PHYSICAL REVIEW B VOLUME 43, NUMBER 2 15 JANUARY 1991-I

Disorder effects on the density of states of the II-VI semiconductor alloys Hgp 5CdQ 5Te, Cdp 5ZnQ 5Te, and Hgp 5Znp 5Te

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The electronic structure of substitutionally random 3 & B C alloys of zinc-blende semiconduc-tors AC and BCdeparts from what a virtual-crystal approximation would grant both because of (i) a chemical perturbation, associated with an electronic mismatch between atoms A and B, and because

of (ii) a structural perturbation (positional relaxation) induced by a size mismatch between 3 and B. Both effects on the electronic density of states are studied here for Hgo 5Cdo &Te, Cdo 5Zno 5Te, and Hgo 5Zno 5Te in the context of first-principles self-consistent supercell models. We use our recently developed "special quasirandom structures" [A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Ber-nard, Phys. Rev. Lett. 65, 353 (1990)] concept whereby lattice sites of a periodic structure are

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ments '

reveals, however, that the nonstructural
theories do miss some qualitative features. It is obvious,
for example, that the lower site symmetries of the A3B,
AzB2, and AB3 clusters (C3„Dzz, and C3„respective-
ly), which surround C atoms in fourfold coordinated A, „B C alloys could produce effects which are absent in the higher (T&) symmetry of the virtual (AB)4 clus-ter. Atomic displacements producing unequal A—C and B—C bond lengths allowed only in the lower sym-metries is just one such example. Simple symmetry-preserving nonstructural theories do not represent such distinct effects associated with the existence of a distribu-

tion of low symmetry environments; instead, it is as-
sumed at the outset that the (configurational) average of a
distribution of low symmetry configuration can be re-
placed by an "effective, " high symmetry configuration.
This can have significant implications on the description
of optical and structural properties. A few recent exper-

imental observations are pertinent to this point. x- (i) Extended

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x0.2
3
P4 P6

I

) () x0.5

I

I

co 0

(b) p~
20 — x0.5
15-

10-
5-

o 0

P3

(

r

x0.2

P4

CdTe

P5

Hg Te

P6

P6

, x0.5j
10-

5-
l

'

- 12.0

P2 P4
I I

„gp,
III, I

-8.0 -4.0 0.0
Energy (eV)

4,0 8.0

FIG. 2. Total DOS of (a) ZnTe, (b) CdTe, and (c) HgTe, eval-uated at their respective zinc-blende equilibrium lattice con-stants. Peaks at different regions are labeled as P1—P6. Notice the change of scale for the P1 and P2 peaks. Zero of ener is
at the VBM.

ea s. ero o energy is

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(a)

(c)

Qe

Q Te -0.450
Q Hg 0 407

QT =0.930
QH -0 360

Q Te -0.529

QT =0.080
Q Hg-1.765

Q =1.386

Q Hg -0.229

EOH

P4

P3

P2

Qe

DOS was broadened using a Gaussian-like function with
full width at half maximum (FWHM) equal to 0.2 eV (un-
broadened DOS are given for comparison; e.g., Fig. 10
below). Full relativistic effects, including spin-orbit in-
teraction through a second variation proceTs7 6j ET aBT /Xi319 Tf 404

arel79.44 Td (are)Tj E8T BT X93 9.18 Tf 160.78bin69 Td (including)Tj E0 BT /X33 9.07 Tf 160.7856 rgie9 Td (effects,)Tj ET BT /Xi307 Tf 475.11iTd (variat

to

variation

broadened for proceTs7 6j ET T BT /549 7.51 Tf 153.33iTd (variation)Tj9116BT /Xi3 9.14963 Tf 5499.3d (ularaussian-like)Tj ET1BT /X62f0.58 Tf 167z.22-blende0.67 Td (was)Tj ET BT /416 9.1496

teraction

including effects, (FWHM)are

2pr

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11f(O) ff S (CT),

taken over all vertices of figure f =(k, m). There are
Dk equivalent figures per site. For an ordered periodic
structure o.=S we will take the lattice-averaged product
(denoted by an overbar) II&(S) over all symmetry-
equivalent figures in the lattice. While for a particular
(ordered) structure S we have a distinct set (II&(S)]
which defines this structure, in a binary random (R) alloy we must take the configurational average (denoted by an-gular brackets) over all 2 structures [o]. The result is known analytically:

(IIk)„=(2x—1)", (3)

so that at x = —, ', for example, all correlation functions vanish, except (IIO &) =1.
Standard approaches for constructing models for ran-dom substitutional networks attempt to approach the statistical limit of Eq. (3) using a site-by-site occupa-tion of the N lattice site; this approaches the

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V. TOTAL ENERGIES, EQUILIBRIUM STRUCTURES, AND BAND GAPS

A. Structure of the SQS-N

x, = ——, ', z, =O (A);

xz =—3, zz =0 (B);
(6)

In the present work we study the total energies and
density of states of Cdo ~Zno ~Te, Hgo 5Zno 5Te, and
Hgo 5Cdo 5Te using the SQS-4 model. The predictions of the SQS-4 model were also tested against the more accu-rate SQS-8 model in some cases.
The SQS-4 structure [Fig. 5(a)] has the space group Cz, (Pmn2&) with primitive orthorhombic unit cell vec-
tors

a=(——, ', —, ', 0)i)a,

x, = —, ', z, = —,

'

(C);

x4 = ——3, z~ = —,

'

(C)

that lead to equal nearest-neighbor bond lengths

R(x)=R~c =Rsc =V'3/4a (x),

in contrast with experiment. This highlights the need
for relaxation.

The SQS-8 structure [Fig. 5(b)] has the space group C, with the monoclinic unit cell vectors

b=(0, 0, 1)a,

c=(1,1,0)ga.

(4) a=(l, —, ', ——, ')a,

b=(—, ', ——, ', 0)a,
The atomic positions (in Cartesian coordinates) take the general forms

r,,

=[gx,;gx;;z;]a,

r, ~= [—il/4 —gx,;ri/4 —gx;; —, '+z,]a,

where i = 1, 2, 3, and 4 corresponds to occupation by 2,
B, C, and C, respectively. In the macroscopic random al-
loy (infinite supercell size) there is no unique crystallo-graphic direction. We mimic this in the finite SQS-X by setting the ce11 externa1 parameters to its idea1 values

(g=r)=1 for SQS-4). This is further supported by our
total-energy calculations for ordered compounds, where
we find that, despite the long-range order, the noncubic
distortion in the isovalent A,B sublattice is less than 1%.
The dimensionless cell-internal parameters x,. and z, represent the structural degrees of freedom that are not determined by symmetry; they need to be relaxed to
achieve a minimum in the total energy given the cell
external vectors (a, b, c). In the unrelaxed structure the
cell internal parameters take the "ideal" zinc-bien de
values

c=(1,1,2)a.

As argued in the above, we have taken the ideal values in Eq.(8) for the. cell external parameters. The atomic posi-
tions (in Cartesian coordinates) take the general form
(i =1—16)

r; =[x,.

,x;,z,]a.

For the unrelaxed structure the cell internal parameters x, and z; take the "ideal" values

x, =O, z, =O (A);

x2= —, ', z~=O (3);
x3= ——, ', z3=2 (A);

x4=0, z~=2 (3);
xs=O, zs= 1 (B);

x6= —, ', z6=1 (B);

x7= ——, ', z7= 1 (B);

(a) SQS-4

- 4L

(b) SQS-8

B1 [113] rA~~!,. 4E~g

xs = —, ', zs =2 (B);
x =—'

z =—'(C)'

xio 4 zio= —,

'

(C) '

x„=——, ', z„=—,

'

(C);

(10)

IL
F

WF r
3-

L
F

2

B A' ~
FICi. 5. Crystal structure of the special quasirandom struc-tures (SQS) of the type (a) SQS-4 and (b) SQS-8 for the x = —'

al-

loy.

x,2= —, ', z,2= —,

'

(C);

xi3= —„', zis =—'

(C);

xi' 4 zis 4

(C) '

x, 5

= —, ', z, 5

= —,

'

(C);

x,6= —, ', z,6= —,

'

(C).

Note that the SQS-8 structure has two variants, obtained

by switching the 3 and B atoms. They differ only in the
rather small, three-body II3 correlation functions and
yield essentially identical total energies (within 2 meV/4-

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atoms). In

a proper calculation, however, the results for
both structures should be averaged. This average (giving
II3 =0) contains all five possible nearest-neighbor (C-centered) tetrahedra A4, A3B, A2B2, AB3, and B4 in the ratio 1:4:6:4:1as required by the random (Bernoulli) dis-tribution at x = —,

'. We will see below (Sec. VIC) that
SQS-8 calculations of the density of states often refiect contributions of such tetrahedra in this ratio.
The equilibrium atomic positions in the SQS model are obtained by minimizing the total energy

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al relaxation, omitted in the VCA and the CPA can be
seen by comparing the relaxed values in Eq. (13) to the
unrelaxed SQS-4 values b,Hz calculated at the same mo-
lar volume, i.e.,

AH~

=189 meV/4-atoms (Cdo 5Zno 5Te),

bHR =213 meV/4-atoms (Hgo &Zno ~Te)

.

(15)

C. Band gaps

We have calculated the direct band gaps at

I for the
equimolar alloys in the SQS-4 model as well as the corre-sponding band gaps in the binary constituents. The opti-cal bowing coefficient [Eq. (1)] is given at x = —, '

as four
times the (crystal field averaged) difference between the average band gap of the binary constituents and the cal-culated band gap of the SQS alloy. Our calculated values
are

b(Cdo ~Zno 5Te)=0. 35 eV, b (Hgo ~Zno, Te)=0.23 eV,
b(Hgo 5Cdo &Te)

=

—0.02 eV

.

These compare reasonably well with the observed low-

temperature values of -0.23 eV, " -0.14 eV, and 0—0.23 eV, '

for Cdo 5Zno 5Te, Hgo &Zno 5Te, and
Hg05Cdo ~Te, respectively. Our results differ, however, from previous CPA calculations, e.g.

, for Hg, Cd Te
Hass et al. obtain -0.27 eV, and Herding et a/. find
0.36 eV. For HgZnTe Berding et aI. obtained b=0.79
eV. (This calculation corresponds to T=O

K and should
hence be compared with low temperature measured
values that give

b -0.14—0.15 eV. The experimental
value at room temperature is, however, larger.

) Part of
the

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V. This model considers the influence of volume defor-
mation on the averaged constituents, but does not in-
clude the chemical effects (i.e., charge transfer) or posi-
tional relaxation. Like the VCA, this approximation re-
sults in an identical number of DOS peaks in the alloy
and its constituents.

(ii) Second is the DOS of the unrelaxed SQS-N [using the parameters of Eq. (6), hence the same bond lengths as in the QVCA model]. Since, however, atoms are not averaged in this SQS model, comparison with the QVCA results reflects the effects of the (constant-volume) chemi cal perturbation. Previous studies indicated that the S-CPA mimics the results of this model for lattice-matched Al& Ga As if weak to medium chemical perturbation is
assumed in a tight-binding model.
(iii) Third is the DOS of the relaxed SQS-N (using the parameters of Table III). Comparison with the DOS of the unrelaxed structure provides a measure of structural relaxation effects on the DOS.

SQS-8. We have averaged over the two variants of the SQS-8 (see Sec. VA) which contain all five A4, 338, A2Bz, AB3, and B4 tetrahedra in the random probability
ratio 1:4:6:4:1.The results are given in Fig. 6(d). Com-
paring the DOS in Figs. 6(c) and 6(d) we see that, except for some Gne changes in the shape of the DOS, all the basic features (splitting, broadening, etc.) are contained in the SQS-4 model. Hence, in the following discussion, un-less necessary, we will use SQS-4 structure to describe the feature of the alloy DOS.
A number of previous DOS calculations exist for
Hg& „Cd Te. Spicer et al.,

' ' Shih et al., and Chen
and Sher used a combined empirical pseudopotential
and tight-binding Hamiltonian in a four-orbital per atom
(s, 3p) Gaussian basis set to perform single-site CPA cal-culations in the diagonal-disorder approximation. The

B. The lattice-matched alloy Hgo, Cdo &Te

Figure 6 depicts the DOS of Hgo &Cdo 5Te; because of the close lattice match between the constituents,

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nine tight-binding parameters were adjusted to fit the
band energies of the binary constituents in a number of
high-symmetry points in the zone,

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20-

x0.5
at
aeq

x0.2

ZnTe (a}

0

~ ~

sublattice potential produces a splitting, an effect which is qualitatively missing in standard CPA models (where all C atoms are taken to be chemically identical). Althoug P1 has mostly the orbital character of Te,s, different

Inspection of the electronic charge densities in the P1 re-ion in the alloys [e.g., Figs. 9(c) and 9(d) for H Z T]

shows that the split components are associ- g05 05 ated with different tetrahedral coordination about Te (a "ligand-field" effect). For Cdo sZno sTe in the SQS-4
structure

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2.8

2.6—

Relaxed Equal bond
lengths

CdTe

Relaxed

2.4—
0
ZnTe

antibon ding
P5

a(P5)

increased 2.0—
Hg Te
~O r

- 5.0— CdTe

- 5.2

- 5.4—

bonding
P3

ZnTe

w(P3)
decreased

- 5.6—
Hg Te

FIG. 11. Calculated relaxation-induced energy-level shifts in the peak of the projected sp bonding and antibonding states for Cd() qZno 5Te and Hgo 5Zno 5Te systems. For convenience we have aligned the ZnTe states of the two unrelaxed systems. "Longer" and "shorter" refer to changes in bond lengths (rela-tive to the VCA average) upon relaxation; see Fig. 1 and Table I ~

tions of the arrows. Our LAPW calculated relaxation-

induced shifts in the bonding and antibonding energies
are depicted in Fig. 11. We see that they agree with the
qualitative trends expected above. The net effect of
relaxaT Bn structural relaxation is, therefore, to (a) reduce the

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a((THE)Tj ET BT /X313 8.11 T1 Tf-likTf 546 659.44 Td (tn)Tj E62BT /X313i13 8 Tf 259.89 370.33 Td (are)Tj E8 BT /X313 8.11 T2 Tf-likTf 546 659.44 Td cted

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relaxaT 2e

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ar.d).44 669.89 Td (abov1s)Tj ET1BT /X623 8.32 Tf 422.11 680.44 Td (76)Tj 46T T /X623 7.94 TseT

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(ter)Tj 440 BT /1i1 7.94 TC259.89 370.3
above.

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a(I)Tj E123 8./Xi1 7.04 Tf 1 151.78 410.11 Td (4W)Tj 5TXi13 /Xi1BT 94 T~183.11 672.22 Td (CdTn)Tj ET33 8.509X 7.04

a(.)Tj E27 BT /97/ 7.94 T&As:3.11 672.22 Td (CdTo)Tj 45T BT /9713 9.1 Tus 690.67 Td (antibon(Th8)Tj 475 BT /98i 8.64 Tf Tf 109

abovTe

1nd

iv)16.11 680.44 Td 857Y

Ts7

state8

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has the advantage of treating all relaxation effects on
equal footing and permitting effective use of first-
principles electronic-structure methods. The accuracy of
the SQS approach can be systematically improved by in-
creasing the size of the unit cell. While we prefer the
SQS-8 model, many of the basic features are already con-tained in the SQS-4 model. On the other hand, in this ap-proach one has to use different SQS's at different compo-sitions x. When x is close to 0 (or l), large SQS's have to be used. In this respect, the molecular CPA can treat more efficiently trends in alloy properties with composi-tion, as long as an accurate Hamiltonian is used.

ACKNOWLEDGMENTS

We thank M. Herding and K. Hass for useful discus-sions and comments on this manuscript. This work was supported in part by Director, OSce of Energy Research [Division of Materials Research of the Office of Basic En-ergy Sciences (OER-BES)], U.S. Department of Energy under Grant No. DE-AC02-77-CH00178. We are partic-ularly grateful for a special "Grand Challenge" grant of computer time from OER-BES.

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