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Predicting structural energies of atomic lattices

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The complexity of current ab initio quantum-mechanical calculations of the total energy of given distributions of atoms on a periodic lattice often limits explorations to just a few configurations. We show how such a small number of calculations can be used instead to compute the interaction ener-gies of a generalized Ising model, which then readily provides predicted energies of many more in-teresting configurations. This is illustrated for A1As/GaAs systems.

I. INTRODUCTION II. METHOD

The prediction of the stable crystal structure of a given compound has traditionally been carried

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P(cr)=[(1—x)P(A)+xP(B) j+bP(o.),
where the excess property is

EP(o)=. g g Dk [III, (cr) i) j—pk

m&Ok&1

(4)

and i)=1 when k is even and ii=(2x —1) when k is odd. %e see that this cluster expansion needs to capture only the deference AP(o) between the property P(o) of some structure 3 & „8 and the linearly weighted sum over the
same

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(i) Define a set of %, periodic crystals A B represent-ing a range of compositions and atomic plane orienta-tions G; Table I and its caption give 27 examples (includ-ing the binaries) for the fcc symmetry.
(ii) Calculate quantum mechanically from band-
structure theory the excess total energy b,E(s) of these X, periodic structures. Here, the ion-ion, electron-ion, and electron-electron (Coulomb, exchange, and correla-
tion '

) interactions are treated self-consistently in an ab
initio fashion. The electron-ion terms are represented by
nonlocal pseudopotentials; the wave functions are ex-
panded in a basis set of M =150 plane waves/atom, and all Hamiltonian matrix elements are computed by extend-ing all integrals and lattice sums to convergence. Since for the example studied here (A =A1As and 8 =GaAs) the end-point compounds have equal molar volumes, all
calculations are done at a fixed (theoretically obtained)
equilibrium volume. Great care was exercised to assure
that the calculated excess energies b.E(s) have the same precision (within 0.1 meV/atom) for all structures; we use precisely equivalent basis sets, Brillouin-zone sampling, ' and stringent self-consistency conditions. These calculat-ed energies AE(s) for all ordered structures (defined in Table I and its caption) are shown in Fig. 1; they exhibit
a nonintuitive distribution of energies whereby certain
atomic-plane orientations [e.g., (111)]have the lowest en-ergies, others [e.g., (201)] have the highest ones.
(iii) To examine the expansion (4), we first fit all of the
X, =27 calculated excess energies to a set of Xf (X, in-
teractions [pz J, systematically extending the range of

i

'

I

'

i

14i-!

CA

CH

QW2
~ j2
CP

m 8

(k, m) to obtain convergence. Using only Nf =13 terms produces an excellent fit" with the root-mean-square er-ror of 0.097 meV, comparable to the intrinsic relative precision of the ab initio calculations. More importantly,
these interactions pk show convergence with the size of
F, e.g.,

the pair (k =2) energies decay with interatomic

separation m: they are —0.8075, —0.0279, —0.0225, —0.0051, —0.0001, and —0.0075 for m =1, 2, 3, 4, 5,
and 6, respectively. The same is true for the three-body

terms p3 i =+0.0075 p3 ~

=—0.0021, and p3 3
=+0.0003, while the four-body terms are rather small: p4, i =+0.0009 and p4 2

=—0.0034.
(iv) Given this rapid convergence, we now select the figures that give the largest contribution Dk pk to the
energy and use these to predict the energies of other
structures. In addition to the normalization terms (0, 1)
and (1,1), we use the pair interactions (2, 1), (2,2), (2,3), and (2,4) [the (2,4) pair has a higher multiplicity DF than

the (2,6) pair]. Using just these six figures and X, =6
structures, denoted in Table I by asterisks, we obtain by
direct matrix inversion of Eq. (4) a set of six interaction
energies, given in the caption of Table I. These are now used to predict the energies of the remaining 21 struc-tures, whose energies were not used in the determination

of the pf's. Table I shows that direct calculations on only
6 configurations can be used to predict the quantum
mechanically calculated excess energies with useful pre cision: the prediction error (0.13 meV; a similar value is
obtained by selecting other structures) is just slightly
larger than the intrinsic precision of the direct calcula-
tion. This analysis shows that the informational content
of the complex total-energy calculations on various
Al Ga As + structures depicted by the symbols in Fig.
1 can be reduced to -6 interaction energies and that
these su%ce to predict the structural energies of other configurations. Of course, the rate of convergence will depend, in general, on the chemical nature of the solid and may vary when long-range elastic or screened elec-
trostatic interactions are present. Our previous studies'
show that the same set of structures and interaction ener-

gies do apply, however, to many other III-V and II-VI in-tersemiconductor compounds. Applications to
transition-metal alloys' indicate that a similar conver-
gence can be obtained. This opens the way for calcula-
tions of formation energies for lattice structures that are too complicated to be treated by direct ab initio methods. A few examples follow.

III. APPLICATIONS

A. Random Al& „Ga„As alloys

0
0.2 0.4 0.6 0.8 1.0

GaAs Composition x AIAs

FIG. 1. Ab initio calculated formation energies of the various
AlpGa~Asp+~ ordered structures of Table I. The solid line
gives the calculated energy AEz of the random Al, 6-a As al-
loy. The symbols refer to the structures defined in Table I.

W'e can predict the formation energy AE& of a random
A i B„alloy by replacing 111, (o) in Eq (4) by its
configurationally averaged value (2x —1)". Using the in-
teraction energies [pf]

from the %,=Kf =6 set we get
the excess energy of the random alloy depicted in Fig. 1
by the solid line. (Using instead the larger set with
%+=13 interactions produces differences ~0.05 meV.)
The value at x = —,

'

is within the experimentally deter-
mined range. ' A ground-state search' with the Ising

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Hamiltonian (4) using our interaction energies [pk
shows that the system will phase separate into
A1As+GaAs at T=O. Note that, despite this, some or-
dered structures have a lower formation energy than the
corresponding random alloy at the same composition
(Fig. 1), hence metastable ordering could exist.

40—

1

]

I
i

I
i

I
l

I

p layers of AC
in continuous BC

[201] 36.65

B. Suyerlattices

It is possible'

"

to predict from Eq. (4) the formation
enthalpies of (A1As) (GaAs) superlattices as a function of the repeat periods (p, q) and layer orientation G sim-ply by calculating the geometrical correlation functions' III(p, q, G) and using the interaction energies that were determined previously from our fit (Table I). For repeat periods (p,p) we obtain the order of the formation
enthalpies bE(111)& bE(001) & EE(110)& bE(113)
& bE(201). In the few cases where our hE can be com-pared with direct ab initio superlattice calculations (for
structures not included in our basis set), the agreement is

good, e.g., for the p =q =3(111)oriented superlattice the result obtained from our cluster expansion, 11.4
meV/cell, is in very good agreement with the extensive
first-principles calculations of Bylander and Kleinman, '
yielding 11.6 meV/cell.

C. Quantum wells

I 30—

U)

c 20

CO
~ ~

(QI)0

[113]„25.96

[110] 22.15

[001] 14.95

[111] 11.44

l i I i I i I

2 3 4 5

Number of AC layers, p

FIG. 2. Predicted interfacial energies of quantum wells con-sisting of p layers of AC embedded in a continuous BCbarrier.

The cluster expansion can be used to extract the inter-facial energy for the interesting case of (BC) (AC)z(BC) quantum wells, i.e., p layers of AC
embedded in a continuous barrier made of' BC. The re-
sults are shown in Fig. 2. We predict that a [ill]- oriented well is the most stable while the [201]is the least stable in this series; the energy of the latter converges rather slowly to its asymptotic limit. The di6'erent be-haviors versus p and, for Axed p, versus orientation Cx can
be understood in terms of the number of mixed A-8 atom

pairs at the interface for each geometry. '

D. Isovalent antiyhase boundaries

Another interesting application is the determination of the energy of an antiphase boundary (APB) in a given or-dered structure. We have considered an APB in which
the atoms of the mixed sublattice (isovalent A and B
atoms in A i B C) are interchanged across the inter-

face. This type of APB was found to occur experimental-ly in high densities (mostly perpendicular to the growth
direction), both in lattice-matched' and in lattice-
mismatched ordered ternary compounds. Direct first-principles supercell calculations of such APB energies would be difficult, requiring O(30—40) atoms/cell (Ham-
iltonian matrices of square dimensions of 6000X 6000) in
order to separate the contributions of two consecutive
APB's. We have considered the effects of differently
oriented APB's on the formation energy of the ordered
CuPt (CP) structure (the monolayer GaAs-A1As superlat-tice oriented along the [111]direction) and of the ordered CuAu (CA) structure (monolayer superlattice along the
[001] direction). We define the APB energy 6AFB(G) as
the difference between the energy of the (CP + APB) sys-tem and that of the perfect CP structure. Since there are two APB's per cell, the energy associated with each is

TABLE II. Calculated APB energies (in ergs/cm) for di6'erently oriented APB's in the CuPt or-dered structure of A1GaAs2. For nonstoichiometric APB's, the value given is the average of the ener-gies of the two Ga and Al APB's [Eqs. (5) and (6)].

Stoichiometric

Cupt

Nonstoichio metric

orientation
energy

111
+ 1.658

001 —0.170

110 —2.388

110
+2.019

113
+0.679

111 —5.988

orientation
energy

101 —2.074

111

113
2.