that the exchange constants in-
crease with decreasing Mn composition because of the
enhancement in the symmetry induced interaction be-
tween band-edge states and Mn d states; this trend agrees
with the experimental data.
The overestimation of the exchange interaction energy
constants is a characteristic of the LSD calculation. '
Since LSD underestimates the exchange splitting of Mn 3d, and 3d, states, it also reduces the p-d energy separa-tion (see Fig. 7). This will increase p-d hybridization; consequently, the superexchange coupling between Mn ions and electrons increases.

We find that the ZB phase of MnTe is metastable com-

35 TOTAL-ENERGY AND BAND-STRUCTURE CALCULATIONS FOR.. ~ 2363

TABLE X. Observed formation enthalpies 5(MX2), elemental cohesive energies E„the ionic correction A(M, X)=II"+I~'—2+x, and the compound cohesive energy E,(MX2) and its "lattice energy" [see Eq. (A4)].

System
MXp

CaF2
CaC1,
CaBr2

CaI,

—hH (MX2)
at 300 K
(Kcal/mol)'

292
190
163
128

35 TOTAL-ENERGY AND BAND-STRUCTURE CALCULATIONS FOR... 2365

vironment there is no special direction (i.e., no c direction).
This parameter g along with u can be used to minimize strain
energy in ordered alloys arising from bond-length and bond-
angle mismatch. See also, G. P. Srivastava, J. L. Martins,
and A. Zunger, Phys. Rev. 8 31, 2561 (1985).
W. A. Harrison, Electronic Structure and Properties of Solids (Freeman, San Francisco, 1980), p. 174.
A. Fazzio, M. J. Caldas, and A. Zunger, Phys. Rev. 8 30,