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Electronic structure and density of states of the random Ala 5Gao 5As, GaAso ~PO 5,
and Gao 5lno 5As semiconductor alloys

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The electronic density of states (DOS), charge densities, equilibrium bond lengths, and optical bowing
of the direct band gaps are calculated for three perfectly random semiconductor alloys within the first-principles pseudopotential method using the concept of "special quasirandom structures" (SQS's). The SQS's are periodic structures with moderately large unit cells whose sites are occupied by atoms in a way designed to reproduce the structural features of the infinite, perfectly random substitutional alloys. In avoiding averaging over atoms (as in the virtual-crystal approximation) or over atomic environments (as in the site-coherent-potential approximation), this approach is capable of revealing the multisite nature of chemical disorder, as well as atomic-relaxation effects. We show how the existence of different local
environments about chemically identical sites leads to splittings and fine structures in the density of
states, and how atomic relaxations are induced by such nonsymmetric environments and lead to significant modifications in these DOS features. The calculated alloy bond lengths and optical-bowing coefficients are found to be in good agreement with experiment. Relaxation-induced splittings in the DOS are offered as predictions for future photoemission studies.

I. INTRODUCTION

Isovalent zinc-blende AC and BCsemiconductors tend
to form stable and continuous substitutional solid solu-

tions A& „BC when grown above the miscibility gap temperature. ' X-ray diffraction, '

nuclear-magnetic-
resonance chemical-shift measurements, Raman scatter-
ing, and extended x-ray-absorption fine-structure
(EXAFS) experiments show that while low-
temperature vapor-phase growth often leads to substan-
tial deviations from randomness (e.g., to short-range clus-tering ' or even to long-range ordering'), liquid-phase or
melt-grown alloys tend to organize microscopically in
near-random atomic arrangements. ' There, the occu-
pations of the "mixed

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tuations in different properties survive averaging. The
various theoretical approaches applied previously to de-
scribe the electronic structure of random alloys differ in
their treatment of this issue.
The virtual-crystal approximation' (VCA) averages
the potentials of all atoms in the alloy, hence, all Auctua-tions are lost. The failure of the VCA in accounting for
distinct A-like or 8-like spectral features is well docu-
mented for both semiconductor'

'

and metal" alloys.
The

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proach with nonlocal pseudopotentials constructed by
the approach of Kerker. Exchange and correlation
effects were treated within the local-density approxima-
tions using the Ceperley and Alder potential as
parametrized by Perdew and Zunger. The wave func-
tions were expanded in a basis set with about 150 plane
waves per atom (kinetic energy cutoff of 15 Ry).
Brillouin-zone integrations were performed by Fourier
quadrature using

a set of 21

k points equivalent to 29 fcc
special points. For the DOS calculation the eigenvalues are obtained directly at

a set of 73

k points (equivalent to
85 zinc-blende

k points), including high-symmetry points.
We have checked the convergence of the

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E 25—
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15

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w)0—
fh

Ch

e
O

P1

P3 E

M

E iM

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dissimilar bond lengths and angles) and "chemical disor-
der" are excluded by construction. Note that we include
the VCA step only as a benchmark against which other
results can be compared, not as a viable alloy theory.
(iii) Chemical dis-order sects: We next calculate the
DOS in the SQS8 model at the volume V, keeping howev-er all bond lengths and angles equal to those in the virtual
lattice ("unrelaxed SQS"). Like in the VCA calculations of step (ii), structural disorder is excluded, but unlike it, chemical disorder effects are included: distinct A and B atoms are retained with no averaging. Note that unlike the SCPA, this model retains the chemical fluctuations arising from the existence of different A and, separately, different B sites. A recent test compared the results of this model in the context of a tight-binding description to those obtained in the SCPA (where all A atoms are aver-aged and so are all B atoms) for a case where structural disorder is negligible (the lattice-matched Alo 5Gao 5As system). It was found that the SCPA captures well chem-ical disorder effects in the spectral ranges where the

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A. General features

Figure 5(a) and Table II show that when the density of states of GaAs and AIAs are aligned using a common zero of energy (the valence-band maxima), the As-like Pl structures and the cationlike P3 structures occur at dis-tinctly different energies in the two

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E. Comparison with the method of superposition
of periodic structures

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I

m .(a) E 20-
C5
C4

~ 10-
M
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0-
th

-(b)
Pe 20
V

0

~ ~" 10-
:P

CS

O 0
- 12

pie

-8

P3A

Alp. 5Gap 5As

4

Z W„D„(ordered)

n=p

Alp. 5Gap. 5As:
SQS8

6A P6B

-4 0
Energy (eV)

FIG. 11. Comparison of the total DOS of Alo 5Gao 5As as ob-
tained (a) from averaging SQS8, and SQS8„[identical to Fig.
5(c)] with (b) the model of "superposition of periodic struc-tures" [Ref. 29(c)] where the density of states of the five ordered
structures Al& „Ga„As4 (0~ n ~4) given in Fig. 10 are super-
posed with random probability weights. [This is distinct from averaging LDOS shown in Fig. 7(f).]

It has been suggested previously '

that the electronic

density of states of a random alloy could be modeled by
superposing those of a number of ordered structures each
containing a distinct repeated cluster. For example, the A4 or B4 clusters appear as a repeated motive in the
zinc-blende structures A C and BC, respectively, the
AzB~ cluster appears in the (001) monolayer superlattice (AC), l(BC), (The CuAu-like structure, or CA), and the 33B and AB3

clusters appear in the "Luzonite" struc-
tures A 3BC4 and AB3C4 (denoted as L 1 and L 3, respec-
tively). To examine this approach we have calculated the
DOS of the five periodic crystals 3C, 33BC4, 32BzC4, AB3C~, and BC (Fig. 10) and superposed them using as
weights the Bernoulli probabilities appropriate to x = —,

'.

The resulting DOS [Fig. 11(a)] compares reasonably well to that obtained in the more accurate SQS8 model [Fig. 11(b)]. In particular, both models show the splitting of
P3 structure and the broadening of P5 peak. However,
we notice from Fig. 10 that the long-range order can sub-stantially modify the "cluster" extracted from these or-dered structures. While the total DOS obtained by the
method of superposition of periodic clusters is rather
similar to what is obtained from the SQS, the partial DOS
can difFer. First, note that ordered structures of the same
global composition (e.g., CA and CH) differ in their coor-
dination arrangements. For example, relative to an 3
atom at the origin, the CA structure has 4, 6, 8, 12, 8, 8,
and 16 3 atoms in shells 1 through 7, respectively,

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same composition can lead to significant errors unless

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symmetry

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laxed case occurs just in this energy region. These mixed states are t'he most sensitive to the structural relaxation.

We notice, moreover a change in the energy onset of P1 ~ peak with relaxation, reQecting

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pert and co-workers find that the introduction of the
structural disorder tends to increase the

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sitional disorder is larger in lattice-matched systems.
Structural relaxation contributes in

a different way to the
bowing of GaAso 5Po

~
and Gao 5Ino ~As. To explain this
different behavior we notice that the top of the valence
band in Gao &Ino &As has more In than Ga character (see also the Appendix), while the bottom of the conduction band has more Ga than In character. Structural relaxa-tion increases the In—As bond lengths thereby raising the energy of the bonding valence-band maximum (VBM), while the reduction in the Ga

—As bond lengths
raises the energy of the antibonding states at the
conduction-band minimum (CBM). The net effect is

a

slight increase of the direct band gap with respect to the unrelaxed configuration. In GaAso 5Po ~, on the other

hand, both the VBM and the lowest conduction state at I have more As than P character. Since structural relax-
ation increases the Ga—As bond lengths, this reduces the band gap giving

a positive contribution to the band bow-
ing. In all cases the total bowing b =bvD+bcE+bsR is positive, leading to

a reduction of the direct band gap.
The reduction is biggest for Gao &Ino 5As that presents
the largest lattice mismatch. Neglect of relaxation leads
to an underestimation of the bowing coefficient of about 42% in GaAso 5PO

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and to its overestimation of about
18% in Gao &Ino 5As.
In the case of Gao 5Ino 5As and Alo 5Gao ~As random alloys there is

a substantial spread in the experimental
optical bowing parameters. The reported values range
between 0.32 and 0.61 eV for Gao ~lno ~As (Ref. 50) and
between

0 and 0.37 eV for Alo 5Gao ~As. ' For
Gao 5Alo 5As the most recent determination of the direct gap bowing by Bosio et

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