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Atomic-scale structure of disordered Gat „In„P alloys

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Extended x-ray-absorption fine-structure experiments have previously demonstrated that for each
composition x, the sample average of all nearest-neighbor A-C distances in an A & „B C semiconductor
alloy is closer to the values in the pure (x—+0) AC compound than to the composition-weighted (virtual) lattice average. Such experiments do not reveal, however, the distribution of atomic positions in an al-loy, so the principle displacement directions and the degrees of correlation among such atomic displace-ments remain unknown. Here we calculate both structural and thermodynamic properties of Ga& „In„Palloys using an explicit occupation- and position-dependent energy functional. The latter is taken as a modified valence force field, carefully fit to structural energies determined by first-principles
local-density calculations. Configurational and vibrational degrees of freedom are then treated via the
continuous-space Monte Carlo approach. We find good agreement between the calculated and measured
mixing enthalpy of the random alloy, nearest-neighbor bond lengths, and temperature-composition
phase diagram. In addition, we predict yet unmeasured quantities such as (a) distributions, fluctuations, and moments of first- and second-neighbor bond lengths as well as bond angles, (b) radial distribution functions, (c)

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II. THERMODYNAMIC DEFINITION
OF THE ATOMIC STRUCTURE OF AN ALLOY

We start our discussion by

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that minimize F'r '= (hE)

r—T(AS)r.
F[I g

j''(x, T)); [R;)]

=min. (2.6)

b,E'„„'s [IR,.

)]+6,E„;b[{R,")]=min. (2.8)
Note that the correlation functions or the spin variables do not appear explicitly in Eq. (2.8) as they are

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Unlike Ising-based methods, '

'

the convergence of a
truncated Ising series is not involved. The main approxi-
mation is now the use of a par ametrized Born-
Oppenheimer surface E[[S;};[R; }] without explicit elec-
tronic effects. Unlike the free-energy minimization
method of Srolovitz and co-workers, we used unap-
proximated S pg Eyjb and Syjb Unlike the Monte Car-
lo embedded-atom approach of Chakraborty and Xi, ' we
do include Eyjb and Syjb terms neglected in Ref. 31.

IV. METHODS OF CALCULATION

A. Structural optimizations
and Rnite-temperature Monte Carlo calculations

The excess configurational energy AE„„„will be de-
scribed here by an effective elastic potential which in-cludes bond stretching and bond bending terms

b.E,o ag[[S,};[R, }]

= g V;, + g V

ij Go ijk6o

(4.1)

exp(5E) /kii T) if 5E)0

t

accept 1 other wi (4.2)

where T is the temperature of the sample, and k~ is the

where VJ and Vzk are the two- and three-body interac-

tions between the neighboring atoms i,j and i,j,k ac-

cordingly. The details of this potential are given

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B. Fitting the ternary valence force field (VFF)
to first-principles calculations

The methodology described above will be applied in
what follows to AC=GaP, BC=InP alloys which have
received prominence due to their applications in photo-
voltaic solar cells, high-power quantum-well lasers, light-emitting diodes, and high electron mobility transistors. '

In addition, experimental data exist for the
alloy bond lengths,

"

mixing enthalpies, ' and the phase

diagram. Previous theoretical results include calcula-tions of alloy bond lengths using local-density-approximation (LDA) calculations, '

the radial force
model, tight-binding perturbation theory, valence-force-field calculations, '

and empirical potential calcula-
tions. '

In addition, cluster expansion calculations of thermodynamic properties have been reported in Refs. 34 and 51.

The excess configurational energy bE'„„'„sof Eq. (4.1) is modeled here by the valence force field (VFF) of Keat-ing (see also Refs. 14 and 53):

4

hE',o„'„s=g g 2

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IbEvFF(s, V,pI„PG„fi„,fG,)]. For each of the struc-
tures, the excess energy of the relaxed cell was calculated
where the cell external coordinates (i.e.,

the 3X3 matrix
which describes the parallelepiped shaped unit cell) as
well as the cell internal coordinates (i.e.,

the atomic coor-

dinates tensor) were relaxed using a Monte Carlo algo-rithm at T=O. To fit the VFF to the LDA, we define a cost function which expresses the difference between the VFF and LDA excess energies as a function of the three

parameters P,„pG„f,„,and fG,:

«PIn-P-Ga fin fGa)=

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TABLE I. Formation enthalpies hH for ordered structures of InP/GaP, where A =GaP and
8 =InP. The structures are described as (AC)~(BC)~ superlattices with layer repeats (p, q) and orien-
tation G. The formation enthalpies were calculated using LDA, the original Keating VFF potential (VFF) (Refs. 52 and 53), our ternary potential (T-VFF), the potential of Khor and Das Sarma (KDS) (Ref. 49), and our modified KDS potential (M-KDS). The units are meV/four atoms, and the symbols define structure names (as defined in Ref. 55).

Formula Potential [111] [001]

Orientation

[201] [113]

Row average
deviation'

LDA
T-VFF
VFF
KDS
M-KDS

CP
144.2
132.4
133.6
98.7
86.7

CA
90.3
93.5
87.5
83.8
84. 1

CA
90.3
93.5
87.5
83.8
84. 1

CA
90.3
93.5
87.5
83.8
84. 1

CP
144.2
132.4
133.6
98.7
86.7

6.6
5.9
22. 1
26.7

LDA
T-VFF
VFF
KDS
M-KDS

a1
128.0
127.4
128.7
94.0
88.0

Pl
81.9
90.8
87.3
86.5
85.5

yl
46.6
43.6
58.9
104.9
98.1

y1
46.6
43.6
58.9
104.9
98.1

y1
46.6
43.6
58.9
104.9
98.1

5.0
9.8
47.1
45.0

W,B
LDA
T-VFF
VFF
KDS
M-KDS

cx2

126.7
109.1
109.7
30.9
38.3

P2
79.1
77.2
72.8
26.0
32.4

y2
45.6
45.7
59.4
59.3
58.9

y2
45.6
45.7
59.4
59.3
58.9

y2
45.6
45.7
59.4
59.3
58.9

5.0
14.9
47.4
44.0

AB3
LDA
T-VFF
VFF
KDS
M-KDS

V1
110.4
112.4
113.5
66.3
62. 1

Z1
72.9
80.3
78.0
61.8
61.0

Y1
54.3
53.6
60.8
90.8
76.8

F1
32.0
34.0
43.6
68.6
66.9

8'1
62.9
63.8
72.0
99.9
82.0

4.6
10.9
45.8
35.9

A2B2
LDA
T-VFF
VFF
KDS
M-KDS

V2
141.8
132.1
132.6
44.6
51.1

Z2
90.6
94.1
91.1
41.5
47.1

Y2
60.7
60.2
78.1
84.4
76.9

CH
29.8
40.2
57.1
91.9
85.7

8'2
61.0
62.4
75.8
86.9
83.6

6.0
16.0
60.8
53.0

A3B
LDA
T-VFF
VFF
KDS
M-KDS

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Qi p(GaP) & ao p(InP) (5.8) This is the reverse of the situation in the pure binary ma-terials, where the VFF values are'

+in-p ga-p. (5.9)

B. The finite-temperature phase diagram

Figure 3 shows the x-T phase diagram of the Ga, In P alloy. The circles connected by dashed lines denote the results of the -42 Tf 120185f 104.89 59f 167.a,

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can be

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0

M

A

8i-p-j

x~=0.90

I I ~ BIRCH%-kMk@. i ~ I ~

x~=0.75

C

I ~ ~

I I

l

x~=0.10

x~=0.50

I

%P

Ij CCCCI I CC I I CCI'
jjjj PR I I 5 I I Ic cc cc c

=:.....Wl
x~=0.25

,

::I

x~=0.90
i—In-j

,

.:..

:.:, I

x~=0.75

,,.

:;:I,

x~=0.50

I:::

x~=0.25

Ii':::

~ .".4 ~ ":;" %:.k3~-. ~'.j I I
x~=0.10
I'

I ~ I

(

I I I Ii) I I ~ I

I

~ I I

=0.90 In
8i-Ga—j

I I I ~

j

I I I I i 1

I I ~

I::,

.

x~=0.50

x~=0.25
I:::::. -:

x~=0.10

4::MN:i-'::::il*:k::k'. % I I) I I ~ I

I ~ I ~
~ I ~

I ~ ~ ~

I I I I
I

~ ~ ~ III I ~

x~=0.25

~ I.

x~=0.10

x~=0.90

i—j—k
Total::::,:;::C":,::,.

,

::,.

::,
,

:I

x~=0.75

4:4'"'~:,";f::::. '.;.

'::.-',::;",:

.

~w~~PX~g+g+gkylgpb@ NPQ+Q)hgwvbh'

x~=0.50

100 105 110 115 120 100 105 110 115 120 100 105 110 115 120 100 105 110 115 120

Angle (Deg)

FIG. 9. Histogram plots of the bond angle distributions of the chemically random Ga& In P alloys for some selected composi-

tions x. Results are given for bond angles around the P atoms (8; p,), the In atoms (8; &„,), and the Ga atoms (6; z,,

). The total

bond angle distribution is (6;J q). The dashed vertical lines denote the tetrahedral bond angle of the zinc-blende lattice (109.47').

bond angles open up, while in Ga-rich alloys a significant
number of bond angles close up. Our simulation further
shows that the bond angles around either anions or cat-
ions are rather soft, exhibiting significant deviations from
the tetrahedral values. In contrast, as Fig. 4 shows, the
nearest-neighbor bond lengths are rather rigid, being close to the ideal values in the binary constituents.

D. Pair-correlation function

R(r)= f p(r)dr.

T

(6.2)

The pair-correlation function is plotted in Fig. 10 for r & 2 A, as there are no bonds shorter than 2 A. The first
peak represents the first shell (nearest neighbors) bond
length, the second represents the second shell, etc. The dashed lines denote the bond lengths in the virtual alloy of composition x. For comparison, we also give results
for pure GaP and pure InP (x =0 and 1). For these pure compounds, the pair correlations exhibit sharp peaks as all bond lengths and bond angles are equal. In the first

Figure 10 describes the pair-correlation function of chemically random Ga, In P alloys for various compo-sitions. The pair-correlation function R (r) is the average radial atomic density p(r) in the interval between r and r+4r, where r is the bond length and Ar is the width of the histogram

alloy shell (s= 1), the peak of the GaP and InP is split into two subpeaks. The left subpeak represents the short-er Ga-P bond and the right subpeak represents the longer
In-P bond. (This can be seen more clearly in the nearest-
neighbor distance distribution in Fig. 5.) From the
second shell on (s ~ 2), the peaks of the alloy are
broadened as the alloy is formed. The centers of the
peaks (r(x)), are located in the virtual lattice

(r(x)), =xr, „c+(1—x)r, ~ c,
shown in Fig. 10 as dashed vertical lines..

virtur152 2peaET BT /XTg.

compositieTf 469.67 318.78 Td (r8ths)Tj ET BT /Xi12 8.93 426 2f 426 250.72R 282.33 33d (cat17j ET BT /XhosXhorT BT /Xi12 9.33 Tf6 Tf 481.104.67 77(in)Tj Eplacem /Xi12 9.11 Tf 531.3.89 470.5.67hist7re)Tj ET BBT /Xi12 11.68 Tf 37 246.12 etc.hist0575.7t4/Xi12 94.67 229ET /X97 2297 T33 Td (,)Tj ETAppendiXi12 8.56 Tf 168.445.56 292 T33 Td),for

r575.7to/Xi12 9.16 Tf 352.67 411 104r22 379inc-blende thess 1).()Tj ET laET T /Xi12 9.42 Tf 1259.4439f (thj ET BT 100T BT /Xi12 15.7 Tf 30138.11 7 Td (thj ET BT 110T BT /Xi12 15.7 Tf 89 385.22 Td Td (t89 329angle)Tj ET=O2 8.9 Tf 251.89 296.78 Td5384.786 as

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0~H
0

0

Q

0

~ W

cf
C4

1

I
l

x~= 1.00
(
I

(rnp)
I I.

II

+~=0.90
I

l,L

I

I
Ii

@~=075 I

I

,

'L iL,

I

I

x~=0.251 I
I

II. ii
x~=0.101
I

a, j.

I

I

I
I

I

I

Il,

I

I

I L&II

I
I

~g„h I'

, J il

I

1

'

x~——0.0$
I

I (G~p)
I I

II

I

I

I

6

Bond Length (j)

FIG. 10. The pair-correlation function of the

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Atom Type T=40K T= 120K T=300K

Qn QG Qln In/Ga

In/ Ga

In/Ga

{100) {100)

FIG. 12. Schematic diagram of four possible displacements
of the P atom in the random Gal „In„Palloy resulting from its nearest-neighbor

nn53dghbor

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ments for the species a. As seen in Fig. 15, this explains why both UQ, and U,„ increase in In-rich alloys. Note that the composition dependence in Fig. 15 is monotonic; no evidence of a drop in U is found at any intermediate composition similar to that found in some II-VI ter-
naries.

(iii) While the static displacement maps (Fig. 11) show that the anion has a larger probability than the cation to reside at off-center positions, the dynamic displacements

(Fig. 15) show U,„)Up) Uz,. In fact, the anion MSDD

changes monotonically with composition from Up UQ, in pure GaP, to Up —UI„ in pure InP. The different peaks of the anion in the static displacement map (Fig.
11) are related to the different anion off-site locations in the five different clusters Ga, „In„Pfor n =0, 1, 2, 3, or
4. One may expect different vibrational modes (and pos-sibly different vibration amplitudes) for different clusters, but these cannot be observed in the MSDD representa-tion, as the probability of the different clusters is mono-tonic with x (see Appendix B).

C. Short-range order

Cowley's short-range order (SRO) parameter is given b

79

p

A/B

&A-B =1— (7.5)

C4O CQ
CS

1 I I I
I

I I I I
I

I I 1

I I I I
I

I I I

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they use Ko,i, =Ki„i =0 in Eq. (86).
Substituting Eq. (81) into (86) gives

R o p

(x) R o& p

+(4Ko&p +ko&p)x —nKo&p

Rin'i (x}=Rin-~+(4Kini +~in~}x —«t'ai

(87)

A~,p=0. 036 A,

A)~p =0.050 A

The solid lines in Fig. 5 depict the histogram of P'"'(x }
vs R„c(x) using Eqs. (82) and (87), and the numerical

values hr, (n =2)=E(1,0,0), hr2(n =2)=s(0, 1,0),

br3(n =2)=s(0,0, 1),

(C3)

where P'"'(x) is given in Eq. (82).
(iii) In the n =2 cluster there are two long In-P bonds and two short Ga-P bonds, so the P atom is displaced along one of the six (100), (100), (010), (010), (001), or
(001) directions (the middle of the two bonds). Let s be the amplitude of the P-atom displacement along the (100} direction. The three possible displacements of the P
atom in the n =2 cluster are

from our calculation of Table IV, and
0

E~&p = Kg&p =0.02 A

fit to the width of the histograms of the MC results.

(89)

where c & 0, and Ar4, Ar5, and Ar6 are similar terms but

with E (0. The probabilities of the six displacements are
equal to

P[br;(n =2)]=P'" '(x)/6. (C4)

APPENDIX: C: A MODEL
FOR THE DISPLACEMENTS OF THE P ATOM

6„
br3(n)= —(1,—1,—1),

(C1)

5„ br 4

(n)= —(—1 1 —1) ~3 7 7
and the probabilities of the four displacements are equal
to

P[hr;(n =1,3)]=P'"=' '(x)/4, (C2)

To understand the essential features of Fig. 11 we con-sider a model which assumes that the displacements of the P atoms reAect the properties of its four nearest
bonds in the five different Ga& „In„P clusters. The
mixed (cation) sublattice is assumed to be unrelaxed with respect to the ideal fcc positions. Specifically, the model assumes the following.

(i) In the n =0 and 4 clusters, the four bonds connect-ing the P atom are equal, so the P atom is located in the tetrahedron center.

(ii) In the n = 1 cluster there is one long In-P bond and three short Ga-P bonds, so the P atom is disp1aced away from the longer In-P bond, in one of the four (111),(111), (11 1), or (111) directions (according to the In-P bond
direction). Since the random alloy is homogeneous and
isotropic, all of these directions have an equal probabili-ty. In the n =3 cluster, there is one short Ga-P bond and three long In-P bonds, so the equilibrium locations of the P atom are in opposite direction relative to the n =1 cluster. Let 5„denote the displacement amplitude of the

P atom along the bond direction in the cluster n (5„)0).
The four possible displacements of the P atom in the n =1 and 3 clusters are therefore

6„ br, (n)= —(1, 1,1),

3

5„
br2(n) = —(—1,—1, 1),

For simplicity we choose

5()=—5()= —, '[&R,„,())—&R, ())], (C5)
where &R,„~(x)) and &Ro, ~(x}) are the In-P and Ga-P
average bond lengths in the random alloy. It is easy to see from the geometry of the cluster that

E(x)=cos —[&R,„i(x))—&Ro, i (x))], 9

2

(C6)

where 0 is the tetrahedral bond angle [8=109.47',
cos(8/2)=1/V3]. Figure 12 demonstrates the possible displacements of the P atom. Thus in a three-dimensional representation of P-atom displacements there are 15 possible locations for the P atom. These are related to the Ave different nearest-neighbor local clusters Ga4 „In„around the P atom: One undisplaced location is in the center of the n =0 and 4 tetrahedra, four dis-placed locations are in the (111),(111),(11 1), or (111) directions of the n = 1 clusters; four locations in n =3 are opposite to those of the n =1 clusters; and six displaced locations are in the (100), (100), (010), (010), (001), and
(001) directions of the n =2 clusters. These locations are represented in Fig. 11 by the three projected (100), (110), and (111)planes.
In order to make the model more realistic and closer to the statistical results, we broaden the projected displace-
ments b,r,.

(n) by a symmetric Gaussian

G(bx, by)=e (C7)

where ~ was chosen arbitrarily to be equal for aH dis-
placements. The results of the model are shown on the right-hand panels of Fig. 11. We see that the model qual-itatively matches the

n

(111ET BT /X5s3er8 Td (statistical)Tj ET19 10.32 f 548 204.44 Td (to)Tj ET n

0ual-

in10(0)Tj ET BT ET BT /Xi19 11.2 Tf 110.78 137467 Td .89

to.44 Td (C2)

1108ond

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We got the following rms displacements for the binaries Zn Te and CdTe: Uz„(Zn Te)=0.071 A, UT, (Zn Te)=0.060 A, UT, (CdTe) =0.065 A, and Ucz(CdTe) =0.080 A compared to the experimental results of