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First-principles calculation of the formation energies of ordered and disordered phases of A1As-GaAs

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The total energy of ordered and disordered phases of AlAs-GaAs systems is expanded in a series
of multiatom interaction energies determined from first-principles linear muffin-tin orbital and
linear augmented-plane-wave calculations of simple superstructures. These interaction energies are
used to discuss the stability of different superlattices and that of the random alloy.

I. INTRODUCTION

Wei and Zunger' have shown that the total excess en-

ergy per cell b,E(n, G) of lattice-matched (AC)„(BC)„ superlattices with layers repeated along the direction 6,

bE [n,G]=E[(AC)„(BC)„;G] nE [AC] —nE [BC],—

pie short-period structures can be used in conjunction with this energy-expansion method to predict the excess energies of longer period (A1As)„(GaAs)„superlattices in different orientations as well as the energy of the random Alo ~Gao 5As alloy. General conclusions on the relative
thermodynamic stabilities of these systems are drawn.

II. APPLICATION TO AlAs-GaAs SYSTEMS

can be represented with respect to the equilibrium ener-gies of pure AC and BC as a reasonably rapidly conver-gent series of k-atom m-neighbor interaction energies

K M

bE [n, G]= y y gk (n, G)~k,

k m

(2)

Here, gk (n, G) are geometric constants representing the occurrence frequency in the superlattice (relative to its constituent binary solids) of k-atom "figures" whose A and B sites are separated by up to the mth nearest neigh-bor (given in Tables I and II of Ref. 1). The utility of this
analysis' lies in the ability to deduce the set [Jk) by
performing directly self-consistent total-energy calcula-tions for X simple periodic structures [sI involving AC and BC, and using the inverse form
N

Jk, = & Mk(s)] 'b, E(s)

s=1

to find X values of Jk. Provided that convergence of

Eq. (2) can be demonstrated for this set of K values of Jk, this expansion affords simple calculations of AF for

more complex structures [s'I,

alTj ET BT BT /Xi0 9.2 Tf 80.4.56 192(drawn16))Tj ET labo ETuT /Xi0 9.41 Tf 437.4 175.33 Td

bE

P 53a

bE

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point zinc-blende compounds A1As and GaAs [for which
AF. =0 by the definition of Eq. (1)]. (ii) For 50%—50%
composition we use four (A1GaAs2) structures: the
"CuAuI" (denoted CA, with space group P4m2), chal-
copyrite (denoted CH, with space group I42d), "CuPt"
(denoted CP, space group R 3m), and the
(A1As)2(GaAs)2 (001) superlattice (denoted Z2). (iii) For the 25%-75% (A13GaAs4) and 75%-25% (A1Ga3As4) compositions we use four structures: two "luzonite" (denoted Ll and L3, for each of the two compositions, re-spectively; space group P43m) and two famatinite (denot-ed El and F3, space group I42m). Table I of Ref. 1 gives the expansion coefficients gk (s) for these structures and Refs. 7 and 8 give pictures of these crystal structures. Along with these ten structures, we use ten interaction energies Jk. These include the following. (i) Four pair (k=2) interactions between the first, second, third, and
fourth neighbors J... J,„J... »d J, 4., respectively.

(ii) Two three body (-k=3) interactions: J3, (between first

neighbors) and J3 z

(where two of the three sites are
second neighbors). (iii) Two four bo-dy (k=4) interac-
tions: J~, (between first neighbors) and J4@ (where one
pair is second neighbor). (iv) The one-site J,,

and the

constant term Jo &. The first column of Table I gives the
LMTO-calculated excess energies for these (and other, see below) structures. Using Eq. (3) with N=10, we ob-tain the values of the ten interaction energies denoted in
Table II as "set I."
To assess the importance of the k) 2 ("many-body") interactions, we have used as "set II" the same ten struc-
tures, but retain only the four pair interactions J2
(1 ~m ~4) in the expansion of Eq. (2), along with Jo, and Ji,. (In this fit, the excess energies of A13GaAs4 and
A1Ga3As4 are averaged.) A least-squares fit to these six
interaction energies produces the values denoted in Table
II as "set II." Table I shows the good quality of the fit
[root-mean-square (rms) error of 0.7 meV]. Using these
four pair-interaction energies, we give also in Table I the

TABLE I. Calculated excess energies AE for AlAs-GaAs superstructures. Energies are in meV/(4 atoms), except those for (001), (110), and (111)superlattices which are in meV per cell (4n atoms). For structures and J's used in diferent sets, see text. The asterisk denotes those values used in the fit, excluding the reference energy hE =0 for GaAs and AlAs; other values are predicted.

Direct
LMTO

Series expansion to LMTO
Set I Set II Set III
10 struct. 10 struct. 6 struct.

10 J's 6 J's 6 J's

Direct
LAPW

Series expansion to LAPW
Set I Set II Set III

Direct
pseudo-
potential'

(001)

n =1 (CA)
71 =2 (Z2)
n =3
n=5
n =7

32.0
35.2
33.3
30.0
28.7

32.0*
35.2*
35.2
35.2
35.2

33.0*
35.2
3S.2
35.2
35.2

32.0*
35.2*
35.2
35.2
35.2

13.8
11.8

13.8*
11.8*
11.8
11.8
11.8

13.8

11.8*
11~ 8
11.8
11.8

13.8*
11.8*
11.8
11.8
11.8

14.9

1.7

(110)
n =1 (CA)
n =2
n =3
n=4
n=5
n =7

32.0

50.4

43.0
45.5

32.0*
51.5
58.0
58.5
58.5
58.5

33.0*

=3

32. 2
32.

=1

32.

=1

32.

40

51. 0

32.

=1

32.

=7

32.

=7

13.

8

struct.

13. 6

8

stru =3

58.

5

5

58.

8

struct.

9

struct.

=7

struct.

=7

struct.

=7

8* 13.

28.

14. 9

struct.

8

(001)

n

(001)

n

n =2 A13GaAs4 (rms) 8* 32. 32. 35.

meV/(4

=3

0*

8*

8*

and n

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predicted values [from Eq. (2)] of the energies b,E(n, G)
for structures not included in the fit. Comparison with
the directly calculated LMTO values shows a rms error
for predicted structures of 2 meV/(4 atoms). This good

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with that of Cohen and Schlijper,

"

who deduced attrac-

tive pair interactions for AlAs-GaAs,

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