PHYSICAL REVIEW

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ning tunneling microscopy. ' '

Indirect evidence for

SRO comes from nuclear magnetic resonance, ' Ra-
man scattering, infrared reAectivity, photo-
luminescence, '

and photoreAectance. Some experi-

ments on semiconductor alloys"' '8 ' '

report

clustering-type SRO (a

& 0), others' ' '

report anticlus-

tering (a (0), and some' '

suggest near-perfect ran-
domness (a=0). Despite these extensive studies, little is
known about the effects of SRO on band gaps. Be-
cause some degree of SRO or LRO is always present in
the technologically important III-V semiconductor al-
loys, a good understanding of their effects on the

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for the single, special configuration cr, without using any

cluster expansion. (P) is thus approximated by P(o,).
For the random binary alloy A& B„ the correlation
functions

(H~

) are known trivially, i.e.

,

(IIf

) =(2x

—1) f, where kf is the number of vertices in
figure f.

A special configuration which matches these correlation functions up to

a maximum figure is called"

a

"special quasirandom structure" (SQS). Surprisingly, one can find periodic SQS's with only

—16 sites that have
zero deviations from the "ideal" correlation functions for

pair figures up to the seventh atomic shell. Direct calcu-lation ' of their band structure reproduces remarkably well the results obtained with huge supercells. This ap-proach has been applied to various properties of semicon-ductor ' ' and transition-metal alloys.
While previous applications of

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TABLE I. VFF results (Ref. 53) for relaxed {subscript r) and unrelaxed (subscript ur) Gao, Ino, P SQS. hH and V are the forma-tion energy and volume per GaInp2 formula unit, respectively. The equilibrium bond lengths are R z, p =2.360 A, R ~ p =2.541 A.

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The analytic form and the parameters for the pseudopo-tentials are given in Ref. 59. As shown

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state are those with dominant contribution in Eq. (10)
from one particular state ink). We define the diagonal,
symmetrized spectral density function A„(k,E) for
configuration o. as

~„, (k E)= g l(n, Rklv&l'l(E E—), (11)

R, v(o.)

where the sum runs over the Nz operations R of the
zinc-blende point group, and over all electronic eigen-
states v(cr) of configuration o. with eigenvalue E. An
accurate theory of alloys would involve a sample with
N~ ~ sites, so its spectral function A„„(k,E) will be a
quasicontinuous function of E. The SQS approach can be
thought of as sampling this spectral density at a finite
number of wave vectors K in the SQS Brillouin zone (we
choose capital letters with overbar for these wave vectors
to distinguish them from wave vectors in the zinc-blende
Brillouin zone).
This discussion makes it clear that the quantity P(o)
having a well-defined configurational average (P & [Eq.
(2)] is the spectral density of Eq. (11). This is so because (i) the spectral density depends only on the configuration of atoms (through the Hamiltonian) and is defined for any
configuration o, and (ii) it is invariant under the space-
group operations of the host lattice (by summing over all
eigenstates). In the SQS approach, we approximate the
configurational average by its SQS value, i.e.,
(A„(k,E) & = A„s&s(k,E). Hass, Davis, and Zunger ' have shown that the spectral density obtained from a SQS-8 tight-binding calculation indeed yields a good ap-
proximation to a well-converged supercell calculation
with -2000 atoms.

(A„(k,E) & can be expanded in terms of its moments, '
e.g.,

its first moment is the expectation value of the ener-
gy eigenvalue of l nk & in the alloy,

f

dE E(W„(k,E) &

(.„(k)& = (12) f

dE(A„(kE) &

In principle, the integration limits are Eo= —~ and
E, = ~. When several peaks are present in the spectral
density, we calculate "restricted" moments in finite,
nonoverlapping energy intervals [Eo,E,] around each
peak. Comparing (E„(k)& with its unperturbed counter-

part E„(k) (from VCA or from the linear average of the constituent eigenvalues) gives us information about opti-cal bowing, whereas the second moment of (A„(k,E) &
measures level

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1.0

Xl (c)

1.0

0.8

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TABLE III. Band gaps E, bowing coefBcients b (in

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TABLE IV. LDA-corrected band gaps in eV (measured from the top of the valence band) for three alloy systems at different states of order: perfect randomness (a=ad=0), clustering-type SRO (a= 6

),

and CuPt-type LRO (g=1). Here, Eg denotes the average gap of the binaries at their equilibrium
volumes. Chemical symbols in parentheses denote the sublattice on which the VBM and CBM are lo-calized, respectively, and D denotes that the state is delocalized.

System

AlQ 5GaQ 5As

GaQ 5InQ 5P
AlQ 5InQ 5AS

r„
X„

r„I„

Eg

2.27
2.18
2.16
1.78

Random

2.22
2.17
2.06
1.65

2.13
2.16
1.93
1.56

SRO
a=—1
6

(Ga/Ga)

(In/Ga)
(In/D)

1.86
2.10
1.57
1.49

(D/Ga}

(In/Ga)
(In/D)

used to describe the wave-function localization in cluster-ing alloys.

2. Quantum well -picture of carrier localization in clustered alloys

I. Impurity picture of carrier localization in clustered alloys

%'e first consider the CBM. The CBM wave function
in Alo 5Gao 5As and Gao 5Ino 5P is strongly localized on Ga-rich clusters (Table IV). In Alo sino 5As, the CBM is weakly localized on the In-rich clusters. The chemical trend pertinent to this observation follows the order of atomic s-orbital energies, which increase in the sequence

Ga~In~Al (LDA values are —9. 16, —8.46, and —7.83 eV, respectively). Because the CBM wave func-
tions in the clustered alloys are mostly s-like (they derive

mainly from I „),this correlation implies that the clus-
ters act as "impuritylike traps": it is well known that an isolated isoelectronic impurity binds a carrier if the difference between its local potential and that of the host atom exceeds a critical value. An isolated Ga impurity in an A1As or InP host crystal is not strong enough to bind an electron. Because the strength of the local po-
tential is determined by its depth as well as its range, a
natural question arises: At what critical size n will an 3„ cluster in a BC host crystal show a bound state? To in-vestigate this question, we have performed EPM calcula-tions on A1As supercells containing 512 atoms where a cluster of n A1 atoms is substituted by Ga atoms. The case of Al, „Ga As is particularly simple because there is no size mismatch between GaAs and A1As, and the lo-cal potential differences between Al and Ga reAect purely
chemical difFerences. Our findings are (i) A Ga„cluster
in an A1As host with n

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changes in the energy spectrum —as described by the hy-
drostatic deformation potentials —is dramatic: GaP
transforms from an indirect-gap material at X to a
direct-gap material, whereas InP transforms from a
direct-gap material to an indirect-gap material at X (Fig.
5). Therefore, in the coherently phase-separated
GaP/InP system, the CBM is localized on GaP, rather
than on InP, as would be the case if the constituents
would relax to their respective equilibrium volume (in-
coherent phase separation). This establishes the
"quantum-well picture, "where the electrons are assumed
to obey an effective-mass-like Schrodinger equation with the potential given by the properly lined-up band edges.
In Fig. 5, the CBM of the +=0 and —,

'

alloy are also
shown, as obtained from SQS-8. Note that localization of
the CBM wave function in the clustered alloy on Ga
agrees with both the impurity picture with its s-orbital
rule outlined above, as well as the quantum-well picture
(valid when coherent phase separation is complete, and il-
lustrated in Fig. 5). This qualitative agreement is not ob-
vious, and the evolution of the electronic spectrum when going from a single isoelectronic impurity via a cluster (or quantum dot) to bulklike domains in a host crystal is not well studied at present.

3. Hole localization

So far we have discussed conduction-band (or electron)
localization. The physical mechanism leading to localiza-
tion of the VBM (or hole) wave function is qualitatively
similar. We have to consider whether an isoelectronic
substitution is attractive or repulsive to holes. The holes
at the VBM in the III-V semiconductors are p-like and
segregated mostly on the anion sublattice. The p-orbital
energies in the free Al, Ga, and In atoms are almost equal. Nevertheless, it was shown by Wei and Zunger
that the relative position of the I », state in III-V
common-anion systems is mostly determined by p-d
repulsion of the cation orbitals. Because in Al the d or-bitals lie above the p orbitals, the I », states in the Al
binaries are expected to be pushed below the ones in the
Ga and In binaries, where the orbital order is opposite.
Therefore the p-d repulsion argument suggests that the
holes will localize on Ga and In clusters in A1& Ga As

and Al, In As alloys, respectively. The predictions of
this simple two-level model indeed agree with the direct
calculations on clustered alloys, as shown in Table IV. In
a common-anion Ga/In system, p-d repulsion alone does
not give a clear indication where the holes are expected
to be localized. Let us use the quantum-well picture in-
stead. We need the valence-band offsets between the con-

stituents (assumed to be zero in Fig. 5) hydrostatically
strained to the alloy volume V. This allows us to predict where the holes will be localized when coherent phase separation occurs. In AlAs/GaAs, the VBM in GaAs is
about 0.50 eV higher than that of A1As. The valence-
band offset in hydrostatically strained A1As/InAs is not
directly available, but it can be estimated from the epitax-
ial A1As/InAs (001) system, where uniaxial strain ap-
plies. The offset of the crystal-field and spin-orbit-
averaged VBM has been calculated to be -0.45 eV72 ET BT /Xi10 8.99 Tf 5tf 132.44ET BT /Xi14 73.11 Td &antum-well

eV72 BT /Xi10dIn

Tf 2545g

of t(00 BT /Xi10 9ET BT /Xi10 9.67 Tf 148.674Tj ET 7 6t-44 637 6t-

wo

4 Td (than)i10 9.17 Tf 175.33 647.44 Td (c8.22 14669 6.33 1rons)Tj EAlj ET BT /Xi10 9.26 T3.89 6. 3 T214 to dir3.(plie214)Tj ET BTT /Xi10 9.38 Tf 139f 98.44 37onst

ones00 (that)Tj E BT /Xi10 6.63 Tf 24 115.4.89 Td (that)Tj E5.33 647.44 Td (c8..89 Td41 Td (m1(ones)Tj AljT BT /Xi10 8.51 Tf 188.564nd)Tj 214)T

Ad Tdt

Ad Tding

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TABLE VI. Average & 0 &~ and its standard deviation of the number of mth shell neighbors of opposite type in SQS-N and the corresponding value (0 & „in an ideal infinite cell [Eqs. (A 1) and (A2)]. inc denotes the shell coordination number.

First
shell

c =12

Second
shell

c=6

Number of opposite neighbors in SQS-X Third Fourth Fifth shell shell shell

c=24 Nc =12 Nc =24

Sixth
shell

Nc=8

Seventh
shell

Nc =48

&Om &si2

&0. &

& O,„&s,z
&0.&„

6+1.8
6+1.7
6+1.7

7+0
7+0.8
7+1

3+0.5
3+1.2
3+1.2

3+0
3+1.2
3+1.2

SQS-8 with a=0
11.5+1.1
12+2.4
12+2.4

SQS-8 with
12+0
11.3+1.9
12+2

(random alloy)
6.5+0.5
6+l.7
6+1.7

1

Al =
6+0

&

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D. B. Zax, S. Vega, N. Yellin, and D. Zamir, Chem. Phys.
Lett. 8 8, 105 (1987).
R. Tycko, G. Dabbagh, S. R. Kurtz, and J. P. Goral, Phys.
Rev. 8 45, 13452 (1992).
D. B. Zax, D. Zamir, and S. Vega, Phys. Rev. 8 47, 6304
(1993).
A. Kobayashi and A. Roy, Phys. Rev. 8 35, 5611 (1987).
25I. Sela, V. V. Gridin, R. Beserman, R. Sarfaty, D. Fekete, and H. Morkog, J. Appl. Phys. 63, 966 (1988).
I. Sela and R. Beserman, Phys. Rev. 8 39, 3254 (1989).
R. Manor, O. Brafman, D. Fekete, and R. Sarfaty, Phys. Rev. 8 47, 9492 (1993).
H. W. Verleur and A. S. Barker, Phys. Rev. 149, 715 (1966).
2 S. Yamazaki, A. Ushirokawa, and T. Katoda, J. Appl. Phys. 51, 3722 (1980).
S. Perkowitz, L. S. Kim, and P. Becla, Phys. Rev. 8 43, 6598 (1991).
S. Lai and M. V. Klein, Phys. Rev. Lett. 44, 1087 (1980).
L. Samuelson, S. Nilsson, Z.-G. Wang, and H. G. Grimmeiss, Phys. Rev. Lett. 53, 1501 (1984).
E. F. Schubert, E. O. Gobel, Y. Horikoshi, K. Ploog, and H. J. Queisser, Phys. Rev. B 30, 813 (1984).
S. Shirakata, T. Nishino, and Y. Hamakawa, J. Appl. Phys. 63, 484 (1988).
35A. Dimoulas, Z. Hatzopoulos, I. Stoemenos, and A. Christou,
Superlatt. Microstruct. 8, 117 (1990).
R. C. Kittler and L. M. Falicov, J. Phys. C 10, 1667 (1977).
Y. Fu, K. A. Chao, and R. Osorio, Phys. Rev. 8 40, 6417
(1989).
3 R. Magri, S. Froyen, and A. Zunger, Phys. Rev. 8 44, 7947
(1998 Tf 164.8 Tf 251.7Tf 257.47232.44 499.67 Td (K.)Tj ET BT /Xi171.33 407.78 Td (44,)TjBT /Xi13 8.594mef 178.78 BT /Xi1378 Td (44,)Tj

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penetrating clusters instead ofjust one.
2For a review, see I. M. Lifshitz, Usp. Fiz. Nauk 83, 617 (1964) [Sov. Phys. Usp. 7, 549 (1965)].
S.-H. Wei and A. Zunger, Phys. Rev. Lett. 59, 144 (1987).
s4D. J. Wolford, in Physics of Semiconductors: Proceedings of

the 18th International Conference, Stockholm, 1986, edited by O. Engstrom (World Scientific, Singapore, 1987), p. 1115. 8~R. G. Dandrea (private communication).
S.-H. Wei (private communication).