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First-principles calculation of alloy phase diagrams: The renormalixed-interaction approach

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We present a formalism for calculating the temperature-composition phase diagrams of isostruc-tural solid alloys from a microscopic theory of electronic interactions. First, the internal energy of the alloy is expanded in a series of volume-dependent multiatom interaction energies. These are determined from self-consistent total-energy calculations on periodic compounds described within the local-density formalism. Second, distant-neighbor interactions are renormalized into composition- and volume-dependent effective near-neighbor multisite interactions. Finally, approx-imate solutions to the general Ising model (using the tetrahedron cluster variation

of

3198 L. G. FERREIRA, SU-HUAI WEI, AND ALEX ZUNGER

where X„and Xz are the number of A and B atoms, re-
spectively. Each lattice site i can be occupied either by a
8 atom (in which case the spin variable is denoted S;= 1)
or by an A atom (where S;=—1). One then seeks to find
for each (x, T) the density matrix p(o., V) and from it the
ensemble average (over configurations) of the internal en-
ergy (bE(y, V)) and entropy, for all phases y

(disor-
dered, ordered, phase coexistence, etc.). The solutions which are energy minimizing both with respect to volume and probability distributions define the excess enthalpy and entropy

dered structures is a subgroup of that of the disordered phase. In this case we will have more figures and smaller Df's.
In a coherent binary (A„B,) or pseudobinary
(A 8, C) systein, the substituting species (A and 8) are restricted to reside on the ideal lattice site, in which case a single external volume V defines uniquely the size

and shape of each figure f. Hence, J&(V) is independent
on the space group of the system (or on the equivalence
or inequivalence of the figure f). In this case, one can
define the "average in lattice product"

bH(y, T)=H(y, T) xH&(—T)—(1 x)H&(—T),

bS(y, T)=S(y, T)—xS„(T)—(1—x)S~(T)

(1.2) IIf(o) Qllf (lf o)
f 1f

(1.5)

for each phase y. Using the conventional common
tangent construction (seeking x and T where the free energies. of two phases equilibrate) one then constructs the phase diagram.
Even neglecting excess vibrational energies and limit-ing the discussion to phase interconversions on the same type of lattice at all compositions, this is still a formidable task, involving 2 calculations of bE(o, V) at each V and performing a statistical ensemble average on such sys-tems (indeed, no exact calculation of the partition func-tion exists for three-dimensional infinite systems). Hence, the standard lattice

FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:. -. 3199

ps(n) =g'p(tr),

where the primed sum over o denotes a multiple sum over all configurations o. containing n at the vertices of subfigure g at l. The simplification is achieved by decorn-posing the subfigure g into a hierarchy of its subfigures h,
hence, like

3200 L. G. FERREIRA, SU-HUAI WEI, AND ALEX ZUNGER

lated subband" ' '

(e.g., narrow d bands in transition
metals) or empirical parametrization of the near-neighbor
Hamiltonian matrix elements ' '

are often used to par-
tially avoid this problem. The advances in modern
electronic-structure computational techniques, ' ' how-
ever, make it now unnecessary to limit d,&„ to a small
value.

Statistical solutions to an Ising Hamiltonian with d;„, fixed at the first nearest neighbor and varying d„„have shown that most aspects of the phase diagram are accu-rately captured when d„„ includes four-body counting figures. For example, the reduced transition temperature kz T, /12J2 for a nearest-neighbor pair-interaction fcc Is-ing ferromagnet is 1.0, 0.9142, 0.8354, 0.840 45, 0.833 94, and 0.829 81 if d„„includes sites, pairs, tetrahe-
dra, double tetrahedra, the tetrahedron-octahedron, and the double tetrahedron-octahedron, respectively, com-pared with the numerically accurate value of 0.816 27 ob-tained in high-temperature expansions. Hence, relative to the latter value, the errors in k&T, /12J 2are 22.5%, 12%, and 2.3% for sites, pairs, and tetrahedra, respec-tively. For many applications, an error of 2—5% can be tolerated. Note, however, that we do not know the efFect on T, of increasing d„„when the interaction range d;„, itself is long (e.g., d„„=—d;„, is equal to a few neighbor
distances). This important question remains open at the present time.
The minimum range d;„, of multiatom interactions needed to capture the essential physical

FIRST-PRINCiPLES CALCULATION OF ALLOY PHASE DIAGRAMS:... 3201

the same system, provided that those phases differ from the set of ordered structures only by substitutional order. This is our first (of two) key approximations.
Connolly and Williams have implemented this ap-

proach using five fcc ordered structures for Is j, i.e.,

lim-

iting d;„, to first fcc nearest neighbors. This selection is unconstrained in that (i} it does not provide information on the magnitude

ap-

3202 L. G. FERREIRA, SU-HUAI WEI, AND ALEX ZUNGER

bors, we will "fold" distant-neighbor interactions into
effective volume- and composition-dependent interac-
tions IJf(x, V)] within the figure U. In the present il-
lustration U is taken as the fcc tetrahedron of nearest
neighbors. This folding is performed under a statistical
assumption —our second key approximation —stating that if a figure has two spin variables separated by a dis-tance larger than d„„they will be assumed to be statisti cally uncorrelated in the following sense. Consider a figure P consisting of sites a, 13,..., co. By the definition surrounding Eq. (1.3) its spin product is

Jf(x, V)=Jf(V)+ g C~(2x —1) ~

Jp(V).

Dp k —k

~K. f'
(2.21)

(IIf) QIIf(n)P (2.22)

Use of the orthogonality relation (2.9) and Eq. (2.12) to write the correlation functions (IIf) in terms of the probabilities P„gives

H~=S Sp.. S (2.14)

where S are the spin variables (taking up values of +1).
If the figure P is not contained in U, we assume no corre-
lation and set

Using this result in Eq. (2.20) we arrive at

(bE(V)) =QP„bE(n, x, V),

where

(2.23)

((S —q)(Sti—q~)...

(S —q))=0, (2.15) bE(n, x, V)=N g DfIIf(n)Jf(x, V).

fcU

(2.24)

where

q=&S& (2.16)

(with a similar definition for spins on other sites}. In the case of the disordered phase,

Our method [Eq. (2.15)] of calculating

product

3204 L. G. FERREIRA, SU-HUAI WEI, AND ALEX ZUNGER

ly satisfied: even constant-Uolunze bond relaxations great-
ly affect the values of bE (s, V), and hence Jf(V).
(iv) Nature of the ground sta-te structures T.he nature
of the T =0 ground-state ordered structures can be found
in conventional methods ' only if a small number ofJ's
are retained in Eq. (2.1). Having calculated the left-hand
side of Eq. (2.1), the prediction of the lowest-energy or-dered phases at T=0 among the set ts I

is available at

the outset, independently of any truncation of the sum of Eq. (2.1) to a few J's.
(U) Statistical correlations. The inclusion of many-spin
statistical correlations within a range d„„tra'nscends the
limited statistical correlations used in simpler models.
The method developed here permits therefore the con-
sideration of rather general forms of "chemical disorder"
(through inclusion of variational, nonrandom correlation functions) as well as "positional disorder" (through relax-ation of atomic position vectors in minimizing the total energy).
(Ui) Control ouer types ofinteractions included Inter. ac-tion parameters Jf are included in a hierarchia1 manner,
based on their established magnitudes, not in an ad hoc
fashion. For a sufficiently large set of interactions, the re-
sulting phase diagram is unique.

B. Limitations

There are two main limitations to our method

(i) The choice of IJf(V)I. Many calculations of alloy phase diagrams are based on the assertion that in-
teractions corresponding to a "small" number of bodies k
and a "few" neighbors m are sufficient to obtain a con-
verged representation of the internal energy. These asser-
tions are often based on the success of fitting certain
features of the phase diagrams (e.g., order-disorder tem-
peratures for Cu, „Au„) using just nearest-neighbor in-
teractions. However, first-principles calculations of Jf(V) reveal (e.g., see Fig. 2 below) that one may have to keep many Jf(V)'s in the expansion of Eq. (1.10). Furth-
ermore, to treat an incoherent system (e.g., a lattice-
mismatched superlattice), one may have to include even
more Jf's because of the removal of the degeneracy of the Jf s. In fact, the only method that is reasonably safe here is to attempt di6'erent choices of interaction range and
observe numerically the convergence of the result (see
below), a rather laborious procedure. Note, however,
that in our formulation Jf(V) is expressed as total ener
gies, not interaction potentials, hence the convergence of the energy expansion is rather fast.
(ii) Number and choice ofspecial structures. The num-
ber ofJf(V)'s determined by the range m, „ofneighbor-ing interactions decides the number of structures needed, For instance, inclusion of all interactions up to km„=4
requires for m „=1 (nearest neighbors) 3m, „+2=5
structures, for nz, „=2 it requires 8 structures, and for
m „=3it

FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:.

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. 3205

We include in this group also the two-layer (AC)z(BC)2 superlattice, also along (001) (denoted Z2).
For (2,0, 1) structures, we have at 50%%uo-50% composi-tion (ABC2) the chalcopyrite (CH) structure, whereas at compositions of 25%-75% and 75%-25% we have the
famatinite structures (Fl and F3, respectively). In the
absence of the common sublattice C, these are the tI8 (for chalcopyrite) and DOE& (for famatinite) structures familiar
in metallurgy. '

Note from Table II that the (0,0, 1)
structures differ from the (2,0, 1) structures by interac-
tions beyond first neighbors.
Finally, for the (1,1,1) structures, we have at 50%-50%
composition the layered trigonal, CuPt-like (CP) struc-
ture (L 1&, in the absence of sublattice C), while for com-positions of 25%%uo-75%%uo and 75%-25% we have the Xl and X3 structures,

3206 L. G. FERREIRA, SU-HUAI WEI, AND ALEX ZUNGER

TABLE II. Lattice average spin products IIk (s} [Eq. (1.5)] for the ordered structures of Table I and the Z2 structure. For the
random structure q =2x —1.

IIk,gs)

0 1 2 3 4 5 5 7 8 9 10 11
interaction

A,m

L1 CUAU L3

Figure 0~m AC A38 AB AB3

Chal. CuPt F1 F3 Z2 X1 X3
BC ABC' ABC' A38 AB3 ABC' A38 AB3 Bagel

1 1 1 1 1

0 -1/2 1/2 0 -1/2 1/2 q
0 -1/3 0 -1/3 0 0 1/3 1/6 1/6 q~
8 -1 1/2 -1/2 0 1/2 -1/2 0 0 0 qs
4 J4=J4 ~
5 K2~22

2

6 M2&2, 4

=-- —= 6

1 1 1/3

1 0 0 q4
2/3 2/3 1/3 0 0 q2
1/3 1/3 -1/3 1 1 q2
7 K3%3,2
8 K4&4,2
9 L2=J2,3

12 1 0
12 1 0

12 -1 -1i2
- 1/3
- 1/3

0 1 1/3
0 1 1/3

0 -1/6 1/6 0 1/6 -1/6 q
- 1/3 -1/3 -1/3 -1/6 -1/6 q4

0, 1/3 1/3 -1/3 1/6 1/6 q

10 Ls&s,s ~ 24 -1 1/2 0 -1/2 1/6 -1/6, - 0 0 0 q3

and one at (1,0,0) passes

40 FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:... 3207

TABLE III. Calculated formation enthalpies 50'"' of ordered phases Ga4As„Sb4 „and Ga„A14 „As4, equilibrium lattice con-stants a,',"' and volumes V,',"', bulk moduli B(„)and their pressure derivatives B(„).The ordered structures are depicted in Table I.

Structure

Zinc-blende

(n =0)
Luzonite

(L1; n =1)
CuAu-I

(CA; n =2)
Luzonite

(L3; n =3)
Zinc-blende

(n =4)
Cupt

{CP; n =2)

3208 L. G. FERREIRA, SU-HUAI %"EI,AND ALEX ZUNGER 40

O

gg 1000

800

AE(n, v)

600 Ql
CP

400

u 200

LU

Gasb
Relative Volume

GaAs

FIG. 1. Total excess energy of ordered Ga4As„Sb4 „struc-tures belonging to the (0,0, 1) ordering vector (n = 1,2,3) and for the end-point compounds (n=0,4).

B. Energy scales and precision

Equations (2.3), (2.4), and (2.27) show that the scale of the internal energy of the alloy is determined by AE(s, V). There are three characteristic energies: (i) the formation enthalpy

FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:... 3209

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32IO L. G. FERREIRA, SU-HUAI %'EI, AND ALEX ZUNGER

—E~, „a„c,(» V I&oI) (5.9)

The total excess energy b,E(s, V) of Eq. (2.2) is the sum of
the three terms of Eqs. (5.7)—(5.9), i.e.,

EE(s, n, V) =EEvD(n, V)+bEcE(s, n, V)+DER(s, n, V)

=E~ ~ c (» V, [u,q I

)

——. '(4—&)E~c(V~c).'nEac(Vac—)—

(5.10)
The formation enthalpy KH(s, n) of ordered phase n is
the value of i5E(s, n, V) at the equilibrium volume V„
which minimizes b,E(n, V).
Figure 3 depicts the three functions bEvD(n, V),
i5EcE(s, n, V), and DER(s, n, V) for a few structures s of Ga~As„Sb~ „. Their sum [Eq. (5.10)] is shown in Fig. 1, whereas Table III gives their values at equilibrium. This analysis demonstrates the following points.
(i) Since b,EvD(n, V) is common to all structures of a fixed stoichiometry X„(e.g., for s =CA, CH, and CP at X„=—,

'

), structural preference energies in lattice-

to form A4 „B„C4,also at the volume V. The "charge exchange (CE) energy involved is

bEcE(s, n, V)=Ex, „a„c,(s, V, [uo1)

,

'—(4—n—)E„c(V) —,

'nE~—c(V). (5.8)

In this step we do not relax the cell-internal degrees of freedom (denoted as Iu I

). Third, allow the cell-internal
structural freedom to relax from IuoI to Iu, I. The
structural (S) energy involved is

bEs(s, n, V)=E„~c (» V, Iu,qI)

mismatched systems are decided by bE&(s, n) +bEcE(»n). Since bEvD=DEs=0 in lattice-matched systems, the structural preference energies are deter-mined by EEcE(s, n) alone.
(ii) All such ternary semiconductor phases are structur
ally frustrated in the sense that it is impossible to have, at
the same time, "ideal" (tetrahedral) bond angles and
"ideal" (i.e., zinc-blende) bond lengths. Binary AB
tetrahedral compounds (e.g., zinc-blende or L lz) can be
strain free in this sense. This is the principal reason
why n13 8.83 Tf.32 TEif 466 647 8.94 104 583.44cell- Td (semiconductor)Tj ET BT

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FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:...

alone and modeling it by the excess electrostatic
Madelung energy AEM, d,I„„ofthe ordered structures
with respect to equivalent amounts of zinc-blende
AC+BC. A simple electrostatic model gives the excess Madelung energy (per four-atom cell)

= 1

bEM, d,i„„(s,2)= (azar', q —P, b,g) (5.11)

where d is the bond length, b,q =qz(AC) —qs(BC) is the difference in charge between the binary compounds, and bg=g&(ABCz) —Qs(ABC&) is the corresponding difference in the ternary ordered phase, and where

+ZB= 1.6381

Pc~=0. 1220,

pcH =0. 1253,

Pc@=0. 1868

(5.12)

are geometrical constants. Clearly, only if the charge exchange b,Q in the ternary phase exceeds that in the binary structures by more than a critical value (b,g/bq)„;, can the ternary phase have bEM, &,&„„&0.
We find

1.83, CuAu —I

(b,g/Qq)„;„= 1.81, chalcopyrite
1.48, CuPt.

(5.13)

In GaAs-GaSb and GaAs-A1As, b,g/hq does not exceed these critical values, hence AEM,„,&„„g&0. The order of stability of Eq. (5.4) obtained in our total-energy calcula-tions (Table III}is consistent with the values of P, given in Eq. (5.12). This suggest that other contributions to b,ECE(s, n) (e.g., on-site Coulomb energy) are less im-portant.
(vi} The order of stabilities in lattice-mismatched sys-
tems [Eq. (5.5)j is decided primarily by bE,(n) of Fig. 3
[since bEcE(s, n)

in

3212 L. G. FERREIRA, SU-HUAI WEI, AND ALEX ZUNGER

Connolly-Williams set (3, B, CA, L 1, and L3) used pre-
viously

FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:... 3213

TABLE VII. This table gives, for each set of GaAs-GaSb structures and its corresponding set of interaction parameters (listed in Table VI), the ratio between the predicted energy [using the

3214 L. G. FERREIRA, SU-HUAI WEI, AND ALEX

FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:... 3215

Finally, for M2 we have
Cz'4 =1, others null.
2. Three-body-interaction K3 =J3 z

(6.4)

Using Eq. (6.1) we obtain

& 11„&=Zq & Il,, & —q', (6.6)

Let a and p denote the sites that are second neighbors (Table II), and y the nearest neighbor to a and p. Fol-
lowing

1)

3216 L G FERREIRA, SU HUAI WEI AND ALEX ZUNGER

—(5)(V)—J (V)+)J (V')—4J3(V)—2J4(V)
EE4(5)(V)—J (V)+J (V)+6J~(V)+8J3(V)+2J4(V)

2. Addition of other pair interactions

(6.15d)

(6.15e)

14

8-

(6.16a)
(6.16b)
(6.16c)
(6.16d)
(6.16e)
where

F~(V) =3K~(V)+12L~(V)+6M2(V). (6.16f)
3. Additional three and fou-r body intera-ctions
Finally, when we also include the interactions K3 and K4, the effective equations of state (denoted as M =10) depend on IP„)

FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:...

used, instead of s „(P,V) to calculate the thermodynamic equilibrium. For instance, the equilibrium volume is given by the equation

dc,„[X(V, T), V, T] ax aE„ ~n
dv & "av a

+& "av

markable x dependence in the energies. In this case, the energy maxima occur at the stoichiometric compositions x =X„,as one readily verifies by equating the derivatives of Eqs. (6.16) to zero. In Sec. VIII C, we will further dis-cuss the effective energies c, of Figs. 4 and 5.

=0 (6.18)

E. Calculated thermodynamic quantities

because the first term is zero due to Eqs. (2.29) and (2.30), and the second due to Eq. (2.26). Therefore we can work with Y,„[x(V, T), V, TJ or Z„[x,V,q(x, T), T] as a temperature-dependent, but state-of-order —independent effective equation of state.
Figure 4 depicts the effective equation of state
E„[x(V,T), V, T] for GaAs„Sb& „, and Fig. 5 depicts Z„(x,T) for Al& Ga„As. No lattice mismatch was per-mitted in the latter case, so that no volume variation can be considered. In both cases, the temperature depen-dence is so weak that it cannot be seen in the scale of the
figures. This implies that (when phonon contributions
are neglected) V, (x, T) is also nearly temperature in-
dependent. One observes in Figs. 4 and 5 that, by in-
creasing the number of ordered structures the energies at
the minima (enthalpies of formation) decrease, and the
curvatures (or the effective bulk moduli) also decrease. In the case of Fig. 5, the new configurations introduce a re-

QH(x, T)=bH(x, T)/x (1—x). (6.19)

The formation enthalpy bH(x) of ordered compounds is
the equilibrium value b,E(s, V,) of Eq. (2.2). The free en ergy is

F(x,T)=bH(x, T) TS ' ' —TES(x,—T) (6.20)

(where S is the ideal mixing entropy), the excess free en ergy is

The folded interaction energies IJk(x, V) I of Eq. (6.13) [or the effective equations of state in Eq. (6.23)] can now be used in the context of the generalized Ising problem to solve for the correlation functions (IIf }or the probabili-ties P„and the equilibrium volumes [Eq. (2.27)]. Evaluat-ing (bE(V) }for the various phases enables the calcula-tion of the basic thermodynamic properties of these phases. We next define the main thermodynamic quanti-
ties calculated and discussed in Sec. VIII. These include

the disordered alloy excess mixing enthalpy bH(x, T) of
Eq. (1.2) and its "interaction parameter"

O. i5

. AlsGa (n=1}

-(a)

0.05-

At4 (n=O) 0-

s(M) (x,T)
Set 3+2L

A/Gas (n=3)

Gag (n=4)

At2Ga2 (n=2)

b,F(x, T)=b.H(x, T) TES(x, T—),
and its "interaction parameter"

QF(x, T)=bF(x, t) Ix—(1—x).

(6.21)

(6.22)

The amount by which the

(328ET BT rXi20 8.81 Tf 541.11 719.89 Td (The1cts)Tj ET oi20 9.9

(n

and0Tj ET BT =PT /Xi20 10.01 Tf 78

bH30].x,

(60Tj ET BT /Xi20

of25Tj ET BT f i20 8.62 Tf 148.22 409.11 TET BT8T BT 32.67 52159.

t ET BT7i20 9.1 j20 9.05 Tf 434.4T BT /Xi20 8.95 Tf 385d

theT BT /Xi2067 442.67 Td These fu3 374.67its

zj ET B1

O. alloy alloy x, (of)T7Td (30T /FIG /Xi20 9.1 Tf 509.11 5608)Tj E BT /Xi20 8 10.69 Tf 54.44 536. Td (nj9.42 BT /Xi20 ETj ET B "7.216 EBT /Xi20o8.86 Tf 178.44 611.854 360.3BT /X16 EBT /Xi2- instanceV„/Xi20 9.16 Tf 537.354 Td („3

ar52T /Xi20 9 ET BT /Xii20 9.62 Tf 91.78 551 419.22BET 15(x,

ar52T py

ET 15(lloy

3218 L. G. FERREIRA, SU-HUAI %EI, AND ALEX ZUNGER

Set 3+2L:

A, B, CA, L1, L3

1700 - "0~ "i~ "2~ "3s "4

V„=(1—X„)V„c+X„V~c,

B„=(1—X„)B„c+X„B~c,

B„'=(1—X„)B„'c+X~B~c,

(7.1)

1600—

1500—

1400—

1300—

1200—

11QQ—

1000

900

800

700 "

6QQ '-
500—

hC 400—

300—
200—
100

CL

1700 -

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1600—

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0
0
0
l
1

l
l
1

I
I 0
0
I
0
Io
I
OI
I
I
I
I
I

Peritectic

Chalcopyrite

Io
10
l0
1

a

j,

Ga4Sb3As Ga4SbAs

I
l

',

,/CuAU-i „

lt
I a aS I l %P I I ai I

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

Atomic Fraction x GaAs

FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:... 3219

TABLE X. Comparison of the input parameters V„,B„,B„',and b,H„[Eq. (5.1)] of the LAPW calcu-lated EE(s, V) excess energies [using Eq. (7.1)] with the efFective values obtained by fitting the effective energies Z„(V) of "set 5+2L" to the same equation, (5.1). A =Sb, B =As.

Struct.

V„(cm /mol)
Input Effec.

B„(GPa)
Input Effec. Input Effec.

AH„(kcal/mol)
Input Effec.

A4C4
A142 9.18 Tf 427.44 663.ut

FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:... 3221

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FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:... 3225

5a tteq

where

hB ha
4B a

(8.1 1)

and

~ =—(~c+ac)
B=,

'(B~c-+B~c»

« =(&ac—&~c»

(8.12)

F. Mixing enthalpies and free energies

In contrast with the predictions of contemporary semi-
conductor alloy models, ' we find (Figs. 11 and 13)
that Q~ is composition dependent. Its values at the lim-
iting concentrations x ~0 and x~1 provide the "limit-ing partial heats of solution, "showing that it is consider-
ably more difficult to dissolve the larger atom (Sb) in
GaAs [Q(GaAs:Sb)=-4. 5 kcal/mol] than to dissolve
the smaller As atom in GaSb [Q (GaSb:As) =—3.8
kcal/mol]. The dependence on x is considerably weaker
in the lattice-mismatched Al& „Ga As system (Fig. 13; note the finer scale relative to Fig. 11).
No direct experimental measurements of Q~ or QH ex-ists for semiconductor alloys. The currently available
values' are 6t to the data of the liquidus and solidus
lines (hence, are appropriate to high temperatures), as-
suming simple thermodynamic models in the fit pro-
cedures. In cases where different 6t methods were at-

tempted for the same system, ' ' QH of 4—4. 5
kcal/mol are obtained for GaAs„Sb& „. This is in very
good agreement with our calculated value (Fig. 11) of

AB (Bgc B c)

Since hB and Aa have opposite signs for semiconduc-tors, ' 5a is always negative in the harmonic theory. In
reality, however, the pressure derivative B' of bulk
modulus is positive. The bulk modulus of the compound
with large lattice constant will have a sharp increase
when it is compressed and the one with smaller lattice
constant will have a decreasing B when it is expanded.
This indicates that the deviation 5a should be smaller

than what harmonic theory would predict (i.e., a,q

is

closer to Vegard's rule) and could be positive as found in our study for Ga(As, Sb).

-4.0 kcal/mol at x =0.5 and a temperature T= 1000 K (the average of the melting temperatures of the constitu-ents). Various authors have used empirical models to es-
timate QH(x =0.5) for GaAs-GaSb. These include the
recent model of Sher et al. '

(QH=3. 67 kcal/mol), the
elastic model of Martins and Zunger (QH =4.58
kcal/mol), the phenomenological delta lattice parameter

(DLP) model of Stringfellow' (QIr =3.35 kcal/mol), and the empirically adjusted model of Fedders and Muller (Q~ =2.76 kcal/mol).
For Al, Ga As our calculated value is

QH(0. 5, T)=0.3 kcal/mol at T =1000 K, compared with
experimental estimates '

' of 0—1.6 kcal/mol. Calculat-
ed values range from QH of —0.07 kcal/mol by Sher et al. '

to 0.11 kcal/mol by Van Vechten. Balzarotti
et al. estimate bE(n)=n(4 —n)JY from diffused x-ray
scattering, yielding in this pair-interaction model
Q(0. 5)= 43bE(2) =3&=1.6 kcal/mol.
The enthalpy and free-energy interaction parameters of Figs. 11—13 and 16 show a marked temperature depen-
dence. This dependence is neglected in regular and
quasiregular solution models and represented phenome-
nologically as Q(0. 5, T)=a bT in o—ther models. The
nonideal entropy hS of Eq. (6.20) is always negative (as
the actual system is more ordered than the random sys-tem), contributing a positive —TAS term to the free en-
ergy. Interestingly, the excess enthalpy b,H(x, T) be-
comes less positive as the temperature is lowered (Figs. 11
and 12). To understand the mechanism by which the sys-
tem reduces

—

11

tely

L. G. FERREIRA, SU-HUAI WEI, AND ALEX ZUNGER

I (a)
0. 10-

0-

—0.05-

hC

3 0. 05-
il

C
O.
Cl

AspSby

As4

hP„(x, T)
Set 3+2I

AspSb2

hPn (x, T)
Set 4+2L

As4

GaAsxSbt-x

(C)

As2Sbp

hP„(x, T)
Set 5+2L

As4 Sb4

As2Sbp

Pn (x, T)
Set 6+2L

As4

0
Gasb

0. 25 0. 50 0. 75 1.0 0
GaAs GaSb

0. 25 0. 50 0. 75 1.0 0
GaAs GaSb

Concentration x

0.25 0. 50 0.75 1.0 0
GaAs GaSb

0. 25 0. 50 0.75 1.0
GaAs

FIG. 17. Excess cluster probabilities [Eq. (6.23)] for GaAs„Sb,

the concentrations of single mixed species (around their corresponding compositions X„), hence reducing hH(x, T), as seen in Fig. 11. Since in the absence of clus-tering the enthalpy of the disordered phase is higher (see
the

3228 L. G. FERREIRA, SU-HUAI WEI, AND ALEX

FIRST-PRINCIPLES CALCULATION OF ALLOY PHASE DIAGRAMS:... 3229

fcc-based phase-separating alloys. The method requires calculation of the excess total-energy functions b,E(s, V) for an optimal set of ordered structures Is} (e.g., from the local-density formalism). These energies are used in Eq. (2.3) to find the interaction parameters Jf(V) (using the inverse of the matrix given in Table II). These in-teraction parameters are then inserted in Eq. (6.17) to find five efFective equations of state c.„(V). Finally, these effective equations of state are used as input to any stan-dard method for solving

3230 L. G. FERREIRA, SU-HUAI WEI, AND ALEX ZUNGER

tions in Alloys (Academic, New York, 1955).
3 Equations (1.9) follow from the orthogonality of the products

IIf g IIf(lf o)IIf'(lt', o)=2 5f f'5,

,
If (f li') does not f'f
coincide with (f', lI) there are unpaired spin variables 0, in the left-hand side of the above equation. The orthogonality

results from summing over all the spin variables R; (1 and —1). See Ref. 40 for details.
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FIRST-PRINCIPLES CALCULATION