~ 't lj' 'gl gl'Ii+i] I+i] I I ji~ li' ~~ /] I ~

'I+ ii~

2562 SRIVASTAVA, MARTINS, AND ZUNGjER

GaP Ga3lnP4 GalnP& Galn3P4 InP

1 1

R{n)
00 inP

~~l do
R]„p {X} inp 80—

CL

o&
U

CL

C

o

0

60— Q3

O
C
G5

co 40

C:
(D

t5
C3

Isa„lnq „P

RG~p (X)
jn)

I

20

dG p

0.0 0.25 0.50 0.75 1.0

Composition x

FIG. 1. Percent charge (in units of dtop doRp) of the' near-
neighbor bond lengths in ordered phases (~) and in random alloys (~).

of a iteratively by displacing the atoms to obtain the equili-brium conditions of zero Hellmann-Feynman forces. '0
For the end-point crystals GaP (n =0) and InP (n=4), we find calculated equilibrium lattice constants QG p and a~ p that are within 1.5'/0'of experiments, like in other recent
calculations. " We find InP to have ~eaker bonds than GaP
(the cohesive energy —Et~[atop] is smaller by 4 kcal/mole than that of GaP)

of

31 ATOMIC STRUCTURE AND ORDERING IN SEMICONDUCTOR ALLOYS 2563

charge transfer. Figure 2(b) shows the self-consistently
calculated deformation-induced charge transfer
b,ps(r)

=p[GaInP2, a,{~2), distorted)

—p[GaInP2, a,{~2), undis-
torted] and Fig 2. (c) shows similarly Ap (r) for Gain3P4.
They indicate substantial charge redistributions: the stabler
Ga-P bond (with

a deep Ga pseudopotential) acquires more
charge than it lost in the previous step to the In-P bond (with the shallower In pseudopotential). The corresponding polarization (pol) energy is

6E".

"

—= 6

E

—6Ev""

=

—2.

5
kcal/mole for

n =2 and constitutes the main driving force
for stability. The tota1 excess energy of the ordered com-
pound is 5Eo=hE{" = (hE n+AE~"")+ (hE E+gE~') We find AE,„=

—1.48 kcal/mole for the chalcopyrite. The
ordered simple tetragonal structure is only 0.

1 kcal/mole
less stable; similarly the luzonite and famatinite structures
are also close to one another in stability.

A few observa-

tions are in order. First, the closeness of the ordered phase energies AEg for these polytype pairs suggests that all are likely to form kinetically at growth temperatures, but the choice of growth (i.e.

, substrate) orientation might discrim-
inate them: the chalcopyrite is a (2,2) superlattice in the
(2,1,0) direction whereas the simple tetragonal CuAu-I-like
structure is

a (1,1) superlattice in the (1,0,0) direction. We
hence predict these particular superlattices to be intrinsically (not accidentally') stable against alloy formation below an
ordering temperature To

= (PHD+ b, Eo)/LSD Secon. d,
these structures can be identified by their fingerprint diffrac-
tion beams. They are (+1,0, 0) and (+1, +1,0) for lu-
zonite and (0, + 1, + 1/2) for chalcopyrite, 7 whereas both the farnatinite and the simple tetragonal structures have in
common the (0,0,

+ 1) and

(

+ 1,

+ 1,0) beams, but the
former also has the

(

+ 1,0,

+ 1/2) beam. Third, our
analysis suggests that alloys formed from closely lattice
matched binaries with

a large difference in bond stability in
the direction

2564 SRIVASTAVA, MARTINS, AND ZUNGER

ductor alloys. Voile we have assumed a perfectly random

solid solution, the physical idea leading to /J, HD(x)) 0 (cf.

Fig. 3) also suggests that in actual samples, the concentra-
tion fluctuations3 (as well as clustering') may be reduced
through the Boltzman factor exp —[b, E~"~(a)/ kT], reflect-
ing the smaller-than-random existence probability of the
highly strained species. Our analysis simply predicts this
tendency for homogenizations of the species to be enhanced
as ha increases, leading also to a temperaure dependence' and nonparabolicity in i) HD(x).
For Ga„ln~ „P, we find that the experimental' /J. HD(x)
curve for the disordered alloy, with a maximum at
B,HD(1/2) =0.72 kcal/mole (experimental uncertainty in
this value is around" 6 50%) is consistent with an excess
stability of an ordered GaInP2 of AEeq 03 kcalimole.
Our calculation (yielding —1.5 kcal/mole) overestimates
this stability due to "Brillouin zone effects, "7 i.e.,

reso-

nances between periodically arranged bonds present in the
ordered compound but not in the alloy.
We can use our calculated bond lengths RAg(a) and RgP (a} for the ordered structure, to obtain their sample averages'5 R (x) in a disordered alloy

R~c(x) = X cu)(P" [x(a)]R/P (a)

n=o

where co)/=4 —n (or cu$P= n} is the number of AC (or
BC) bonds. A similar expression pertains to Rs~(x). The dashed lines in Fig. 1 show the calculated results, indicating
a bimodal distribution similar to that observed for other al-

loys, but R (x), in a random alloy, deviates from the corre-
sponding do values significantly more than do the bond
lengths R '

in the ordered phases.
%e conclude that the stability of the ordered structures arises from the fact that they are strain reducing (i.e., small b,Evn+ i5.Ev~), reflecting their ability to simultaneously ac-commodate the two dissimilar bond lengths in a coherent
fashion (solid circles in Fig. 1). When small, this allows
the stabilizing chemical charge transfer terms to take over (the net electron flow is from the less stable bond to the
more stable bond). Such ordered systems are predicted to

have a Vegard-like lattice constant, much like their random analogs at the same concentration (hence the latter could be used as a convenient substrate for growing the former), a sharp bimoda1 distribution of bond lengths with displaced anions, and positive "optical bowing" (although with some-what larger gaps than their random