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(aj Diamond symmetry (b) Zinc-blende symmetry

FIG. 1. Representation of structures with (a) the diamond
and (b) the zinc-blende symmetry in (2 B)& C2 alloys. A
solid circle indicates an A"' atom, an open circle a B atom,
and a shaded circle a C' atom. For clarity, the structure in (b)

represents the maximum possible zinc-blende ordering, with all 3"' atoms on one sublattice and all B atoms on the other.
Real zinc-blende samples hTf 193.674op726Tf 263.44 570.89 Td0.56 244.78413rv ET BT /Xi1 8.53 Tf 189.59 520.4d (samppartij ET BT /Xi1 8.1 Tf n)Tj ET op3Tf 230.44

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models of the ZB~D transition have neglected octed

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hole. Compensation can then occur through charge
transfer from donor to acceptor bonds. This creates a
distribution of positive and negative charges. The energy
associated with this process can be conveniently modeled

by considering (A "8)„/(C2)„superlattices (SL's). In
superlattices, two types of AZ, =+1 bond interfaces
occur: In [110]SL's, both donor and acceptor bonds are
present at the same ("neutral, " or nonpolar) interface,
while in [001] and [111]SL's, only one type of hZ, =+1 bond is present at each (charged, or polar) interface. In unreconstructed [001] and [111]SL's, only partial com-
pensation may take place if the period is long enough,
since the band gap acts as an upper limit to the potential drop across charged interfaces. However, reconstruction can further lower the energy through swapping of atoms
between interfaces, allowing thereby for a more effective
compensation within each interface. Full compensation
is expected in nonpolar [110] SL's and all other struc-tures, including alloys, where long-range fields are absent.
According to the model of Dandrea, Froyen, and
Zunger, the excess energy of nonisovalent lattice-
matched SL's can be approximated well by a combination
of Ising-like nearest-neighbor interactions between neu-tral atoms and electrostatic terms due to charge transfer. Since the energies are measured with respect to the segre-gated end-point compounds, and since stoichiometry be-
tween the 3

" and 8 elementary constituents is main-
tained, only the difference between the average energy of the two types of (neutral) b,Z„=+1 bonds and the aver-age energy of the two types of normal bonds is a relevant parameter when electrostatic terms are not included.

The total excess energy before charge transfer (q =0) is

E „,(q =0)=(ND+N~)5,

tions between compensating charges [q;] (usually —,

'

and ——, ', in units of the electron charge) placed, in the model,
at the midpoints [R,] of the b,Z, =+1 bonds. (The small
variations in bond length between donor and acceptor
bonds are ignored and the average bond length of the
nearly lattice-matched 3 8 and C constituents is
used in the model.) These interactions are assumed to be
screened, independently of distance, by the average static
dielectric constant eo of the two components, so that we
have

e q;q.

M" e~~o;&, R —R~ (5)
The total excess energy is the sum of Eqs. (1) and (3)—(5):

E~„,(q)=E~„,(q =0)+E„+Ec,„I.
Here, E„+Ec,„& is the total-energy change that can be

assigned to hZ, =+1 bond energies due to charge
transfer, including the (negative) compensation gain and the (positive) intrabond Coulomb energy. The total pair-wise energy can also be written as

Ep„,(q) =(ND+N„)J(q),

bH=E „,(0)+E„+Ec,„I+EM,d

.

Previous models ' ' ' ' have retained only the

E „,(0) term.
It is convenient for a thermodynamic treatment of the
problem to regroup the contributions of Eqs. (1)—(5) as

bH =Ep„,(q)+EM,d,

where

where ND and Xz are the total number of donor and ac-
ceptor bonds in the structure (ND =Nz for
stoichiometric systems) and the average excess energy 5

of the bZ, =+1 bonds before charge transfer occurs is expressed in terms of bond energy differences as

where

J(q)=5+bJ(q).

In this expression, the bond charge-transfer energy is

b J(q)= ——,

'E (0)q+ —, '(UII+ U„)q

(10)

2~ (siii-IV+ eiv-V eiii-V eiv-Iv)

After charge transfer, three additional terms appear.
(i) Transfer of a charge q from a donor to an acceptor state initially separated by a gap of Eg(q =0) produces an energy gain (to first order in q) of qE (q =0). A compen-
sation gain,

In Sec. III we show how the energy parameters 5 and (UD+ U„) [and, therefore, J(q = —, ')] are obtained from
this model through first-principles superlattice pseudopo-
tential total-energy calculations for the lattice-matched
systems (GaP)„/(Si2)„and (GaAs)„/(Gez)„. The accura-
cy of this model in predicting calculated SL energies is
then demonstrated.

E„p=,

'

(ND +N„)E (—0)—q, (3)

Eco I

'(ND +Nz)(UD + U—z)q (4)

where UD and U~ are intrabond Coulomb repulsions in
the donor and acceptor bonds.
(iii) Finally, an excess Madelung energy EM,d

results

from the sum of screened long-range electrostatic interac-

therefore arises.

(ii) The excess or deficit of compensated charges on the AZ, =+1 bonds now produces an excess intrabond
Coulomb energy, due to both electrostatic and exchange-
correlation terms, given by

III. CALCULATION OF ENERGY PARAMETERS
AND TESTS OF THE MODEL

The excess energy and charge-transfer values were cal-
culated for 13 (GaP)„/(Siz)„SL's by the semirelativistic
self-consistent pseudopotential method using a plane-wave basis with cutoff energy of 15 Ry. These were used to obtain a fit of the energy model of the previous section.
The Madelung energy was calculated by the Ewald
method, with a dielectric constant taken to be the aver-
age (co=10.4) of GaP and Si. The parameters 5 and (Uz, + U„) were extracted from a least-squares fit to the

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0 3 (a)
-

q=O
~ 0.2-

0.1— 40
~ I
~00

(b) I
y) 0.2-

M

o q=0 01-
LU

0.0

(GaP)„(Si2)n

Np+NA —N

'

[001]
n=1

M P

Np+NA-N/2

[001] [001] [110] [111]
fl=2 0=2 (i=2 ll=1
rec.

M P MP ~MP M+p

FIG. 2. Formation enthalpy (with respect to the separated
constituents) of some (Gap)„/(Si2)„superlattices, according to
the charge-transfer model (M) and to pseudopotential calcula-
tions (P) [Ref. 29]. The sublattices are classified in (a) and (b)

according to their number of AZ, =+1 bonds, AD+X&, and are denoted by their orientation and repeat period n. The bars
for "n =2 rec" indicate the average energies of reconstructed
structures obtained by swapping cation and anion atoms on
different (001) planes, as described in Ref. 29.

pseudopotential total energies for fixed values of Eg(0). The degree of arbitrariness in the choice of E (0) was of little consequence to the fit: Changes in Eg(0) are offset
by changes in (UD + U„) so that both b J(q) and 6 are
relatively insensitive to E (0) over a reasonable range of
values.

The resulting energy parameters for GaP/Si are

0.

fit:

for cntial

AZ, AZ, 0.

The

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energy

values fo some

the

pah(period)Tj ET BT 1896 9.12 Tff 75956 104.22("P" ((0))Tj ET BT /Xi5 8.423 Tf 65922 (with sd (the)Tj ET BT /Xi5 9.39 Tf 9582f 205.67 Td (obtained)Tj ET BT /Xi5 8.674Tf 1658122 94.56 energy

the model

"M"Eg(0).

The

q=0

cation

igstructed 0. arend

lcula- cation

AZ, 0. n

that cTd (cROYEN,)Tj ET BT /Xi 10.49 Tf 165344 679.89duonable

a

cntial

AZ,

AZ,

U„)

the

[Ref.

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(b)

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that

the

some

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and

the

q=0 for

in

atoms

b (ucording cvalues. Np+NA

energy

values

of

=+1 GapGe/(SSL'values with

cmodel

The

parameters

0.=2 fit:

AZ,0. are 43

the

cd (was)Tj ET BT /Xi5 10.31 Tff 93.44 124.89 Td (of)Tj ET BT /X1 8.12 7Tf 537Tf 124.89 Td (the)Tj ET BT /Xi5 9.98734 6737Tf 124.89 Td (model)Tj ET BT /X73

cad (cdROYEN,)Tj ET BT /Xi 10.49 Tf 143.56 605.67showesulting

inperiod dmentTd (0.)Tj ET BT 8Xi5 9.86 T 2035.11 86.67Analysihanges

total

atoms

for

q=0

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—

0.

0.

—

q=0 01- I

d (0.)Tj ET BT /Xi5 8.643Tf 289.56 669.11„pGe/((q=0)Tj ET BT /6X65 4.446Tf 226958 636„ (are)Tj ET BT /X75 14.40Tf 156 200.44 Td '([111])Tj ET BT /Xi5 14.40T d (0.)Tj ET BT /Xi5 8.64i5 9.45.11 134.78GapGe/(tions 0. [Ref.

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infor for relbonds,

the

b

(q) relbonds,

to

E

d ((0))Tj ET BT /Xi7 9.25 Tf 214388 668.11 T omlcula- igs (cation)Tj ET BT /X67 9.21iTf 144244 636.33ga T(tions igs 12.42rf 54267 679.78 (igs (cat66.78 Td (of)Tj ET BT /X1j ET636.22 Td mj ET BT9,)Tj ET BT /Xi5 9.1811f Td mj ET BT9,)T67 20448T6 94.56 Td e 109ET BT /Xi315.83.22 29467

energy

0= 669.11casd (in)Tj ET BT 15 8.94 4549.4 Tf 205.678J Td ((q))Tj ET BT /4i5 8.443449.4 Tf6.33tyge relcula-

changes q=0

0. the

E

charge-transfer (b (0 0= b) F in ps

de 4 v

th

and

planes, by[Ref.

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havior, depending on composition

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TABLE II. Contributions to the formation enthalpies of unrelaxed GaP/Si superlattices and alloys. All energies are in
meV/atom. (ND+N~)/N gives the relative number of AZ„=+1 bonds. The formation enthalpy in the model without charge
transfer is AHM(0) =E~„,(q =0) [Eq. (1)] and the pairwise energy with charge transfer is E~„,(q) [Eqs. (9)—(11)]. The first few terms in the excess Madelung energy are shown next: Contributions E„ form nth neighbor bond pairs [Eqs. (13) and (14) and Fig. 4]. The

remaining terms in the Madelung energy are denoted by E„, while the total excess Madelung energy is
EM,d

=E, +E2 +E3,+E» +E„. The next two columns represent the total formation enthalpy from the model,
EHM =E~„„(q)+EM,~, compared to that from the pseudopotential calculation, AHP [Ref. 29]. This comparison shows the model captures the important physical ingredients of the excess energy of nonisovalent systems. Superlattices of (GaP)„/(Si,)„are denoted by the repeat period n and orientation G. The line for "2 (rec)" displays average energies of reconstructed structures obtained by swapping cation and anion atoms on different (001) planes, as described in Ref. 29. The maximum entropy (Max-S) zinc-blende (ZB)
and diamond (D) structures are described in Sec. V.

Structure

ND+N~
N

b H~(0) Ep„r(q)

Superlattices

E Erem EMad AHM AHp

[001]

[110]

Max-S
Max-S

n
1

2

2(rec)

ZB
D

1

2
1

4

1

6

1.097
1.172

210
105
105

210
105
70
52

105
52
35

230
246

126
63
63

126
63
42
32

63
32
21

138
148

45
22
11

45
0
0
0

0
0
0
Alloys
56
46

—52
0

—52 —26 —17 —13

—14 —22

—23
12
0

—23
12
8
6

—34
0
0

—6 —10

—23
12
0

—23
12
8
6

34
17
12

47 —24
12

—12 —3

—6
22

—6 —10

38
18

120
85
60

120
53
36
27

56
37
30

176
166

125
90
62

125
48
38
25

42
30
25

'Estimated to be small in alloys.

III that our model captures the variations in the directly
calculated pseudopotential values and that neglect of
electrostatic effects [compare bH~(0) with bH~] overes-
timates instability and reverses the order of the ZB and D alloy phases.
The truncated model can be used to predict the heats

of solution of some simple substitutional nonisovalent de-fects in the 3"'B and C constituents. Such results can be compared to those obtained from Harrison's universal-parameter tight-binding (UPTB) method for isolated defects. Consider (GaP)i „Si2 as an example. We define the "sublattice heat of solution" Ho, p(Si,Si) as

TABLE III. Same as Table II for GaAs/Ge.

Structure

ND+N~
N

EHM(0) pair (q) E

Superlattices

Erem EMad AHM AHp

[001]

[110]

Max-S
Max-S

n
1

2

2(rec)

ZB
D

1.097
1.172

162
81
81

162
81
54
40

81

178
189

109
54
54

109
54
36
27

54

120
128

35
18
9

35
0
0
0

0
Alloys
44
36

—40

0 —20

—40 —20 —13 —10
—11 —17

—17
8
0

—17
8
6
4

—26

—17
8
0

—17
8
6
4

35 —18
9

35 —5

—4
16

31
15

105
70
52

105
45
31
23

49

151
143

112
68
50

112
38
35
22

35

'Estimated to be small in alloys.

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the energy required to transfer a pair of unbound Si atoms from the bulk of a Si crystal replacing a pair of Ga and P atoms in CraP, so that the two Si atoms remain separated in two different sublattices. This creates four Si—Ga and four compensating Si—P bonds in tetrahedral geometries. Each defect, therefore,

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fcc sublattices of the diamond lattice by

a and P, we call
y;. the pair probability for finding an atom

i on sublattice
a and

a neighboring atom

j on sublattice P. The corre-

sponding site probabilities will be denoted by x; and xJ~. The total configurational entropy of the lattice per site in units of kz is then

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Cumulative sums of terms

in (GaP)„(Si2)n Madelung energies

VI. EQUILIBRIUM PHASE DIAGRAMS

A. Hamiltonian and its solution
0.08
E
O

0.06

0.04

Ul

+ 002

0.00

-0.02

Max SZB
Max SD

[001]n=2

[110]n=2

'X
------------- ~

We discuss next the equilibrium finite-temperature
thermodynamics resulting from our truncated charge-
transfer model using the pair approximation of the
cluster-variation method (CVM). We will comment on
both equilibrium results and on possible metastable
states.

The bulk equilibrium thermodynamics of homogeneous
(A"'B), „C2 solid alloys will be described through
the excess free energy
I I I

1 2 3z 3h

Order of bond pairs

I

Tata)

FIG. 7. Convergence of the excess Madelung energies of maximum-entropy (Max-S) x =0.5 (GaP)& „Si2„alloys in the zinc-blende (ZB) and diamond (D) phases and of two n =2
(GaP)„/(Si2)„superlattices. The order of bond pairs correspond
to the electrostatic interactions of Fig. 4.

AF=bH —TS, (22)

where the excess enthalpy AH includes the pairwise and
interbond electrostatic terms of Eq. (7) and the
configurational entropy S is given in the CVM pair ap-
proximation of Eq. (19). In terms of the pair probabilities Iy;. I, the excess enthalpy is written as

bH =2K +y,, b;, + g N„g pI,",I~kl~ CI,",I~k~~, (23)
where

J(q) for bZ, =+1 bonds
0 otherwise, (24)
(where either Ga or P is located on one sublattice) and less Ga-Si-P (where Ga and P are located on the same sublattice) are found; the electrostatic repulsion between
AZ, =+1 bonds of the same kind then increases the ener-gy of the ZB phase.
(ii) The bond charge-transfer energy E„~+Ec,„~ [Eqs. (3) and (4) and Fig. 6] is higher (less negative) in the ZB phase. This is due to a larger number of Ga and P atoms on the "correct" sublattices, leading to a larger
number of Ga—P normal bonds and, therefore, a smaller

number of Ga—Si and Si—P (b,Z„=+I) bonds. Conse-
quently, the compensation energy (which stabilizes both
phases) is less negative in the ZB phase.
(iii) The "chemical" part of the pairwise energy, E~„„(q=0), is smaller in the ZB phase for the same
hZ, =+1 bond counting argument given in item (ii).
As a combined result of effects (i), (ii), and (iii), we find
(a) a smaller excess enthalpy for both phases in compar-
ison with the no-charge-transfer results and (b) a smaller
excess enthalpy for the D phase than for the ZB phase, in
contrast with the no-charge-transfer result. Effect (a) im ET BT /Xi10 10.58 BT /X310 9.37 T9 Tf 85.6.68 Tf 28c/Xi10 9.95 Tf 314.44 /Xi104Xi10

a

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g, =&s, &, g, =&s, &,
g, =(S,'&, g,=(S,'&,

g, =&S,S,), g, =(S,'S,'&,
g, =&S,'S, &, g, =&S,S,')

.

(26)

Here,

E and
j represent nearest-neighbor sites on sublat-

tices a and P, respectively; the spin variable S; can as-sume the values —1, 0, or 1, according to which atomic species

(2'", C', or

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mates for order of magnitudes of solubilities.
A C impurity atom in solid A B has an excess en-
ergy h6', /2, where b,8, is given by Eq. (16) if no charge-
transfer effects are included or Eq. (15) with charge-
transfer effects. In the very dilute limit no correlation
occurs between different impurities, and a mean-field ex-pression for the entropy is appropriate. The free energy in the x —+0 limit is then given by

Fo(x) =Nx
2 (Nx)![N (1—x)]!
2k~ T

x + [x lnx +(1—x)ln(1—x)]
2 b,C,

(31)

1—x
2

2k~ T 1—x + x lnx +(1—x)ln

1

2

(32)

The

2the

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0.02

I-
CQ

Ul

CD
CD
CD
CD

LL

T=1600 K, q=1/4

-0.02 —, S~

A

-0.04—

-0.06—

0
GaAs

0.2 0.4 0 6
Composition x

0.8 1.0
Ge

FIG. 10. Representative free energy vs composition curve of
(GaAs)& Ge2 for a temperature below the tricritical point.
The dashed and solid lines indicate the zinc-blende and dia-

mond phases, respectively. Points A and B are the limits of phase separation (represented by the dotted line), S is the zinc-blende phase spinodal, and P is the unstable second-order tran-sition.

order transition line terminating at x =0 at a finite criti-
cal temperature T„so that only the D phase is stable for
T) T,. This feature enabled a low (x, =0.3 or 0.4)
order-disorder concentration to be Ptted in previous ap-proaches by adjusting ratios of temperature to interaction
energies. While we have excluded AZ, =+2 bonds, we
note that if their energy were three to four times 6 (as suggested in Refs. 27, 58, and 59), their inclusion in our
model would lead to significant deviations in the phase
diagrams only for T «2000 K.
(ii) As the temperature is lowered, x, increases gradual-
ly, until a tri critical point is reached, at
T =T„=1.826/kz, x =x„=0.727, below which the
transition becomes first order. The presence of a tricriti-
cal point is a well-known characteristic of the Blume-Emery-Griffiths model.
(iii) Below the tricritical point, the first-order transition
is refiected in an (x, T) diagram by a phase-separation re-gion, whose concentration range increases rapidly as the
temperature drops until it occupies the whole 0&x &1
interval

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for the uncompensated case, we find that in the CVM
pair approximation single phases are unstable in most of

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APPENDIX A: SUPERPOSITION APPROXIMATIONS

To introduce interactions beyond the size of the basic cluster (in this case, the nearest-neighbor pair), we use
mean-field-like "superposition approximations, "
that would be exact if there were only one path between two points of the lattice (as in one-dimensional systems or Bethe lattices). For the finite-range energy expression of Eq. (13), we use the probabilities of occupation of first-neighbor bond pairs,

+—[D (k3+ k4)—~(f1+f2)]

N

(B2)

where z =4 is the lattice coordination number.
An isomorphism exists between the complete BEG
Hamiltonian of Eq. (Bl) and the three-species alloy prob-
lem with only nearest-neighbor interactions (to which our
model without charge transfer 43 9.4 ET BT / /Xi15 9.26 Tf 533.56 590.5

cn 5j ET BT /Xi15 9.66 Tf 117.22 579.22 Td (cn 5j Tj

the

Ha6 ET BT definXi15 8.63 Tf 268.11 612.78 T6 (workout)Tj ETXi15 9.18 Tf 70.568 589.78 5d (U.)

po47rea

2Xi15 13.67 Tf 436.8Tj 52.78 1 th40est-neighalong15 8.91 Tf 432.22 667

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tion is antiferromagnetic (J &0). The condition

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Zunger, Phys. Rev. Lett. 66, 2132 (1991), demonstrated by
total-energy calculations that the energy-minimizing surface
geometry of Ga0 5In0 &P is identical to the one observed after
growth but differs from the bulk-stable geometry. See also a
preliminary report in J. E. Bernard, R. G. Dandrea, L. G.
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bygeometry