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Electronic properties of random alloys: Special quasirandom structures

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Structural models needed in calculations of properties of substitutionally random A] B alloys are usually constructed by randomly occupying each of the X

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different diagonal energies for different C atoms). In ac-
tuality, possible nearest-neighbor arrangements around C
include CA38 and CA83 (C3„symmetry), CAzBz (D2d
symmetry) as well as CA4 and C84 (Td symmetry); more
configurations occur when one proceeds to more distant

shells. Each of these CA„84 „(0~n ~4) clusters could
contribute differently to a given phybnrcl

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transitions,

" ' ' which can be thought of as folded (pseu-
dodirect) excitations, and can be described also by the

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lander, and Kleinman; the —1000 atom cell of

Pb, „Sr„Sused by Davis; the -2000 atom model of
(GaAs), Ge2„used by Davis and Holloway; and ear-
lier model calculations by Alben et a/., with
8000—10000 atoms, and by Henderson and Ortenburger
on disordered 8—12 atom cells

calcu3 9.211s667.55 ET BT /Xi3Tj ET BT /Xi3 9.31 T44

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to describe disordered alloys with terms (and accuracy)
equivalent to those with which state-of-the-art methods
address simple periodic crystals. Indeed, since we are
dealing with periodic crystals Is), their physical proper-
ties E can be calculated by (first-principles, self-
consistent) band-structure techniques, avoid-ing the simplified empir/Xi5 11.21 Tf 179.14 be

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than zero (denoted in Table

I as "PE"); these occur at
rather short distances from the origin for small N. Clear-
ly, this standard method for creating periodic, quasiran-

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TABLE II. Special, X-atom fcc quasirandom structures at x = —,

'. This table gives the empirical formula, the unit cell vectors in
units of half the lattice constant, the designation of the SQS-N as a superlattice (SL) and the correlation functions 11„.The square
brackets next to Hz give the degeneracy factor DI, The deviations of HI, from zero measures errors relative to the infinite, per-fectly random x = —,

'

alloy. The designation of the superlattice is illustrated as follows: the notation "A,

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(a) SQ8-2 (b) SQS-4
aE &L ~ &E 4L
%F

4E A~ ~ ~ IE

(c) SQS-8

8) [113]
~ 4 L ~A & &ML

alloy [Eq. (2.8)]. It is, however, a simple matter to apply

~

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TABLE IV. Number of neighbors to a given atom in the SQS-4, the average & 0) of mth shell neighbors of an opposite type, and the corresponding result &0)s for the perfectly random alloy [Eq. (3.2)]. The number of Bneighbors is the shell coordination num-ber (CN) minus the number of A atoms.

Sublattice Occup.

First
shell
CN=12

Second
shell
CN=6

Third
shell

CN =24

Number of A neighbors in SQS-4
Fourth Fifth Sixth
shell shell shell
CN=12 CN=24 CN=8

Seventh
shell

CN =48

Ninth

9632 WEI, FERREIRA, BERNARD, AND ZUNGER 42 A (1), (0,0,0)a A (2), (—, ', —, ',

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Since our interest in the present paper is in comparative
simulations of the perfectly disordered (random) alloy, we
first provide bH(x) as obtained by cluster expansion in
the T~ee (random disorder) limit. By Eqs. (2.7) and
(2.8), we see that at x = —,

'

~H'"(—,

'

) =Do, t &o, i

hence (since Do, = 1), Eq. (2.10) gives

(4.2)

W,

b,H' '(—,

'

)=—g [II,(s)] 'E(s), (4.3)
where E(s) is the excess energy of the ordered structure s at the equilibrium volume V(x = —,

'

) of the random alloy,
and II is a matrix inverse. Equation (4.3) provides a simple way to calculate the mixing enthalpy of the x = —,

'

random alloy from the known total energies of N, period-ic structures, without resort to complex solutions of the Ising Hamiltonian. In Ref. 55(a), we illustr72 /Xi11 9.2ng

illustmT /Xi11 8.5T /8.9911 9.02 In

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13.9, and 16.

5 meV/4 atoms, compared with 19.

5 in the

cluster expansion) appear reasonably well converged.
The fact that hH'"' of random alloys lends itself to
calculation in terms of the

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in good agreement with our result of Eq. (4.5). A
different experimental value of

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E. Electronic structure

The electronic structure of substitutional isovalent
semiconductor alloys exhibits a number of experimentally
established features.
(i) While band-edge transitions remain nearly as sharp
as in the constituents, alloy broadening is observed at other energies.
(ii) "No-phonon indirect transitions" are observed;
while they resemble I ~Xtransitions in the binary, pko-
nons are nevertheless not involved.
(iii) Most transition energies bow downwards with x, i.e.,

their energies lie below the concentration-weighted average transition energies of the constituents. Different
transitions have different bowing parameters.

'

(iv) Valence-band states observed in photoemission are often split into A-like and B-like components.
All of the features can be understood qualitatively by noting that SQS's closely approximate the atomic
geometry of random alloys and that, at the same time,

~1c ~lc ZB

X1c M5c +I 4c

X3, M1, +M2, +I 1,,

1.1, ~R1,+R4,,

(4.8)

where ZB denotes zinc-blende states, and superlattice
states are denoted by a bar. Here, I =(0,0,0); M= (0,1,0), and R =(—, ', —, ', —, ') (in Cartesian coordinates with units 2m./a). For SQS-4, we have the folding relations:

these SQS's are superlattices. Recall that superlattice
states %,(Kr) of band index i and wave vector K can be
analyzed in terms of the states P,.(k,r) of the constituents using compatibility and "folding" relationships. For ex-ample, the (001) superlattice SQS-2 (with repeat period of
1) exhibits the compatibility relations' (shown here as appropriate to mixed-cation superlattices with the origin
on the anion site)

r"(o,o, o), x,"(ool), r."(—,

', —,

', o), x".(——,

', ——,

', o)-r(o, o,o),

X„"(1OO), X,"(O1O), ZzB(-,', ——,

', O),

o)-r.12 432.98 Td (—)Tj ET BT /Xi14 9.58 T3 467.08 449.6 Td (—)Tj ET BT /Xi14 11.98 Tf 109.22 445 Td (,)Tj ET BT /Xi14 13.31 Tf 148.91 448.91 Td (',)Tj ET BT /X

k,

of

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(Kr)

,

4.

K

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by

The

energies

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can

by Xi14 (by)Tj ET BT /Xi14 9.41 T03106.32 350.08 Td (are)Tj ET BT /Xi14 9.52 4 469.309615.86 Td (The)Tj ET BT /Xi14 8.85 f 39.309615.86 Tinverthese

k,

—

S8 (i.)Tj ET BT /Xi14 9.28 Tf321.Tf 2193.2 Td (For)Tj ET BT /Xi14 8.85 f 312.Tf 2193.2 Teacwith

zinc-blende

we

have the

k,

(4.

the

as

by

SQa).

(i)

l-gel(and)Tj ET BT /Xi14 0.68 Tf 1 9.T5 675.65 Td (sp(not(by)Tj ET BT /Xi14 .54 Tf14 9.Tf33113.2 TS (states)Tj ET BT /Xi14 5.54 Tf 114.Tf33113.2 Td epeat)Tj ET BT /X Valence-band 4.

can

be

split

in

the

(.)Tj ET BT /Xi9480.54 Tf3396.16 520.68 Tuctor in

', Td (by)Tis5.01 T024 6BT068Xi14 /Xi7114 10.54 Tf.54 Tf067 65', by9.1 TiQS'sTj ET BT /Xi14 8.3 Tf 47.557.99 2 BT /Xi1BM)](4.)T14 8.59 Tf 465.Tf617.74 Tg03 0 36814.Tf3311Xi14 12.78 T314 8.917 Tf C 6 5659 2 3.2 Td %, components.Tf3 M5c4 R4, repeat states, by T1B 564.5 (%,)Tj ET BT /Xi14 j 68.21 d (+)T T1B 564.5 d BT /i /Xi14 98378/Xi14 01 10539 (9.64 1B 564.5 (T BT /Xi14 9.39 Tf 42f321.4)Tj8)T T1B46.81 T BTj ETET BT /89.02 T1539.580f 2731(R4, 58.33n B40Tj E1385Tf 163.2f 1053131.4955.82 T)Tj c„ states

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TABLE VII.

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TABLE IX. LAPW calculated crystal-field splitting AcF and spin-orbit splitting 6p (all in eV) at the VBM [from Eq. (4.12)] for seven disordered 50%-50% semiconductor alloys and

and

[from

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2:.(a) r

L1c

Ji Ji

iA(1/4, 1/4, -1/4) (c) P(3/8, -5/8, 1/8):

(b) L1c Lie(+X] c)X1c(+L1c)-
Ji Ji

I

UlI

C
LLI

Cl -1.

-

0.31

0

0.16 0.12

L3v

0.32

0.24

L3v

0.25 0.08

0.26 0.09

L3v

L3y L)c Matrix Elements in Ga2AsP SQS-8

(a)". Te
I
I
I
I I
I I

5 I

I' I I

15 (b},",Te, s 15-
r I
~ I D I I
5-

15 (c)
Hg, d

I

Te {1)
Site

Te, p

: h
Il

&%I)r I

' L I

Hg
Site

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The first step measures the "volume-deformation" (VD)
contribution bvD, the

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TABLE X. LAPW-calculated semirelativistic bowing

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CU

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amounts of the binary constituents [i.e., bz of Eq. (1.1)], and then (ii) applying this change to the average of the
measured' (low-temperature) band gaps of the binary
constituents. Since the LDA error largely cancels in step
(i), this procedure is likely to produce a reasonable esti-mate. The results for the predicted direct I v~M~I „ gap are given in Fig. 13 where spin-orbit effects have been included. We see that relative to the average gap [Eg(AC)+Es(BC))I2, the direct gap decreases in the se-quence chalcopyrite ~random alloy ~CuAu ~CuPt. The mechanism for this was discussed in detail by Wei
and Zunger and by Bernard et al. ' These results can

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amine the rate of convergence. This is done as follows:

Using band theory we have first calculated the direct I„,~I „band gap Es(s) of E, ordered structures s = AC, BC, CuAu-like (CA), chalcopyrite (CH), CuPt-

like (CP), the (AC)z(BC)2 (001)superlattice (denoted Z2)
and SQS-4. These values, evaluated at the average alloy lattice constant

a =(a„c+azc)/2 and averaged over
crystal-field splitting are given in the first eight columns of Table XII. Using Eq. (2.10), we then find the X, "band-gap interaction

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TABLE XII. The first eight columns give the (LAPW-calculated, unless otherwise noted) direct band gaps at I (in eV) at the 50%-50% average volume for

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A.

Sher,

M. J.

Vac.1

BVac.Wilj ET BT /Xi26 8.87 T /Xi26 84.72 TT2 Td (Vac. BT /Xi26 8.49 Tf 15Tf 163.52.89 2 Td (Vac..)Tj ET BT /Xi26 8.8 Tf 249.01 Td 2 T)Tj ET R2.47 (B)Tj TsTj ET BT /Xi26 9.38 210.49 3017d 65BT14hTj ET BET BT /Xi26 7.94 Tf 120.92 2876 TdT14hTj ET BET BT /Xii22ET B /X0255 035emm 198.99 s Vel ET BT /Xi26 9.17 Tf 55.6 523..97 Td239.d (VelET BT /Xi26 8.9 Tf 227.48 333.62 .88Tj ET BBT /Xi26 9.09 Tf 230.24 376.564 597.99 s,)Tj BT /Xi26 8.83 Tf 266360 S.

B

B

3(5,)Tj ET75 ET BT /Xi26 8.37 /Xi38.044295 Td (5,)Tj ET

61Td (295.)BunkE7 (1)Tj .18 Tf 68.1 208.29 3797.39 1B. 13333300BT /Xi26 7.86 Tf Tf Tf 555 Td 39 1B.71 (D.))Tj ET BT Tf3 8.1T BT8.3338 7146.47618.9 Td (B)Tj7 j ET B0BT /Xi26Tf 232.5 Tf 55.92 345.

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