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Real-space description of semiconducting band gaps in substitutional systems

R. Magri and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401 (Received 30 May 1991)

The goal of "band-gap engineering' in substitutional lattices is to identify atomic configurations that would give rise to a desired value of the band gap. Yet, current theoretical approaches to the problems, based largely on compilations of band structures for various latice configurations, have not yielded sim-ple rules relating structural motifs to band gaps. We show that the band gap of substitutional A1As/GaAs lattices can be usefully expanded in terms of a hierarchy of contributions from real-space "atomic figures" (pairs, triplets, quadruplets)

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As was proved by Sanchez, Ducastelle, and Gratias, any lattice property can be rigorously expanded by the form
(2) or (4), provided that the expansion in figures is carried
to

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of band gap with composition are sizable. (iii) The status
of our experimental ' '

and theoretical ' under-

standing of the band gaps of disordered ' '

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have calculated the projection of a number of
conduction- ban d states in each configuration onto a I &, epresentatio. Wee usee the lowest-energy conduction band at I th at has a finite I &, projection. No e
many casess thisis does oes not correspond to the absolulute

um of the conduction band at I, or too the conduc-
i

'

ro'ection. This produces,
however, a consistent set of minimum-energy I &,

- i e

states appropriate to the onset n of absorption s or
reflectance expenmen ts. Wee have also averaged over the crystal-field splitting of the valence-band maximum ca-culated as 42, 23, 0.6, and 16.6 meV for CA, CP, CH, and Z2, respectively; see Tablee II for the definitions of these structures).

The LDA calculated I,5,~I &, one-electron one-e ec r band
a s are given in Table II and its caption for the 27 struc-
tures. The various sym o s in
band gaps as a function of composition corn and superlattice

I I

'

I

orientation. Th ese exh ibiti (i) a substantial configurational

~ ~ ~

de pendence d re6ectede in a spread in the values; ii some
systematic trends, e, e.g. 1 1 1] structures have the smalles

a

Tabl0p

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with k& vertices (i.e., a selection of k& out of N sites). Figure 2 depicts a number of such clusters in the fcc lat-tice and Table III defines their vertices. The expansion is defined with respect to an orthonormal set of coeKcients, as follows. One defines the spin product

II~(o)=S, S2 Sk f f f
for each of the 2 figures in configuration o.. The set
I

II&(o)] is orthonormal, [including the "empty figure'* f=(0, 1) for which Ho, (o)=1]in that for two figures f

and f

' we have

P~=2 g II&(o)P(o)..

o.=1

(9)

The series (8) may be reduced using symmetry: denoting by R one of the NL operations of the space group of the lattice (not the space group of a particular configuration o), we have

P(ko)=P(o) (10)

figure f to the lattice property P is given from Eqs.
(6)—(8) by
2N

g II~(o)II~.(cr)=2 6~~. (6)
Equation (6) shows that 2 II&(o) is the transpose ma-
trix of II&(o.); multiplying the matrices in reverse order
one obtains the completeness condition between the two configurations o and o',

and

II+ &

(R. cr)=III(o),
hence, Eq. (9) gives

(12)

g Il~(o)II~(cr')=2 5

f

One can hence rigorously expand any property P(o) of the lattice configuration o. in the orthonormal set of
I

II~(o.) I as
2N

P(a)= g III(o)p& f=1
where the configuration-independent contribution pI of

P(cr) =N g II~(cr)D~pF,

F

(13)

where the "lattice-averaged spin product" (denoted by an overbar) of the prototype figure

gives in

ich

symmetr19T 4 87/Xi4 10.9 84.89 599.44 Td ic2

f.

8)

P

[pF }

can then be used to predict band gaps of arbitrary
structures.

shown in Fig. 2. In addition to the normalization con-stant po, and the site-only p,,

figures we use (i) eight

pair (k=2) interactions [Figs. 2(a) and 2(b)], (ii) four
three-body

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From these results, we conclude the following.
(i) The cluster expansion for the direct band gap [Fig. 3(a)] converges considerably slower than that for the total energy [Eq. (2) and Fig. 3(b)] in that the latter is dom-inated by the nearest-neighbor pair energy J2 2 while the former requires a considerably larger number of higher
terms.

(ii) Nevertheless, the cluster expansion of the band gap is reasonably accurate in that the standard deviation for the fit (Table V) is comparable to the underlying precision of the pseudopotential calculation.
(iii) The cluster energies of Fig. 3(a) exhibit an overall decrease with size, in that the contributions from figures with larger interatomic separations are rather small.

V. CONVERGENCE AND TRANSFERABILITY

We have conducted four tests to examine the conver-

gence of the cluster expansion.
First, we have recalculated Ipk }

from Eq. (23), using

as input only 10 out of 27 structures; the resulting in-teraction energies were then used to predict the band gaps of the remaining 17 ordered structures not used in
the f'tt. The last two columns of Table V show that the

prediction error (relative to the "exact" pseudopotential
values) has increased only to 0.04 eV compared to 0.03
eV in the complete fit; both deviations are close to the rel-
ative uncertainty in the pseudopotential calculations of
the band gaps. Note that T /Xi7 9.99 Tf 276.89 VBT /Xi7 9.32E02.33 T8 fits

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TABLE VI. Band-gap expansion coefficients pk and the analogous expansion coefficients Jk for the total energy [Eq. (2)]. pk (VCA) gives the cluster coefficients for expansion of the virtual crystal approximation to the band gap.

Figure

{0,1)=Jp
(1,1)=J)
Pairs

{2,1)=J2
(2,2)=K,
(2,3)=L2
(2,4) =M2
(2,5)=N~
(2,6)=Oq
(2,7)=P2
(2,8)= Qp

6
3
12
6
12
4
24
3

pk (me V)

1262.86
584.06

—25.68
13.05

20.68 —41.44
6.40
16.80
3.58
11.05

Pk (VCA)

1435.7
740.9

0.00
0.00
0.00
0.00
0.00
0.00
0.00
0.00

5.2638 —0.0059

—0.8054 —0.0156 —0.0018 —0.0044
0.0003 —0.0085 —0.0024 —0.0027
Three body
(1,1,1)=J3
(2, 1,1)=K3
(3,1,1)=L3
(3,2, 1)=L3

8
12
24
24

—12.92 —0.90
10.36
1.10

0.00
0.00
0.00
0.00

0.0083 —0.0025 —0.0008 —0.0004
Four body
(4, 1)=J4
(4,2) =K4
Square

(4,3) =L4

2
12
3
12

17.80 —7.79
22.80
1.17

0.00
0.00
0.00
0.00

—0.0106 —0.0005 —0.0004

0.0035

Es (D4)—E

1(Es)Tj ET BT/Xi8 12.35 ET BT CPi8 12.57 Tf 131.56 464 Td 15 ET BTd (126BT /X/XiXi8 8.5 Tf 119.89 2656 Td 19j E

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eV, i.e., just a bit above the precision of the underlying pseudopotential calculation.

VI. APPLICATIONS
OF THE CLUSTER EXPANSION

The solid lines in Fig. 1 show the predicted band gap of perfectly random Al& „Ga As solid solutions, using Eqs. (15)—(17) and the interaction energies of Table VI. We see that the bowing of (E~(x))z is nonparabolic. Using Eqs. (19) and (20) we find

b2-gody =0.59 eV,

b3»d„=0.64(2x —1) eV,

b~» „d=0.098[(2 x—1) +1] eV,

(27)

i.e.,

two- and three-body interactions are dominant. The comparison of these values to experiment is somewhat clouded by the LDA error on the side of theory, and by the fact that aHoy data is usually displayed as an average over certain composition ranges, on the side of experi-
ment. Recent careful experimental studies '

have re-
vealed, however,

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are the 2"=16 ordered structures A„B4 „(O~n ~4)
spanned by this figure. Then, the alloy band gap can be
written as

SRO effects created by finite temperature equilibrium have but a negligible effect on the direct band gap of A1As/GaAs alloys.

(Es)~ = g Q„(x,T)Es(n). (32)
C. Predicting direct band gaps of ordered structures

4

E
2
1

c

1
~ ~

U)
6$ -3
(3 4

Effect of SRO

0.1
GaAs

0.3 0.5 0.7 0.9
Composition AIAs

FICx. 4. Di6'erence in the direct band gap of AlAs/GaAs al-loys containing short-range order (calculated from the thermo-dynamic model of Ref. 4 at T=300 K) and the perfectly ran-dom alloy (T~ a.).

At T~ oo, it can be shown

"' '

that Q„(x, ~) becomes
the random Bernoulli probability.
To see the effect of SRO on the alloy's band gap, we
use the function Q„(x,T) computed in Ref. 4(b) for
Al, „Ga„As and contrast the band gap (E)z obtained from Eq. (32) with that obtained by substituting in this equation the Bernoulli distribution Q„' '(x, ao) appropri-ate to the perfectly random alloy with no SRO. To exag-gerate the effects, we use Q„(x,T) at a rather low teinper-ature of 300 K (well below growth temperatures), where bQ„(x, T) of Eq. (28) is large. We can use for E (n) in Eq. (32) the band gaps of the 16 structures that are exact-
ly spanned by F,„being a tetrahedron. These consist of
five distinct configurations A (zinc blende), A3B (luzon-ite), AB (CA), AB3 (luzonite), and B (zinc blende) with ratios 1:4:6:4:1. To obtain more accurate results (see
Table VII) we can use the renormalization trick of Ref. 4
whereby Es(n) [denoted EE(n, V) in Eq. (2.13) of Ref 4(a)] is replaced by its renormalized from [denoted e„ in Eq. (2.27) of Ref. 4(a)]. Equation (6.16) of Ref. 4(a) gives
this quantity where all pair interactions are folded in.
Figure 4 shows the difference between the alloy band gap computed with SRO [i.e., using Q„(x,T=300 K)] and
the band gap of the perfectly random alloy [using
Q„(x,~)]. We see that (i) SRO reduces

the band

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x, that

SRO where

are

lastRef.

agr (see)Tj ET BT /Xi10 8.78 56 94.32 125.89 Td (with)Tj ET BT /Xi10 9.26 Tf7498.32 125.89 Td (the)Tj ET BT /Xi10 9.42 Tf 135.32 125.89 Td (model)Tj ET BT /Xi10 10.58

that

the conwell e-range

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of the

tmputed where

to

ai7ET BTT0ET BT /Xi/Xi10 9. 9.26 Tf 55.33 552.44 .89 T (Tj ET30ET BT /Xi10os8.05 Tf 55.33 74.68.56 Td 6A4I))292j ET BT 12.6 Tf.14 31.78 43

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gap of 1.72 eV.
Although computationally expensive, we have calculat-
ed the self-consistent band structure of the former x = —,

'

structure using the pseudopotential method with precise-ly equivalent basis sets and Brillouin-zone sampling used for all other structures. This gave a direct band gap of 1.07 eV, very close to the prediction of the cluster expan-sion of 1.10 eV. This highlights the usefulness of such cluster expansions in the design of materials with specified properties. Note that both values are larger than the linearly weighted average —, 'Eg (A1As)
+
~Eg (GaAs) and then the largest band gap at x = —,

' con-

tained in our "basis set" (e.g., see Fig. 3).

VII. SUMMARY

We have demonstrated that the direct band gap of sub-stitutional A1As/CraAs systems can be usefully expanded

in terms of contributions from a hierarchy of atomic clus-ters. %'e find that two-body and three-body figures are dominant, and that the expansion requires larger figures than needed to express the total energy surface. This ex-pansion enables the prediction of the band gap of random alloys, alloys with short-range order, and gap of complex
ordered structures.

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third layer stacking) vary from 2.3 to 3.3 eV; see, e.g., N. L.
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