

GROUND STATE STRUCTURES OF INTERMETALLIC COMPOUNDS: A FIRST-PRINCIPLES ISING MODEL

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Predictions of the equilibrium crystal structure of simple compounds, e.g., within first-principles total energy methods are usually carried out by searching for the lowest energy among a small number, $O(10)$, of intuitively selected candidate structures. We show how calculations of the total energies of $O(10)$ structures can be used instead to define a first-principles, multi-spin Ising Hamiltonian, whose ground state structures on a fixed lattice can be systematically searched using lattice theory methods. This is illustrated for the intermetallic compounds CuAu, CuPd, CuPt, and CuRh, for which the correct ground states are identified out of more than 65,000 possible structures.

1. Introduction

Recent advances^{1,2} in first-principles self-consistent implementations of the local density formalism³ have produced a wealth of information on the ground state properties of ordered intermetallic¹ and semiconducting² compounds. To find the stable crystal configuration, one repeats the total energy calculation for a few assumed crystal structures that by analogy with related compounds or by "chemical intuition" are expected 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 identification of the stablest structure in this set and possible phase-interconversions among them. While generally successful,^{1,2} 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 "winning" (minimum energy) configuration. One wonders, however, if a different, hitherto unexpected structure could have yet lower energy, or whether linear combination of two other structures with compositions x_α and x_β (and $x_\alpha < x_\sigma < x_\beta$) could have a lower energy than σ (hence, σ will disproportionate into $\alpha + \beta$). Addressing this problem, even for binary A_nB_m compounds on a fixed lattice requires, in principle, calculation of the total energies of the 2^N atomic configurations for each type of lattice (fcc, bcc...). Even limiting N to $O(10) - O(10^2)$, this is a formidable task for first-principles electronic structure methods.³ This problem can be circumvented to some extent by using simplified electronic Hamiltonians (e.g., minimal basis set tight binding) in conjunction with perturbation theory⁴ or

by replacing the quantum mechanical total energy by phenomenological effective pair potentials.⁵ It is the purpose of this paper to demonstrate how one can effectively perform such a ground state search among many [$O(2^N)$] atomic configurations in a *first-principles manner*, using directly calculated (local density³) total energies of only ~ 10 crystal structures. We illustrate this method for the intermetallic systems $\text{Cu}_{1-x}\text{Au}_x$, $\text{Cu}_{1-x}\text{Pd}_x$, $\text{Cu}_{1-x}\text{Pt}_x$, and $\text{Cu}_{1-x}\text{Rh}_x$. These form an interesting set in that while in elemental form, Cu, Pd, Pt, and Rh are all fcc metals, their 50%-50% equimolar compounds exhibit at low temperatures a range of symmetries⁶: CuAu has the fcc-based ($L1_0$) structure, CuPd has a bcc-based ($B2$) structure, CuPt has a rhombohedral ($L1_1$) structure, and CuRh does not exist (it phase separates into pure Cu + Rh). We show that an extensive ground state search (of $\sim 65,000$ configurations) within the local density formalism does predict in all cases the correct ground state symmetries. This opens a practical way for identifying stable crystal 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,^{7,8} where a given lattice type (e.g., fcc, bcc) with N sites is discretized into a set of "figures" f , each being a particular selection of k_f sites (a k -vertices figure) out of the total N sites. The lattice can exist in 2^N configurations σ , each corresponding to a different occupation of the N sites by A and B atoms. Labeling each site i by a fictitious spin variable

\hat{S}_i (+1 if occupied by B, -1 if occupied by A), we define for each figure f in configuration σ the spin product $\Pi_f(\sigma) = \hat{S}_1 \hat{S}_2 \dots \hat{S}_k$. The energy $E(\sigma)$ of any lattice configuration can then be rigorously expanded⁷ into an Ising-like series

$$E(\sigma) = \sum_f^{2^N} \Pi_f(\sigma) J_f, \quad (1)$$

where J_f is the energy of figure f , defined, through the orthogonality relationship,⁷ by averaging over all the configurations as,

$$J_f = 2^{-N} \sum_{\sigma} E(\sigma) \Pi_f(\sigma). \quad (2)$$

These sums can be reduced by symmetry noting that for a space group operation \mathfrak{R} of the lattice, we have $E(\mathfrak{R}\sigma) = E(\sigma)$ and $\Pi_{\mathfrak{R}f}(\mathfrak{R}\sigma) = \Pi_f(\sigma)$, hence, from Eq.(2) $J_{\mathfrak{R}f} = J_f$ so all ND_f symmetry-related figures have equal interaction energies. Consequently, the sum in (1) can be limited to the prototype (symmetry-unique) figures F :

$$E(\sigma) = N \sum_F D_F \bar{\Pi}_F(\sigma) J_F, \quad (3)$$

where the "lattice averaged products" $\bar{\Pi}_F(\sigma)$ are $\sum_{\mathfrak{R}} \Pi_{\mathfrak{R}F}(\sigma) / N g_0$ and $N g_0$ is the number of operation \mathfrak{R} in the space group of the lattice.

While the cluster expansion of Eq.(3) is exact, its utility in practical applications rests on it representing a fairly rapidly convergent series. In practice, many applications of Ising-like theories to phase stability have *postulated* the dominance of just a few (e.g., nearest neighbors) interactions,⁷⁻⁹ often⁸ without calculating them or actually verifying convergence.⁷⁻⁹ Within the spirit of a first-principles approach, we set to calculate the parameters of Eq. (3) from an *ab initio* electronic Hamiltonian (here, the local density formalism³). We do this by selecting (separately for fcc and bcc) a hierarchy of N_F figures $\{F\}$ and a set of $N_s \geq N_F$ periodic crystal structures for which the total excess energies $\{E(s)\}$ are directly calculated self-consistently in the local density approximation (LDA), as implemented by the linearized augmented plane wave (LAPW) method.¹⁰ The $N_s = 12$ structures selected here (Table I) cover a range of compositions and ordering vectors; the $N_F = 8$ figures $F = (k, m)$ that we use include k -body terms separated by up to the m -th neighbors. We use the hierarchy: (i) the empty (0,0) and site-only (0,1) fig-

TABLE I. Comparison of the directly calculated (LAPW) and the cluster-expanded [Eq.(4) using $N_F = 8$ and $N_s = 12$] unrelaxed excess energies (in meV/atom) for the fcc-based structures. The structural symbols are from Ref. 6 except for $\beta 1$, $Z 2$ that are $A_2 B_2$ superlattices, respectively, along the [001] direction, whereas "40" is a $A_2 B_2$ superlattice along the [201] direction. The last two lines show the standard deviation η of the fit for both unrelaxed and relaxed structures. Similar calculations were done for CuPd using 12 bcc-based structures yielding $\eta_{\text{unrel.}} = 3.7$ meV.

Struc.	CuAu		CuPd		CuPt	
	LAPW	Eq.(4)	LAPW	Eq.(4)	LAPW	Eq.(4)
$L1_2$ ($A_3 B$)	-35.1	-38.2	-85.0	-79.2	-115.8	-112.7
DO_{22} ($A_3 B$)	-30.8	-29.8	-75.5	-77.4	-96.7	-97.8
$\beta 1$ ($A_2 B$)	59.9	61.0	-36.4	-42.5	-40.8	-34.6
$L1_0$ (AB)	-33.4	-32.7	-75.9	-78.4	-83.3	-91.1
$L1_1$ (AB)	68.1	68.1	-66.8	-66.8	-111.9	-111.9
"40" ($A_2 B_2$)	-15.2	-15.9	-76.4	-74.8	-63.8	-61.3
$Z 2$ ($A_2 B_2$)	155.3	154.6	-4.3	-3.6	34.7	31.7
$\beta 2$ (AB_2)	46.4	46.7	-48.6	-43.9	-31.2	-31.5
DO_{22} (AB_3)	-9.1	-8.7	-46.4	-47.7	-65.9	-69.8
$L1_2$ (AB_3)	-16.1	-17.2	-53.4	-49.5	-96.3	-84.7
$\eta_{\text{unrel.}}$		1.0		3.1		4.3
η_{relaxed}		15.2		12.2		4.8

ures, (ii) the pair terms (2,1), (2,2), (2,3), and (2,4) for 1st, 2nd, 3rd, and 4th fcc neighbors (5th 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,⁹ since $\bar{\Pi}_F(s)$ and D_F are known for such periodic configurations,¹¹ we can obtain the values of the N_F functions $\{J_F\}$ from a least-square fit⁹ of $\{E(s)\}$ to Eq (3); the fit error (Table 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 effective interactions J_f of Eq. (2) represent a renormalization of all potentially long range terms; J_f is hence a sum of total energies, not an interaction potential.⁵ Since $E(s)$ is generally a function of volume¹¹⁻¹² V , the interactions J_F depend on V , too. It is useful (see below) to transform these $\{J_F(V)\}$ into another expansion in terms of volume-independent interactions \mathcal{V}_F . This can be done by the " $\epsilon - G$ " expansion¹¹ in which we replace the equation of state $E(\sigma, V)$ for structure σ by the function $U(\sigma, V)$ which has the same value for the first three volume derivatives at equilibrium as $E(\sigma, V)$, yielding

$$E[\sigma, V(x)] \cong U[\sigma, V(x)] = G(x) + N \sum_F D_F \bar{\Pi}_F(\sigma) \mathcal{V}_F, \quad (4)$$

where $G(x)$ is a closed-form function¹¹ of the alloy volume $V(x)$, the bulk modulus $B(x)$ and its pressure derivative $B'(x)$. [Reference 11 illustrates that Eq. (4)

reproduces Eq. (3) with excellent precision]. Equation (4) shows that the excess energy of any configuration σ can be separated into a configuration-independent "elastic energy" $G(x)$ 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 problem⁹) which represents configurationally dependent fluctuations about this medium. The relative stability of phases at the same x is hence determined by their substitution energies, while $G(x)$ controls disproportionation of a single phase into multiple phases of unequal molar volumes. In many previous studies, size differences, measured by $G(x)$, were neglected. As shown in Ref. 11, this can lead to substantial errors in the calculated formation enthalpies of compounds whose constituents are size mismatched. To test the transferability of $\{\mathcal{V}_F\}$ we recalculate it from a smaller set of 10 (rather than 12) structures, then, using Eq.(4) we predict the energies $\{E(s')\}$ of the remaining structures $\{s'\} \neq \{s\}$. Comparing these predictions from the cluster expansion to those directly calculated via LAPW gives the "prediction error" (Table II); this is then minimized by increasing the number of figures in the underlying cluster expansion. In addition, we use $\{\mathcal{V}_{k,m}\}$ and $G(x)$ to predict via Eq.(4) the energy ΔH_R of the random alloy [for which $(\bar{\Pi}_{k,m}) = (2x - 1)^k$]; the standard deviation in the ΔH_R values obtained from different expansions is also shown in Table II. The procedure is carried out for both "unrelaxed" geometries (i.e., when the cell volume is varied, but the A and B atoms are assumed to reside on their

Table II. Using different combinations of 10 structures $\{s\}$ (out of 12, see Table I) we calculate $G(x)$ of Eq.(4), then fit $E(s) - G(x_s)$ to find different sets of $N_F = 8$ interactions $\{\mathcal{V}_F\}$. These are then used to predict via Eq.(4) the energies $\Delta H_{s'}$ of the two remaining ordered structures s' (not included in the fit), and the energy ΔH_R of the random alloy at $x = 1/2$. This Table gives (in meV/atom) the average |LAPW - predicted| error for $\Delta H_{s'}$ (" $\Delta H_{s'} \text{ error}$ ") and the predicted ΔH_R obtained from different sets $\{\mathcal{V}_F\}$. The last row gives the standard deviations η . The same procedure yields for CuPt $\eta = 2.2$ and 0.9 meV for unrelaxed and relaxed ΔH_R . Note that even using only 10 structures, the error in predicting the energies of any combination of two independent structures is rather small.

Structures not in fit	$\Delta H_{s'}$ error unrel.	CuAu		$\Delta H_{s'}$ error unrel.	CuPd	
		Pred. ΔH_R unrel.	Pred. ΔH_R relax		Pred. ΔH_R unrel.	Pred. ΔH_R relax
$\beta 1, \beta 2$	1.4	68.4	-6.1	5.5	-47.7	-78.4
$L1_2, L1_0$	2.4	68.3	-8.8	6.0	-47.2	-79.1
$L1_2, L1_2$	3.7	68.3	0.9	8.6	-47.9	-73.5
DO_{22}, DO_{22}	3.7	69.2	2.4	8.6	-50.0	-77.4
$DO_{22}, \beta 1$	2.9	68.9	-1.7	7.9	-49.3	-77.5
η	2.9	0.4	4.2	7.4	1.1	2.0

cubic fcc or bcc sites) and for "relaxed" geometries (energy 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 $N_s = 12$ structure and $N_F = 8$ figures describes the energies of the unrelaxed ordered structures to within the underlying LAPW accuracy.¹⁰ Hence, we will use this expansion to search for the ground state among 2^N lattice configurations. Table II shows a robust prediction of the energies of the random alloy (both relaxed and unrelaxed) using different sets of $\{V_F\}$ and that the energies of unrelaxed ordered structures are predicted for these systems to within 10 meV/atom even if we use $N_s = 10$. To meet this criteria it was necessary to extend the interactions up to the 4th and 5th pair terms for fcc and bcc lattices, respectively. We find that the cluster expansion converges well in these cases, in that the products $D_{k,m}V_{k,m}$ generally decay with cluster size: for CuAu for example, the pair ($k = 2$) terms are (in meV) 270.3, -4.7, 14.6, and -3.0 for $m=1, 2, 3,$ and 4 neighbors, while the 3 and 4 body terms are -19.6 and 1.8 meV respectively. The cluster expansion converges, however, considerably slower for relaxed ordered structures (compare η_{relaxed} in Table I to η_{unrel}). These trends are understandable considering that truncation of the expansion of J_F in Eq.(2) does not guarantee that $J_{\text{eff}} = J_f$. Since relaxation can alter the sizes of the symmetry-related figures (which have the same size in the unrelaxed lattice), truncation of Eq.(2) for *relaxed* configurations could make J_F different from J_f , leading to a slower convergence of Eq.(3) for the same number of figures. This is less of a problem in the random alloy because in this case only the configurationally averaged J_F 's are relevant.

Our strategy will hence be to perform a ground state search using the cluster expansion (4) for the converged expansion in *unrelaxed* configurations, assuming that relaxation does not alter the *symmetries* of the structures on the ground state line (GSL). Having identified out of the many (2^N) candidate structures a few that are ground states, we will calculate their *relaxed* energies directly from LAPW, without a cluster expansion. Notice that we give up at the outset the possibility of distinguishing structures whose energy difference is smaller than our truncation error (e.g., long-period CuPd superstructures stabilized by very weak 8-th neighbor interactions¹³).

Having established a converged Ising-like expansion, the problem of finding its ground state is a classic problem of magnetism of spin lattices.^{7,14,15} The most complete ground state search for fcc lattice was carried out by Kanamori and Kakehashi¹⁴ (KK)(retaining pair interactions up to $V_{4,2}$) and for bcc lattices by Finel and Ducastelle.¹⁵ However, these authors make a number of simplifying assumptions on $\{V_{k,m}\}$ which are not supported by our actual local-density calculations. For example, they neglect the many-body terms $V_{3,1}$ and $V_{4,1}$, assume that $V_{2,1} \gg V_{2,2}, V_{2,3}, V_{2,4}$

(hence, $L1_1$ ordering is disallowed) and take $G(x) = 0$ (hence, neglect strain energies resulting from $A - B$ size-mismatch). Such simplifying approximation can not be used here. We have hence conducted a ground state search of 2^N lattice configurations using our *full* $\{V_{k,m}\}$ sets, but limiting N to 16 fcc (bcc) sites per primitive unit cell. Structures with larger cells could be missed. We hence search $2^{16} \sim 65,000$ structures for each compound.

Our predicted $T = 0$ GSL's are shown in Fig. 1; they consist of straight line segments between "breaking points" (denoted by solid diamond-shaped symbols) that indicate the globally stable ordered structures. The symmetries established clearly from experiment⁶ are also found theoretically, even though we have purposely omitted from the basis set used to extract V_F some of the structures which are known to be ground states.

For CuPt, we find the established⁶ Cu_3Pt ($L1_2$) and CuPt ($L1_1$) phases, i.e., we correctly describe the competition between rhombohedral ($L1_1$) and tetragonal ($L1_0$) symmetries. Two additional ground state fcc structures Cu_7Pt and CuPt_7 ($D1$ and $D7$ in Fig. 1a), having twice the primitive fcc lattice vectors are also identified; these were not included in the "basis set" as they were unsuspected by the normal method of guessing to be ground states. We tested this result by calculating the energy of Cu_7Pt directly from LAPW ($\Delta H = -65.5$ meV/atom for the unrelaxed structure), confirming the cluster expansion prediction ($\Delta H = -62.6$ meV/atom). Indeed we found that an early¹⁶ investigation did propose the existence of the CuPt_7 ($D7$) structure on the basis of electric measurements, (however, this was not directly confirmed by X-ray studies).

For CuPd (Fig. 1b), we find the observed fcc-type Cu_3Pd ($L1_2$) and bcc-type CuPd ($B2$) structures showing that our theory correctly reproduces the delicate balance between fcc and bcc interactions. The cluster expansion also predicts that CuPd_3 ($L1_2$) is (with a numerical uncertainty of 5 meV/atom) a ground state. The $D1$ and $D7$ structures (not observed) are predicted to be candidates for low temperature stable structures.

For CuAu (Fig. 1c) we correctly find Cu_3Au ($L1_2$), CuAu ($L1_0$) and CuAu_3 ($L1_2$) to be on the GSL, however, inclusion of structural relaxation (which is very large for Cu-Au) moves CuAu_3 away from the GSL. For CuRh (not shown) we find that the GSL consists only of phase-separation, as observed.⁶ Figure 1 also shows the calculated excess free energy $\Delta F(x, T)$ of disordered alloys at $T \geq 800$ K, obtained from a cluster-variation^{8b,11} solution (including folded interactions¹¹ up to $V_{4,2}$) with the relaxed cluster energies. We find a reasonable agreement with the measured^{6a} $\Delta F(x, T)$ values.

4. Summary

The major advance here over previous first-principles calculations of phase stability involves a thorough study of the convergence of the Ising series (instead of an arbitrary and convenient truncation), com-

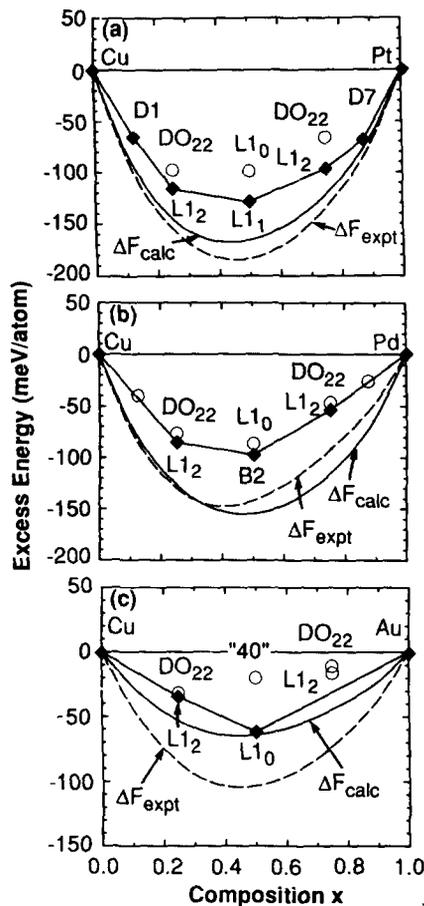


Fig. 1: Ground state lines (solid line segments connecting diamond-shaped symbols) for Cu-based intermetallics. The symmetries are obtained from the unrelaxed cluster expansion, while the energy values displayed (except $D1$ and $D7$ for CuPd) are from relaxed LAPW calculations. For CuRh (not shown) the ground state line gives only phase separation. Open symbols shows the LAPW energies of structures 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 $L1_2$ (LAPW values). Also shown is the calculated and measured^{6a} free energy $\Delta F(x, T)$ of the disordered alloys at $T = 1350, 1350,$ and 800 K for CuPt, CuPd and CuAu, respectively.

parison of different lattice (fcc, bcc) and use of "ground state search" within the context of LDA calculations. A similar approach¹⁷ that uses directly Eq. (3) [with volume-dependent $J_F(V)$] rather than $\epsilon - G$ approximation 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 intermetallic compounds. This removes the need to correctly guess at the outset a set of candidate crystal structures that includes the stablest.

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9. For $N_F = N_s$ one can invert Eq (3) to obtain J_F , as shown by J. W. D. Connolly and A. R. Williams, *Phys. Rev.* **27**, 5169 (1983) for nearest neighbors. Here, however, we use: (i) $N_s > N_F$, (ii) select the set of structures and figures which show minimum linear dependence (Ref. 11a), and (iii) increase the range of J_F to obtain convergence. The weight for structure s in the least-square fit are $w_s = 48M_s/G_s$, where M_s is the number of atoms/cell and G_s is the number of point group operations.
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