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Gus L. W. Hart
gus.hart@gmail.com

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Verifying predictions of the $L1_3$ crystal structure in Cd-Pt and Pd-Pt by exhaustive enumeration

Gus L. W. Hart

Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602, USA

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In 2001, S. Müller and A. Zunger [Phys. Rev. Lett. **87**, 165502 (2001)] predicted a never-before-observed crystal structure in Ag-Pd. Recently, Curtarolo predicted the same structure to be stable in Pt-Cd and Pt-Pd [S. Curtarolo *et al.*, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **29**, 163 (2005)]. The predicted structure is unique in several ways. Though never seen in any other face-centered-cubic-based intermetallic binary compound or ordered alloy, it is relatively simple—it contains only four atoms per unit cell. Furthermore, the structure is the only one of this small size, except the $L1_2$ structure, that cannot be characterized as a simple stacking of layers where each layer contains only one kind of atom. We construct a first-principles-based Hamiltonian and search it for the thermodynamically stable (lowest energy) structures. Using a (practically) exhaustive enumeration of about three million of the most likely candidate structures, we find that this new structure, designated $L1_3$, is indeed a ground state in both Cd-Pt and Pd-Pt. Experimental efforts to validate the predictions are underway.

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I. INTRODUCTION

Crystal structure plays a central role in the properties of intermetallic alloys. Understanding which crystal structures are physically possible and gaining insights about competing phases in multicomponent alloys can lead us to improve existing materials and perhaps design new ones. Thus, knowing what crystal structures are physically realizable is an important component of furthering materials design. Simulation, particularly first-principles calculations, can provide a useful and high-throughput^{1,2} avenue for finding new candidate compounds and structures.

Nature gives us roughly 60 metallic elements to combine to construct possible new crystal structures. We are far from knowing all the intermetallic compounds and ordered alloys that can be formed using these ingredients, both in terms of stable phases (ground states) and likely metastable phases. Thus, a useful step in developing better alloys is finding new compounds, known structures from new combinations of elements, and altogether new crystal structures.

Even in the simple case of binary intermetallic systems (combinations of just two elements) there is plenty of room for new discovery. There are about $\binom{60}{2} \approx 1500$ binary metallic systems. Nearly every one of these 1500 binary systems has been studied experimentally to some degree. In some cases, the experimental data is quite exhaustive. But there is still a great deal that is unknown, and there are a significant number of cases where experimental data is incomplete or misleading.

As an example of incomplete/misleading experimental data, consider the Rh-Ir-Pd-Pt “quartet.” These four elements are chemically very similar, all nearest neighbors in the periodic table. Thus, we expect that all six of the possible binary systems formed from these elements may exhibit essentially the same properties and have similar phase diagrams. Indeed, this idea has been perpetuated for more than 50 years in every known phase diagram compilation.^{3,4} In experiments, three of the six (Pd-Rh, Ir-Pt, Ir-Pd) phase separate at relatively high temperatures, and it was assumed that the

remaining three (Rh-Ir, Rh-Pt, Pd-Pt) would do the same. Surprisingly however, first-principles calculations show these remaining three to be compound forming.⁵⁻⁸

Such examples of incomplete/misleading data in the experimental literature are relatively common. Furthermore, the number of ternary and higher multinary intermetallic systems is immensely larger than the number of binary systems. Thus the room for potential discovery is vast. In exploring the possibilities, we prefer to start where discoveries are most likely. Likely candidates for new compounds have recently been extracted from experimental databases using information theoretic methods.⁹ New compounds and *new structure* candidates have also been inferred using datamining techniques.¹

The purpose of this paper is twofold: (i) outline a new approach^{10,11} for finding new candidate crystal structures, and (ii) verify the predictions of an entirely new structure in two intermetallic systems, Cd-Pt and Pd-Pt. The datamining work that inferred a new structure in Cd-Pt and Pd-Pt, though a seminal contribution to the discipline, is inherently limited—structures not included in the calculated database cannot be predicted. Thus, if the true ground state of a system is not one of the structures considered in the database, it will not appear as a ground state. The approach outlined here avoids this restriction. We exhaustively enumerate essentially all possible structures. Then, coupling this “complete database” with a first-principles-based fast Hamiltonian, we rigorously determine the ground states of the system.

II. ENUMERATING ALL POSSIBLE STRUCTURES

Conceptually, enumerating all possible crystal structures for intermetallic systems is relatively simple. In many intermetallic compounds and solid solutions the atomic sites form a simple periodic array of points. By simple, we mean that these points closely approximate either a face-centered-cubic (fcc) or a body-centered-cubic (bcc) lattice, or the points correspond to the atomic sites of an hcp crystal. Taking this underlying structure (fcc, bcc, or hcp) as a premise, the prob-

lem of finding new candidate structures in intermetallic systems becomes simply a problem of combinatorics—generating all unique combinations of unit cells derived from an underlying structure.

Crystal structures can be systematically generated by extending the ideas of “derivative superlattices.”^{12,13} We briefly describe the method here; details are given in Ref. 11. Given a “parent” cell, fcc, for example, all derivative supercells can be enumerated by first considering all possible *superlattices* based on the original lattice. Listing the basis vectors of the original lattice column wise to construct a matrix A , we can consider the change in basis $B=AS$ where S is a matrix with all integer elements and determinant 1 or -1 . In this case, S is merely a rotation (proper or improper) that leaves the lattice represented by A unchanged (and the basis merely rotated). Matrices A and B then are merely two different choices of basis for the same lattice. On the other hand, if the elements of S are all integers, but the determinant of S is 2, say, then the lattice of B is a superlattice¹² of A with twice the volume of the original (parent) lattice.

By systematically generating all possible matrices S for each determinant size, and then systematically increasing the determinant size, all possible superlattices can be generated, in order of increasing volume. Generating all possible S 's is relatively straightforward because every matrix with integer elements can be represented uniquely in Hermite Normal Form (HNF). Generating all HNF matrices of a given determinant can be done simply by finding all the triple factors of the determinant and using a standard permutations algorithm.^{12,13}

Applying this approach to the case of the fcc lattice, we find 7, 13, and 35 superlattices for $|S|=2, 3$, and 4, respectively. Some of these superlattices are equivalent by the symmetry operations of the fcc parent lattice, and thus the numbers can be reduced to 2, 3, and 7 superlattices, respectively.

Once all unique *superlattices* have been enumerated, we must consider all possible *superstructures*, that is, all possible arrangements of atom types on sites inside each supercell. Although this can be done using standard algorithms for generating all partitions of an integer n into m blocks^{14,15} and permutations of those partitions, it is more efficient to represent all possible configurations as all base- k numbers between 0 and $k^n - 1$ and then remove symmetrically-equivalent duplicates using a group-theoretic approach.^{11,16} For the purpose of this paper, we generate all structures for two atom types (a binary system, $k=2$) with n (and so also $|S|$) less than or equal to four. The result is 2, 3, and 12 unique *superstructures* of volume 2, 3, and 4 times larger than the original fcc parent cell, respectively.

III. FCC STRUCTURES

Using the approach described above, we find a total of 17 fcc-based superstructures with 4 atoms/cell or fewer. These structures are depicted in Fig. 1. For the case of a doubled superstructure (volume twice that of the parent), only two unique structures are possible. These are the well-known prototypes Cu-Au and Cu-Pt (also referred to by their *Strukturbericht* labels $L1_0$ and $L1_1$, respectively), shown in the upper-left corner of the figure.

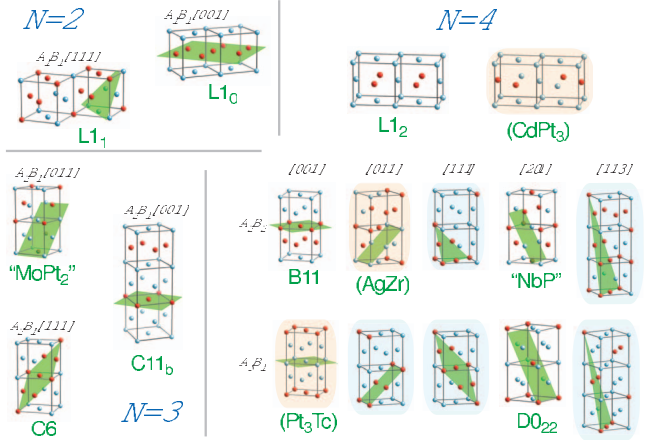


FIG. 1. (Color) The first 17 binary structures derived from the fcc lattice. All have four atoms/cell or less. Structures shown with a green plane can be characterized as a stacking of pure A and B atomic layers. For example the $L1_0$ structure (upper left) is an alternating (A_1B_1) sequence of layers stacked in the $[001]$ direction. All of the two- and three-atoms/cell structures have physical manifestations. Of the four-atoms/cell structures only four have physical manifestations. Three of the others (yellow backgrounds) have been predicted to exist¹ but not yet observed. The other five (purple backgrounds) have never been observed or predicted to exist in any system.

Moving to the next largest cell size, three-atom/cell structures, we find three structures. Again, like the two atom/cell case, we find the structures generated by this combinatoric method have physical manifestations. (Although in the prototypical compounds, the c/a ratio and internal coordinates of the atoms are more bcc like and hcp like in the case of $C11_b$ and $C6$, respectively.)

Continuing with four-atoms/cell, the results are more interesting. There are twelve structures and only four have been observed experimentally. Three more have recently been predicted to exist (yellow backgrounds in Fig. 1). The remaining five structures have never been observed or predicted to exist in any known system.

The structures enumerated in this first group of 17 are geometrically the simplest possible structures based on the fcc lattice. Why is it that some have physical manifestations and some do not? Briefly, the answer is related to the atom-atom correlations, i.e., the bonding configuration (A/A and B/B bonds vs “unlike” A/B bonds). Structures whose bonding configuration is the most *unlike* the configuration that results from random arrangement of atoms are more likely to be found in nature.¹⁰ However, some of the structures deemed likely to exist by this criterion still have not been observed. But recently there have been several predictions that these structures deemed likely by the approach of Ref. 10 are indeed ground states. They simply haven’t been observed or successfully fabricated yet. In particular, the structure denoted “ $CdPt_3$ ” in Fig. 1 was recently proposed¹ to be a ground state in two systems, Cd-Pt and Pd-Pt. Its first prediction as ground state in any compound was in the Ag-Pd system.¹⁷

We refer to this new structure as $L1_3$.¹⁸ This new *Struk-*

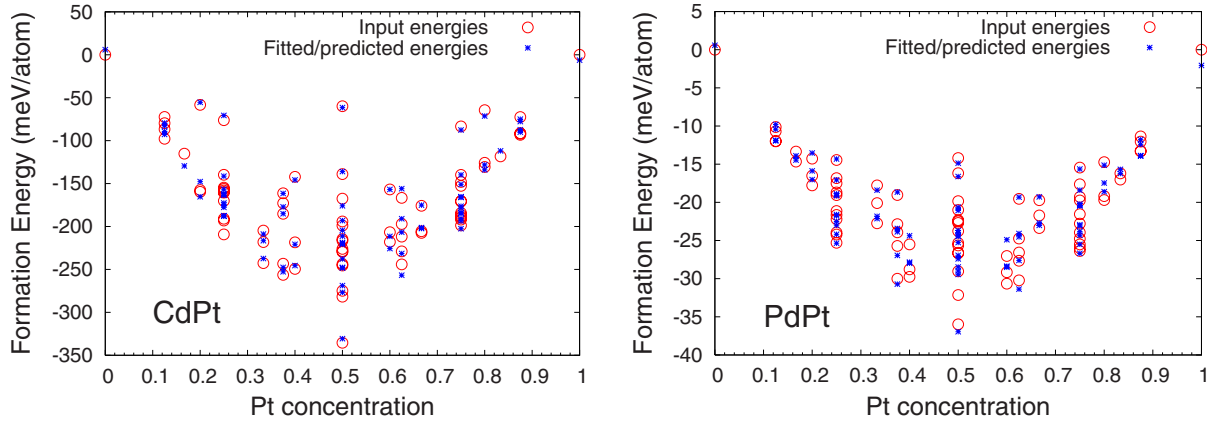


FIG. 2. (Color online) Input energies and corresponding fitted values for Cd-Pt (left) and Pd-Pt (right). The energy scales on the plots are not the same. Input energies are indicated by open circles and the corresponding fitted value is indicated by a bold cross. If the fitting errors were zero, each cross would coincide exactly with its circle.

turbericht designation is in analogy to the two common prototypes in the Cu-Au system, L_1_0 and L_1_2 (see Fig. 1). L_1_3 is to the L_1_1 structure of Cu-Pt what L_1_2 is to L_1_0 . L_1_0 is an alternating stacking, in the $[001]$ direction, of A and B layers of atoms. L_1_2 is similar but every other layer of atoms is not pure B atoms but a 50/50 arrangement of A and B atoms. Likewise, L_1_1 is an alternating stacking of A and B layers of atoms, but in the $[111]$ direction, rather than the $[001]$ direction. In analogy to the relationship between L_1_0 and L_1_2 , L_1_3 is also an alternating stacking of layers in the $[111]$ direction with every other layer a mixed (50/50) layer of A and B atoms. Thus the L_1_1/L_1_3 pair of structures are related to each other in the same way that the L_1_0/L_1_2 pair are, except the stacking direction for the alternating layers is different. Some readers may be familiar with the concentration-wave formalism of Khachatryan.^{19,20} The L_1_3 structure is associated with *two* Lifshitz-type (high symmetry) wave vectors stars, (001) and $(1/21/21/2)$.

IV. DATAMINING PREDICTIONS

The L_1_3 structure was predicted to be a ground state in Pd-Pt and Cd-Pt by the datamining approach of Curtarolo *et al.*^{1,2} The approach combines the accuracy of first-principles methods and the power of heuristic approaches that use prior information. Heuristic approaches extract “rules” from a vast database of experimental results to infer stable crystal structures, but are subject to experimental error/uncertainties. First principles approaches avoid many experimental difficulties but do not take advantage of prior knowledge. This datamining approach generates a first-principles-derived database and then uses this “prior knowledge” to extract statistical rules. These rules can make probabilistic statements about the existence of different crystal structures in a given system. In a tour de force, Curtarolo *et al.* generate a database of 15,000 first-principles calculations and use it to make dozens of new predictions, even predicting entirely new crystal structures in some cases.

The datamining method explores a relatively large number of calculated structures but it does not explore *all* pos-

sible structures. The method can reveal the lowest energy structure among a large group of “contenders” but cannot rule out new, unsuspected structures (those not in the database). Because the datamining approach can only make probabilistic statements about structural stability, to verify (or disprove) the inferences that the datamining approach makes, we apply a method that systematically explores (essentially) all possibilities.

We do this by enumerating essentially all possible structures,^{11–13} as discussed in Sec. II, and then testing each structure in turn. The number of derivative structures (several million) is large to ensure that the global minima have been found. This number is too large to allow for a direct first-principles determination of the energies, so the possibilities must be explored with a “fast” Hamiltonian, such as a cluster expansion.^{21–23}

V. CLUSTER EXPANSION AND GROUND STATE SEARCHES

Combined with structural enumeration, the cluster expansion can determine the energy of millions of structures in just a few seconds. We briefly describe the method here; further details can be found in Refs. 21–23. First, the energies of a relatively small number of different structures (typically 20–70) are calculated. The energies are then fitted to a generalized Ising model.²² If care is taken in such a fitting procedure,^{24–26} the resulting Ising Hamiltonian (cluster expansion) can predict arbitrary *unfitted* structures with near first-principles accuracy. The results are iteratively verified (and the model improved if necessary) using additional first-principles calculations, as described in Ref. 26. Alternatively, the terms of the Ising Hamiltonian can be extracted via a generalized perturbation method where the interactions are extracted directly from quantum-mechanical calculations.^{27–29} Reference 25 (page 2) briefly contrasts the two approaches.

We constructed cluster expansions for both the Cd-Pt and Pd-Pt systems. In both systems approximately 80 input structures were used in the final fit. The energies of these struc-

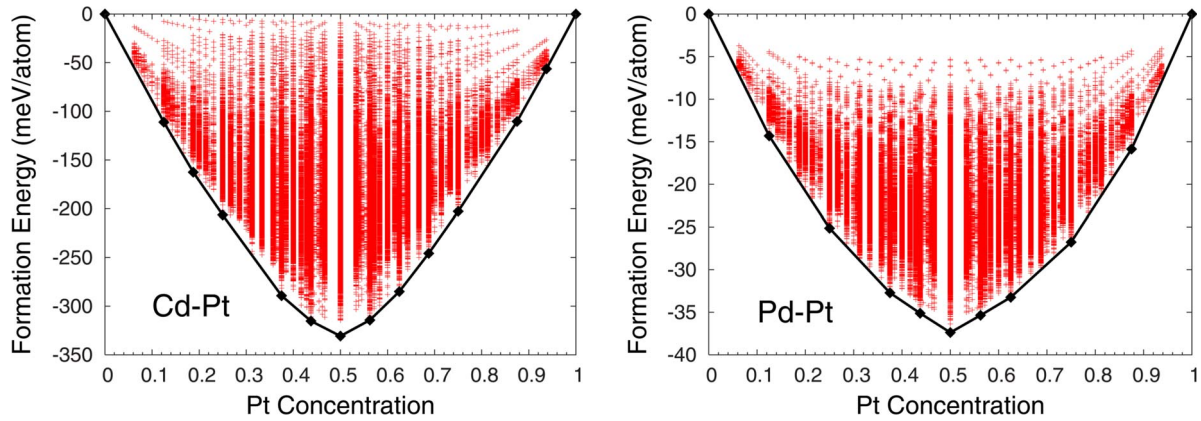


FIG. 3. (Color online) Ground state searches for Cd-Pt (left) and Pd-Pt (right). For each case, the energies of approximately three million structures were computed and compared. The red crosses indicate the energy of each structure, the black diamonds the ground states. The solid black line indicates the convex hull. The $L1_3$ structure is found to be a ground state at 75% Pt in Cd-Pt and at 25% and 75% Pt in Pd-Pt, as predicted by the datamining approach.

tures and their fitted values are shown in Fig. 2. From the figure, we see that the first-principles-calculated formation energies are well reproduced by the cluster expansion. References 24–26 describe in detail the general approach we use for the fitting, selection of input structures, and the refinement of the model.

Using the cluster expansions, we performed a ground state search for each system. In the searches, we compared the energies of approximately three million structures to determine which ones were ground states. The results are shown in Fig. 3. The structures included in the ground state search were all those fcc-derived superstructures containing 20 atoms/cell or less. Unit cells beyond 12 atoms are almost never seen in typical intermetallic compounds. Extending the search well beyond the unit cell sizes of *any* typical fcc-based structure gives us further confidence that the search has been essentially exhaustive—there are only a few thousand fcc-derived superstructures with unit cells of 12 atoms/cell or less but several million with 20 atoms/cell or less.

A full discussion of the complete list of ground states found in Cd-Pt and Pd-Pt is outside the scope of this paper; instead we focus on the inferences of the datamining work on these two compounds and the $L1_3$ structure. Though there are differences between the datamining-predicted and cluster-expansion-predicted ground states (the CE characteristically predicts more ground states than datamining or other methods), there is agreement on the ground states at 1:1 and 1:3 stoichiometries. In both systems we find the $L1_3$ structure to be a ground state—in the case of Pd-Pt, it was found to be a ground state at both 25% and 75% platinum. In the case of Cd-Pt, the $L1_3$ structure was found to be a ground state at 75% platinum, also as predicted by the datamining work.

Experimental efforts to verify the appearance of $L1_3$ in Pt-Cd are underway in collaboration with Candace Lang at the University of Capetown, South Africa, and with David Allred at Brigham Young University. Because of the large differences in melting temperatures between Cd and Pt, achieving samples with the desired 3:1 stoichiometry is challenging. Initial samples have been Cd poor ($\sim 11\%$ rather than 25%) resulting in a apparently two-phase samples.

X-ray diffraction shows weak superlattice peaks. The peaks are a better fit to the $L1_2$ structure than $L1_3$. Our analysis shows that the formation enthalpy of $L1_3$ is significantly lower but at elevated temperature the *free energy* of $L1_2$ may actually be lower. Because the space group of $L1_3$ is a subgroup of the $L1_2$ spacegroup, it's not unlikely that there are two ordering transitions: $\text{fcc} \rightarrow L1_2 \rightarrow L1_3$. New samples are being prepared in hopes of achieving more consistent Cd concentration. Experiments are also underway for Pt-Pd. These results will be reported in a future paper.

VI. SUMMARY

A never-before-observed crystal structure was predicted to be a ground state in two intermetallic systems, Cd-Pt and Pd-Pt. The predicted structure is unique in several ways. Though never seen in any other fcc-based intermetallic binary compound, it is relatively simple, containing only four atoms per unit cell. The structure is the only with four or less atoms/cell, except the $L1_2$ structure, that cannot be characterized as a simple stacking of layers where each layer contains only one kind of atom. The new structure is referred to as $L1_3$, in analogy to the structures seen in Cu-Au and Cu-Pt (that is, $L1_0$, $L1_2$, and $L1_1$).

The structure was predicted to be a ground state in Cd-Pt and Pd-Pt via a pioneering, first-principles-based datamining technique.^{1,2} But because this datamining approach makes *probabilistic* statements about ground states, we combined two other approaches to verify the datamining predictions. First, we described a new method for enumerating all “derivative superstructures” of a parent structure, fcc in this case. Combining this new method with the well-established cluster-expansion approach, we calculated the energy of all possible candidate structures. We indeed find that the $L1_3$ structure is a ground state in both Cd-Pt and Pd-Pt. It's remarkable that such a simple, small unit cell structure has thus far evaded experimental observation.

The datamining approach is a powerful new tool to infer candidate ground structures. In turn, the cluster expansion can unambiguously verify (or refute) its predictions in spe-

cific cases. Furthermore, the cluster expansion, coupled with a search of all possible derivative structures,^{10,11} can suggest *new* structures that should be included in the input databases of the datamining approach so that it can cast a wider net when exploring a class of materials.

Another important reason for finding new stable structures is their importance in nanoparticles. The modification of the bulk phase diagram for nanoparticles is a critical component of understanding phenomena such as nanocatalysis. An interesting illustration is shown by Curtarolo *et al.* in Ref. 30. Such an application is especially interesting in platinum and palladium and their alloys because of their widespread use in catalysts.

Note added in proof. Recently, it was found that the Struk-

turbericht symbol $L1_3$ had been previously defined.³¹ It appears that this symbol has not been used since and that the structure it referred to, an 8-atom fcc-based superstructure, is referred to as $D4$ in the modern literature (though the modern designation is no less arbitrary than the original).

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