1. Introduction

Recent advances 1,2 in first-principles self-consist-
ent implementations of the local density formalism 3 have produced a wealth of information on the ground state properties of ordered intermetallic I and semicon-ducting 2 compounds. To find the stable crystal con-figuration, one repeats the total energy calculation for a few assumed crystal structures that by analogy with related compounds or by "chemical intuition" are ex-pected to be likely competitors for the stable ground state. Comparison of total energy vs volume curves for such a set of "intuitive structures" permits the identifi-cation of the stablest structure in this set and possible phase-interconversions among them. While generally successful,l,2 the predictive value of this approach does depend on one's ability to guess correctly at the.outset a canonical set of structures which includes the "win-ning" (minimum energy) configuration. One wonders, however, if a different, hitherto unexpected structure could have yet lower energy, or whether linear combi-nation of two other structures with compositions z~, and x# (and za < z~, < z#) could have a lower en-ergy than a (hence, a will disproportionate into a + 3). Addressing this problem, even for binary A,,Bra com-pounds on a fixed lattice requires, in principle, calcu-lation of the total energies of the 2 N atomic configura-tions for each type of lattice (fcc, bcc...). Even limiting N to O(1O) - O(102), this is a formidable task for first-principles electronic structure methods, s This problem can be circumvented to some extent by using simplified electronic Hamiltonians (e.g., minimal 2.5type

by formidable replac.80 0 TD 391 1 rg 0.42 Tc 0 Tw (total) Tj 212 0 TD 1 1 1 rg 0.48 Tc 0 Tw 2type total energy by

phenomenological effective pair potentials. 5 It is the purpose of this paper to demonstrate how one can effec-tively perform such a ground state search among many [O(2 N)] equimo-

lax compounds exhibit at low temperatures a range of symmetriesS: CuAu has the fcc-based (L10) struc-ture, CuPd has a bcc-based (B2) structure, CuPt has a rhombohedral (Lll) structure, and CuRia does not exists (it phase separates into pure Cu + Rh) . We show that an extensive ground state search (of ~ 65,000 configurations) within the local density forrnMism does predict in all cases the correct ground state symmetries. This opens a practical way for identifying stable crys-tal structures directly from first-principles calculations, without resort to coherent potential or tight-binding approximations.

2. Approach
Our approach is based on standard lattice theories
of statistical mechanics,L s where a given

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Si (+1 if occupied by B,-1 if occupied by A), we define for each figure f in configuration a the spin product HI(a) = SItS2t...Sk,. The energy E(~) of any lattice configuration can then be rigorously expanded 7 into an Ising-like series

2 N

E(a) = ~ l'I/(a) J! , (1)
!

where Jl is the energy of figure f, defined, through the orthogonality relationship, T by averaging over all the configurations as,

2 N

J1 = 2-~' ~ E(~) ni(~) • (2)
a,

These sums can be reduced by symmetry noting that for a space group operation ~ of the lattice, we have E(~a) = E(a) and II~l(~a) = Ill(a), hence, from Eq.(2) J~! = 3"/ so all ND! symmetry-related fig-ures have equal interaction energies. Consequently, the sum in (1) can be limited to the prototype (symmetry-unique) figures F:

E(~) = N ~ Z)r fIF(~) J~ , (3)
F

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ures, (ii) the pair terms (2,1), (2,2), (2,3), and (2,4) for
1st, 2nd, 3rd, and 4th fcc neighbors (Sth in bcc), and
(iii) the 3-body (3,1) and 4-body (4,1) terms [replaced
by (3,2) and (4,2), respectively, for bcc structures]. As shown by connolly and Williams, ~ since rIF(s) and DR
are known for such periodic configurations, H we can obtain the values of the NF functions {JR} from a least-square fit 9 of {E(s)} to Eq (3); the fit error (Ta-ble I) already provides some measure of the adequacy of the truncation. Note that since E(s) is obtained from a first-principles (LAPW) calculation in which all lattice sums are calculated to convergence, the ef-fective interactions Jl of Eq. (2) represent a renormal-ization of all potentially long range terms; J! is hence a sum of total energies, not an interaction potential, s Since E(s) is generally a function of volume H-12 V, the interactions J~ depend on V, too. It is useful (see below) to transform these { JF(V)} into another expan-sion in terms of volume-independent interactions Y~-. This can be done by the "e - G" expansion L1 in which we replace the equation of state E(~, V) for structure a by the function U(o, V) which has the same value for the first three volume derivatives at equilibrium as E(a, V), yielding

E[~, V(~)] ~ Vie, V(~)] = G(~)+N ~ Z)F fIF(~) VF,
F

(4)
where G(z) is a closed-form function 1. of the alloy vol-ume V(x), the bulk modulus B(x) and its pressure derivative B'(x). [Reference 11 illustrates that Eq. (4)

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reproduces Eq. (3) with excellent precision]. Equation
(4) shows that the excess energy of any configuration a can be separated into a configuration-independent "elastic energy" G(z) of the medium (zero only when all atomic species have the same molar volume) plus a sum of chemical "substitution energies" (the standard generalized Ising problem 8) which represents configu-
rationally dependent fluctuations about this medium.
The relative stability of phases at the same z is hence determined by their substitution energies, while G(z)
controls disproportionation of a single phase into mul-
tiple phases of unequal molar volumes. In many pre-
vious studies, size molar m

Table II. Using different combinations of 10 structures {s} (out of 12, see Table I) we calculate G(x) of Eq.(4), then fit E(s) - G(x,) to find different sets of .N'F = 8 interactions {12F}. These are then used to predict via Eq.(4) the energies AH,, of the two remaining ordered structures s' (not included in the fit), and the energy/XHIz of the random alloy at x = 1/2. This Table gives (in meV/atom) the average] LAPW - predicted I error for AHe ("AHs'error") and the predicted AHR obtained from different sets {PF}. The last row gives the standard deviations 7;. The same procedure yields for CuPt ~ = 2.2 and 0.9 meV for unrelaxed and relaxed &HR. Note that even using only 10 structures, the error in predicting the

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cubic fee or bcc sites) and for ~relaxed" geometries (en-
ergy minimized with respect to all structural degrees
of freedom consistent with their respective space group symmetry).
3. Results

Table I shows that the cluster expansion with
N, = 12 structure and NF = 8 figures describes the energies of the unrelaxed ordered structures to within the underlying LAPW accuracy, l° Hence, we will use this expansion to search for the ground state among 2 N lattice configurations. Table II shows a robust predic-tion of the energies of the random alloy (both relaxed
and unrelaxed) using different sets of {PF} and that
the energies of unrelaxed ordered structures are pre-
dicted for these systems to within 10 meV/atom even
if we use N, = 10. To meet this criteria it was nee-
essa.,'y to extend the interactions up to the 4th and
5th j 42g 0.72 Tc 0 Tw (the j 27.60 0 TD 1 1 1 ructure) rg meV/atom

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(hence, Lll ordering is disallowed) and take G(x) = 0 (hence, neglect strain energies resulting from A - B size-mismatch). Such simplifying approximation can not he used here. We have hence conducted a ground state search of 2 8 lattice configurations using our full {~,,~} sets, but limiting N to 16 fcc (bcc) sites per primitive unit cell. Structures with larger cells could be missed. We hence search 2 ~e .~ 65,000 structures for each compound.

Our predicted T = 0 GSL's are shown in Fig. 1; they consist of

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0

- 10

-150 I AF£~/~"~Fexpt t
- 2 0 ~

50 ~ (b) .... :
0JECu Pd
• N DO22 ~l,

-lOO \,'~'-"~__ .C4 "~, 2 B2 ,,f../. _1
- 150 " ~ Fcalc
AFexpt
- 200 ....

so }(-c) .... :

0~ Cu "40" DO22 Au'

~"..~ O22 0 L12

l
-100 I- J ~------ AFcalc

' ....

0.0 0.2 0.4 0.6 0.8 .0

Composition x

Fig. 1: Ground state lines (solid line segments connecting diamond-shaped sym-bols) for Cu-based intermetallics. The symmetries are obtained from the unrelaxed cluster expansion, while the energy values displayed (except D1 and D7 for CuPd) are from relaxed LAPW calculations. For CuRh (not shown) the ground state line gives only phase separation. Open symbols shows the LAPW energies of struc-tures that are above the ground state line. The cluster expanded values D1 and D7 for CuPd are slightly above the line connecting the end point and/'.12 (LAPW values). Also shown is the calculated a~d measured ~a free energy AF(z,T) of the disordered alloys at T = 1350, 1350, and 800 K for CuPt, CuPd and CuAu, respectively.

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parison of different lattice (fcc, bee) and use of "ground state search" within the context of LDA calculations. A similar approach 17 that uses directly Eq. (3) [with volume-dependent JR(V)] rather than e - G approxi-mation produces nearly identical results. We conclude that such first principles total energy calculations on a small number of periodic structures can be used along with lattice models to effectively search among many

configurations for the global ground state structures of intermetalllc compounds. This removes the need to correctly guess at the outset a set guess the aftlstructures

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9. For N~- = N, one can invert Eq (3) to obtain JF, as shown by J. W. D. Connolly and A. R. Williams, Phys. Rev. 27, 5169 (1983) for nearest neighbors. Here, however, we use: (i) N~ > N~" , (ii) select the set of