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Thermodynamic

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TABLE I. Coefficients [(k, (s)l of the expansion of the total energy (per 4 atoms) of ordered structures [s] in terms of k-body,
m-neighbor interaction energies J[Eq. (2)]. Here CuAu, Chalc., CuPt, Luz, and Fam refer to layered tetragonal, chalcopyrite, lay-ered trigonal, Luzonite, and Famatinite, respectively (see Ref. 4d for pictures). Corresponding ensemble-averaged (k (R) for the
random alloy at x =0.5 are also given.

Structure

Space
group Formula

Two-body
(2, 1 (2, 2 (2, 3 (2,4

Three-body
(3, 1 (3,2 (3,3

Four-body
(4, I (4,2

m(s)
[me V/(4 atoms) l
LAP W Fit

CuAu
Ch ale.
CuPt
Luz
Luz
Fam
Fam
Random

P4m2
I42d
R3m
P43m
P43m
142m
I42m
F43m

ABC2
ABC2
ABC2
A3BC4
AB3C4
A 3BC4
AB3C4
A o.sBo.sC

16 0 —32 0
16 —4 —16 —16
12 —12 —24 0
12 0 —24 0
12 0 —24 0
12 —2 —16 —8
12 —2 —16 —8
12 —6 —24 —12

0 0 0
0 0 0
0 0 0

16 0 48 —16 0 —48
16 8 32 —16 —8 —32
0 0 0

0 —32

0 —16 —8 —24 —8 —24 —8 —24 —8 —32 —8 —32 —4 —24

1 1.5
9.8
7.5
8.4
8.7
7.3
7.7

11.4
9.7
7.5
8.6
8.6
7.7
7.7
7.0

the expansion coefficients); and (ii) at the same time,

~(s, V) can be independently calculated accurately for
periodic structures with use of first-principles band-
theory approaches. Specializing Eq. (2) to the set
cr =[s] and inverting this relation gives
jv

Jt, (V) = g [&k (s)] '~(s, V),

s]

(3)

from which we obtain N interaction energies from calcu-
lations of the total energy functions of N structurally in-
dependent periodic systems. The set of N structures [s}
is selected so that (i) they exhibit at least all nearest-
neighbor local arrangements around a common atom C expected to occur in the alloy [e.g., A4 and 84 in the
zinc-blende structures, 2282 in the layered tetragonal
and chalcopyrite structures, 838 and 883 in the layered trigonal, Luzonite, and Famatinite structures (see Table I)]; (ii) they include the lowest-energy structures; (iii) they exhibit ordering in all principal orientations: [001] and [110] for the layered tetragonal, [ill] for the lay-ered trigonal, [201] for chalcopyrite and Famatinite; (iv) the set js] is converged in the sense that the [Jk]'s cal-
culated from it can reproduce through Eq. (2) the in-
dependently calculated total energy ~(s', V) of struc-
tures s' not included in the original set. The Landau-
Lifshitz structures " ' of Table I satisfy the first three
requirements; we will show below by way of numerical
calculation that they also satisfy the fourth requirement.

We have calculated ~(tr=s) of Eq. (1) for nine or-
dered AI„Ga4-„As4 structures

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[001]-oriented (A[As)2(GaAs)2 superlattice gives
=2.85 meV/(4 atoms), whereas using Eq. (2) with the
data (4) gives 3.6 meV/(4 atoms) (see below). [Adding
this superlattice to the nine structures and refitting gives

similar values: Jq] = —0.758, J22=0.089, J23=0.022,
and J24=0.112. This fit produces ~(s) values which
agree with those of Table I to within 0.1 meV and yields
for the n =2 superlattice ~ =2.85 meV/(4 atoms).]
This demonstrated transferability shows that the expan-
sion of Eq. (2) including up to fourth-neighbor pair in-
teractions captures the essential energetics of substitu-
tional A1As-GaAs systems. The resulting interactions
are repulsive (J2 ~ & 0) between nearest fcc cations, and weaker, mostly attractive beyond this range. Conse-quently, under equilibrium conditions, all of our ordered

Landau-Lifshitz structures [exhibiting ~(s) &0] are
predicted to be unstable at T =0 with respect to decom-position into AlAs + GaAs. However, since low-
temperature phase separation (unlike ordering') is
strongly inhibited kinetically in semiconductor alloys,
we will also study below the free energies of the next
lowest thermodynamic states.

The utility of the analysis of Eqs. (1)-(3) lies in the fact that the knowledge of a converged and transferable
set [Jk] affords simple calculations of the internal en-
ergies of more complex configurations cr through evalua-tion of [gk (cr)] rather than by the more laborious
direct self-consistent calculations of ~(cr). Coupled
with simple models for the entropy, this permits model-
ing of the relative thermodynamic stability of alloys and
longer-period superlattices.
The random Ala sGao sos alloy. —Calculations of spa-
tial correlations for the A[„Ga~ —„As alloy

'
have

shown that (because of the small size and electronega-
tivity difference between Ga and Al) this alloy is very
nearly random (R) above room temperature. For ran-
dom alloys, the ensemble-averaged expansion coefftcients
(R) are again simple constants; they are given in the last line of Table I. Equations (2) and (4) then give the
excess energy of the 50%-50% random alloy: AF(R,x
=0.5) 7.0 meV/(4 atoms). Since this energy is posi-tive, the random alloy is not the T =0 ground state. Coupled with the calculated internal energies ~(O)
of the ordered (0) short-period superlattices given in
Table I, this leads to the following conclusions: (i) Since
we find hE(R) & AE(O) and (neglecting differences in
vibrational entropies) the excess free energies are

~(R) =AE(R) —TS(R) and AF(O) =~(O), where S(R) &0 is the configurational entropy of the random alloy, we predict for A[„Ga~ „As that AF(R) & hF(O)
at all temperatures. In the absence of size mismatch, or-

dered monolayer (n =I) superlattices [with ~(O) &0]
are, hence, always of higher free energy then the the ran-dom alloy of the same composition. This suggests that
the layered tetragonal ("CuAu-like") ordering observed
by Kuan et al.

"

in Al„Ga~ —„As is not driven by bulk

AF'(n, G) =2I[G]/n, n ~ n„ (5)

a relationship derived earlier by Wood, Wei, and Zunger '

from different considerations. This scaling
[Fig. 1(a)], indicating a greater stability per atom of longer (relative to shorter) period, "repelling" (I&0) superlattices, simply reflects the fact that electronic and structural changes attendant upon the formation of an interface are limited to a certain distance from the inter-

face. From Table II and Eq. (4), we find the interfacial energies I[001]=3.6 meV, I[110]=5.8 meV, and I[111]= —,

'

I[100] 2.7 meV, suggesting the [110]inter-
face to be the most unstable, whereas the [111]interface is the most stable in this sequence.

TABLE II. The expansion coefficients g2, (n, G) (per unit cell or 4n atoms) and the excess energy ~(n, G) [in meV/(4 atoms)] of (AC), (BC), superlattices.

G

[OOI]

[I io]

n=1
n~2

n 1

7l =2
Pl =3
n~4
n=l
n~2

—16 —16 —16 —24 —24 —24 —12 —12

0 —16

0 —16 —16 —16 —12 —12

—32 —64 —32 —48

— —

1216422 8.75 TfmTf 419.02 9 70.968 Td (—)Tj ET BT /Xi2 8.63 Tff 426.690.968 TTd (32)Tj ET BT /Xi2 11.87Tf 418.91t

32

—

16—

6 (—)Tj ET /Xi2 9.08 Tf 121.26 6823an.08 TTd (32)Tj T /Xi2 11.33 Tf 449 2

32—fr5 fr5 6I[1052 Tdrame2 8 Tf 434.07 343.673138.72 Td (bul6I[1))Tj E (422 8.75 TfmTf 0Tf 358.6Td (3l6I[1j ET BT=4T /Xii2 8.83 Tf 225.53 263.5 T404.1 T th9.2618gree MT /Xi2 13.28 Tf 46.3 Tf 3317S(R95~ms) — —618gm

th9.25(R))Tj ETK9.25 Tf 104.73 252.1f 33624.8.25(RET BT N/Xi2 8.74 Tf 366.897 286.47.44 5(RET BT /Xi2 8.93 Tf 250.56 412.61 2637.38 55(R))Tj ET Xi2 mi2 9

5216d374lso

f57 45.238Tj ETT urth-neighb 9.15 Tf 71.43 344.1386.76 6 Td45.24252 TdETi9.15 Tf 71.43 344.1 504 406572.45.27d

VOLUME 61, NUMBER 13 PHYSICAL REVIEW LETTERS 26 SEPTEMBER 1988 Comparison of ~(n,