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Ground-state characterizations of systems predicted to exhibit $L_1_1$ or $L_1_3$ crystal structures

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Despite their geometric simplicity, the crystal structures $L_1_1$ (CuPt) and $L_1_3$ (CdPt$_3$) do not appear as ground states experimentally, except in Cu-Pt. We investigate the possibility that these phases are ground states in other binary intermetallic systems, but overlooked experimentally. Via the synergy between high-throughput and cluster-expansion computational methods, we conduct a thorough search for systems that may exhibit these phases and calculate order-disorder transition temperatures when they are predicted. High-throughput calculations predict $L_1_1$ ground states in the systems Ag-Pd, Ag-Pt, Cu-Pt, Pt-Pd, Li-Pd, Li-Pt, and $L_1_3$ ground states in the systems Cd-Pt, Cu-Pt, Pd-Pt, Li-Pt. Cluster expansions confirm the appearance of these ground states in some cases. In the other cases, cluster expansion predicts unsuspected derivative superstructures as ground states.

The order-disorder transition temperatures for all $L_1_1/L_1_3$ ground states were found to be sufficiently high that their physical manifestation may be possible.

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I. INTRODUCTION

A scan of experimentally observed binary metallic phases shows that some appear many times. For example, the familiar prototypes CuAu and Cu$_3$Au (Strukturbericht $L_1_0$ and $L_1_2$, respectively) are found in experimental phase diagrams 51 and 294 times, respectively.$^1$ This is contrasted by the single occurrence of two other simple phases: Cu-Pt (Strukturbericht $L_1_1$), and a 3:1 phase reported in the Cu-Pt system referred to as $L_1_7$ by Müller et al., which we will refer to as $L_1_3$.$^2,3$ All four structures are among the simplest possible fcc-derived superstructures, with four atoms per cell or fewer.

Many frequently observed crystal structures are fcc-derived superstructures. The atoms in these crystals all lie on fcc lattice sites.$^4$ There are 17 fcc-derived superstructures with four atoms per cell or fewer.$^5$ Among them are some commonly observed crystal structures: $L_1_0$, $L_1_2$, MoPt$_2$, D0$_{22}$, C6, and C11b. Other structures in this group, including $L_1_1$ and $L_1_3$, are essentially missing from experimental phase diagrams.

One way to assess the likelihood of a particular structure’s physical manifestation is through a geometric comparison. When atom-atom correlations deviate significantly from the correlations of a random configuration, that structure is more likely to occur. Such “nonrandom” structures have energies much greater than or much less than the random alloy, with the latter ones competing for ground-state status.

This idea was used to assigned a likelihood value to all fcc-derived superstructures up to four atoms per cell.$^5$ $L_1_0$ was found to be most likely and $L_1_2$ was ranked number 4 in the list. $L_1_1$ came in just below $L_1_2$, and $L_1_3$ was found to be slightly less likely than D0$_{22}$, which appears 19 times in experimental phase diagrams, and is slightly more likely than MoPt$_2$, which appears 10 times in experimental phase diagrams.

Will the $L_1_1$ and $L_1_3$ structures appear in systems other than Cu-Pt? If so, in which systems will they occur and how can we identify those alloys? Well-known empirical methods, such as the Hume-Rothery rules$^6$ and Pettifor-type structure maps,$^7$ are one way to predict thermodynamically stable phases and miscibility behavior. These methods analyze experimental data and attempt to establish phase stability trends. Pettifor maps, for example, group together all occurrences of a given structure into well-defined domains, thus helping one to make educated guesses as to what other systems may exhibit the same phase. These methods have their utility and successes, but provide little insight where experimental data are scarce or lacking completely.

In contrast, ab initio high-throughput methods scan a large database of possible ground states exploring a larger space than other heuristic methods. Furthermore, such high-throughput data can be used to construct lattice-based models, which can be used to search over large portions of configuration space. Combining these methods increases the search space beyond what each method can do separately.$^8$

Our goal is to uncover new occurrences of the phases $L_1_1$ and $L_1_3$ by combining the strengths of these two computational techniques. $L_1_1$ and $L_1_3$ phases have only been observed experimentally in the Cu-Pt system.$^2,9$ However, both phases were predicted to exist in the Ag-Pd system,$^{10}$ and $L_1_3$ was predicted to be stable in Pd-Pt and Cd-Pt using a first-principles-based data-mining technique.$^{11,12}$

II. HIGH THROUGHPUT

The high-throughput (HT) approach combines heuristic information with first-principles calculations to predict stable phases. In this method, prior knowledge of experimentally observed phases is used to build a database of candidate ground states. First-principles calculations are then performed on all structures in the database and for all possible binary systems. In this way, the power of prior knowledge is combined with the precision and accuracy of first-principles calculations. Currently, our binary alloy HT database contains calculations for over 630 systems, a total of $\sim$150 000 calculations available in the AFLOWLIB consortium repository.$^{13}$
First-principles calculations were performed within the framework of AFLLOW,\textsuperscript{8,11,12,14–18} which employs the VASP software for computing energies.\textsuperscript{19} Projector-augmented-wave (PAW) potentials were used and exchange-correlation functionals parametrized by Perdew, Burke, and Ernzerhof under the generalized gradient approximation (GGA).\textsuperscript{20–22} A dense $k$-mesh scheme was used to perform the numeric integration over the Brillouin zone.\textsuperscript{23} Optimal choices of the unit cells, by standardization of the reciprocal lattice, were adopted to accelerate the convergence of the calculations.\textsuperscript{17,18}

The effect of spin-orbit coupling has not been included in our calculations because of the following consideration. In Ref. 24, we found that the inclusion of relativistic spin-orbit coupling in transition-metal alloys affects the total energies but leaves differences between competing phases essentially the same. The issue can be understood if one considers that most of the spin-orbit coupling energy comes from core electrons, which are not shared in the highly delocalized metallic bond responsible for the formation energy. Thus, the relativistic contribution to the total energy in the space of concentrations is a linear combination of energies, a simple tilt of the whole convex hull, which does not alter, by construction, the thermodynamic competition between phases.

This data-mining technique explores a large number of candidate ground states, but it only explores the space of (almost) all known alloy structures. The method will successfully find the ground states among a pool of contenders, but can not rule out new, unexpected structures. To find the unexpected ground states, we need a way to rapidly explore more configurations.

To do this, we consider essentially all derivative superstructures of the parent lattices. All possible derivative superstructures are enumerated,\textsuperscript{25,26} then the energies of all enumerated structures are compared to find the ground states. Typically, the number of superstructures enumerated is large (millions) to ensure that we find the global minima. Due to the computational cost, direct first-principles calculation of all enumerated superstructures is not possible. For this reason, a model Hamiltonian must be used to compute their energies.

### III. Cluster Expansion

A useful model Hamiltonian for lattice configuration problems is the cluster expansion (CE). The CE can be used to quickly compute the energies of a large number of configurations. Here, we give a brief review of the CE methodology.\textsuperscript{27–29}

The CE expresses a material’s physical property as a linear combination of geometric figures or “clusters.” In the CE formalism, an atomic configuration is defined by first assigning a spin value for each atomic type. The configurational property of an atomic configuration is then expressed by first averaging over spin products, something typically referred to as correlation functions. These correlation functions form a basis by which a material’s physical properties can be expanded:

$$ E(\sigma) = J_0 + \sum_f \sum_{\sigma_i} \Pi_f(\sigma) J_f, $$

where $\sigma$ characterizes the atomic occupancy on the lattice, $\Pi_f(\sigma)$ represents the averaged spin products over cluster $f$ for configuration $\sigma$. The $J_f$‘s are the expansion coefficients and $N_f$ is the number of clusters of type $f$.

These coefficients are found by fitting the CE to a set of training data, typically first-principles energies of a small group of structures. A genetic algorithm is then used to fit the training data to the CE.\textsuperscript{30,31} The CE predictions are iteratively verified, adding to the set of training data as needed.\textsuperscript{32} When combined with enumeration algorithms,\textsuperscript{25,26} the resulting CE can calculate the energies of millions of derivative structures with near-first-principles accuracy in a few minutes.

Training-data calculations were performed using the VASP software. We used PAW potentials and exchange-correlation functionals parametrized by Perdew, Burke, and Ernzerhof under the generalized gradient approximation.\textsuperscript{20–22} An equivalent $k$-mesh scheme was used for Brillouin-zone integration to reduce systematic error.\textsuperscript{33}

The CE can compute the energy of atomic configurations in large cells very fast, making it possible to perform thermodynamic Monte Carlo (MC) simulations. These simulations require millions of energy calculations and would not be possible without a fast Hamiltonian such as the CE.

### IV. Results

As mentioned previously, the current HT database contains data for over 630 binary systems. This database was searched for occurrences of $L_1_1$ and $L_1_3$ ground states. $L_1_1$ was found to be a ground state in the following systems: Ag-Pd, Ag-Pt, Cu-Pt, and Pd-Pt. $L_1_3$ was found in Cd-Pt, Cu-Pt, Pd-Pt, Li-Pd, Li-Pt, and Ag-Pd.

Cluster expansions were constructed for all of these systems. CE training data consisted of ~100 first-principles calculations. Any new ground states predicted by the CE were verified by first principles and added to the input set. The process of fitting to the training data, performing a ground-state search, and adding any new ground-state predictions to the training-data set was iterated many times to ensure convergence of the CE.

In the figures that follow, several hundred first-principles calculations are shown. These structures were selected for calculation either as part of the initial training-data set, or because the CE predicted them as ground states at some point during the iterative procedure explained above. By verifying all ground-state predictions with first-principles calculations, and making them available as training data, the CE is slowly refined to predict more accurately and more completely cover configuration space.

Ground-state searches were performed by calculating the energies of all structures up to 16 atoms per cell. Rarely are structures with >12 atoms per cell seen in the experimental literature. By expanding the search well beyond this, we are ensured that searches are essentially exhaustive. Converged cluster expansions were used to perform MC simulations for determining order-disorder transition temperatures.

In what follows, we give a short summary of our results for each system studied. Some reported ground states do not have a Strukturbericht designation or an experimental prototype because they have never been observed. We will refer to these structures using a number that represents
their location in our enumerated list. A full crystallographic description of these structures can be found in the Supplemental Material. Additionally, this crystallographic information can be generated using our enumeration code, which is available via SOURCEFORGE.

### A. Ag-Pd

Experimental reports for this system are scarce. It is reported to be a solid solution from the solidus line down to 900 °C, with no reports of ordered phases appearing.\textsuperscript{35-38} First-principles results predict eight ordered phases in this system (see Fig. 1).

#### Ag-Pd system

<table>
<thead>
<tr>
<th>Composition</th>
<th>Experiment (Refs. 35–38)</th>
<th>HT</th>
<th>CE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%) Pd</td>
<td>(Ref. 13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>Solid solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td>CayGe</td>
<td>fcc-154685*</td>
</tr>
<tr>
<td>18.75</td>
<td>Solid solution</td>
<td>Two-phase</td>
<td>fcc-154665*</td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~21.5</td>
<td>Solid solution</td>
<td>Two-phase</td>
<td>fcc-33781*</td>
</tr>
<tr>
<td>25</td>
<td>Solid solution</td>
<td>Two-phase</td>
<td>D0(23)</td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td>D0(24)</td>
<td>~0.7 meV/atom above D0(24)</td>
</tr>
<tr>
<td>31.125</td>
<td>Solid solution</td>
<td>Two-phase</td>
<td>fcc-154439*</td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>Solid solution</td>
<td>C37*</td>
<td>Two-phase</td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37.5</td>
<td>Solid solution</td>
<td>Two-phase</td>
<td>fcc-154395*</td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~42</td>
<td>Solid solution</td>
<td>Two-phase</td>
<td>fcc-18195*</td>
</tr>
<tr>
<td>40</td>
<td>Solid solution</td>
<td>Two-phase</td>
<td>fcc-154685</td>
</tr>
<tr>
<td>50</td>
<td>Solid solution</td>
<td>Two-phase</td>
<td>fcc-154395</td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td>L1(1)</td>
<td>~1.1 meV/atom above tie line</td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td>L1(3)</td>
<td>~1.2 meV/atom above tie line</td>
</tr>
<tr>
<td>~57</td>
<td>Solid solution</td>
<td>Two-phase</td>
<td>fcc-25645*</td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>Solid solution</td>
<td>L1(3)</td>
<td>Two-phase</td>
</tr>
<tr>
<td></td>
<td>&gt;900 °C</td>
<td>L1(3)</td>
<td>~3.7 meV/atom above tie line</td>
</tr>
</tbody>
</table>

On the Ag-rich side, the first-principles phases Ag\(_7\)Pd (Ca\(_7\)Ge), Ag\(_{3}\)Pd (D\(_0\)\(_3\)), and Ag\(_{3}\)Pd (D\(_0\)\(_2\)) are found to be ground states, all of which are well-known experimental phases. The formation energies of D\(_0\)\(_3\) and D\(_0\)\(_2\) differ by less than 1 meV/atom (within numerical accuracy) and thus we report both as the ground state. At composition Ag\(_3\)Pd, we also find an fcc-derived phase (fcc-154685, oS\(_3\)2, #63), the formation energy of which is found to be within 1 meV/atom of the Ca\(_7\)Ge structure.

Other first-principles phases on the Ag-rich side found using cluster-expansion searches are Ag\(_{3}\)Pd\(_3\) (fcc-154665, oS\(_3\)2, #67), Ag\(_{11}\)Pd\(_3\) (fcc-33781, mS\(_2\)8, #12), Ag\(_{11}\)Pd\(_3\) (fcc-154439, oS\(_3\)2, #21), Ag\(_{10}\)Pd\(_6\) (fcc-154395, oS\(_3\)2, #66), and Ag\(_{9}\)Pd\(_{6}\) (fcc-18195, #15). The ordered phase Ag\(_3\)Pd (C37) was found by HT to be ~1 meV/atom lower than the CE tie line.

On the Pd-rich side, the first-principles phase at composition Ag\(_3\)Pd\(_3\) is stable. At composition 1:1, we find a two-phase region with L1\(_1\) and D\(_1\) being ~1 meV/atom above the tie line. Similarly, at composition AgPd\(_3\), we find a two-phase region, with AgPd\(_3\) (L1\(_3\)) appearing ~3.7 meV/atom above the tie line. Thus, the low-temperature stable phases predicted here by CE are somewhat different than what has been previously predicted\textsuperscript{10}, notably, the presence of L1\(_1\) and L1\(_3\) as low-temperature ground states is not confirmed.

The difference in formation energy between the tie line and the L1\(_1\) structure is arguably within the limits of numerical accuracy. It is possible that AgPd (L1\(_1\)) is a ground state in this system. Furthermore, the atom-atom correlations of the two structures at the breaking points of the tie line at ~42 at.% and ~57 at.% were found to be very similar to L1\(_1\), indicating the system may prefer L1\(_1\)-like configurations.

Thermodynamic MC performed at 42 at.% Pd found a transition temperature of about ~70 °C. This low transition temperature explains why no ordered phases have been observed experimentally.

### B. Pd-Pt

Phase diagrams derived from experimental studies show this system to be phase separating (see Fig. 2)\textsuperscript{35,36,40-42} However, a recent experimental study by Lang \textit{et al.} found the system to be miscible at these temperatures, although no ordered phases were reported. Lang reported the kinetics of this system to be prohibitively slow, probably due to the similarity of Pd and Pt.

Computational results reveal a handful of ordered phases, but the ground states predicted by HT and CE differ over the entire composition range, with no single phase being predicted as a ground state by both methods. HT calculations find the following stable ordered phases at low temperatures: Pd\(_3\)Pt (L1\(_1\)), PtPt (L1\(_1\)), PdP\(_3\) (L1\(_2\)), and PdP\(_7\) (Ca\(_7\)Ge).\textsuperscript{11}

CE ground-state searches reveal a different set of ground states, all at different compositions than the HT ground states. There are four phases with monoclinic symmetry at compositions Pd\(_{10}\)Pt\(_4\), Pd\(_4\)Pt\(_3\), Pd\(_3\)Pt\(_4\), and Pd\(_3\)Pt\(_{10}\). There is one phase at composition Pd\(_3\)Pt\(_{14}\) with orthorhombic symmetry and one phase at composition Pd\(_3\)Pt\(_{11}\) with orthorhombic symmetry. Since these phases have never been seen in any binary system, they were not a part of the HT database.
Thermodynamic MC performed at 42 \text{at.}\% \text{Pt} found a transition temperature of \sim25\, ^\circ\text{C}. This low transition temperature, no doubt a result of the slow kinetics reported by Lang et al., explains why no ordered phases have been observed experimentally.

### C. Li-Pd

The phase diagram for this system is mostly known, reporting five ordered phases of known structure and one compound of unknown structure.\cite{35,36,43,44} For Li-rich compositions, the experimental phases Li$_{13}$Pd$_4$ (Cu$_{13}$Si$_4$), Li$_2$Pd (Hg$_2$U), and LiPd (B$_2$) are ground states. One experimental phase of unknown character is reported at composition Li$_8$Pd$_2$. The stability of LiPd (B$_2$) is confirmed by first principles to be stable at low temperatures. Other first-principles phases found to be stable in this region are Li$_3$Pd$_2$ (hcp-982, mp10, #11), Li$_2$Pd (D0$_3$), and Li$_2$Pd (bcc-9), as shown in Fig. 3.

Pd-rich ground states reported experimentally are L1$_3$Pd$_2$(mP4, #10) and LiPd$_3$ (Ca$_7$Ge). First-principles ground states for this region are Li$_3$Pd$_3$ (fcc-625, cf32, #166), LiPd$_3$ (L1$_3$), and LiPd$_7$ (Ca$_7$Ge), confirming the stability of the experimental phase LiPd$_7$ (Ca$_7$Ge) down to low temperatures.

The first-principles ground states Li$_8$Pd$_2$ (hcp-982, mp10, #11), Li$_2$Pd (bcc-9, hP3, #164), and Li$_3$Pd$_3$ (fcc-625, cf32, #166) were found by CE ground-state searches. These phases have never been reported in any binary system, and as such were not included in the HT database.

MC simulations performed at composition LiPd$_3$ find the transition temperature for LiPd$_3$ (L1$_3$) to be 900 \text{^\circ }\text{C}, making this system a good candidate for finding another occurrence of L1$_3$.

### D. Li-Pt

Phase diagrams show three known and two unknown compounds appearing in the Li-Pt system.\cite{35,36,45} (see Fig. 4.) For Li-rich compositions, experiment reports two unknown
The first-principles ground state with structure C32 was not considered by CE searches because it is not a derivative superstructure. HT databases included C32, and found it as a ground state in this system, because it was suspected as a ground state, having been observed in other binary systems. The first-principles ground states Li$_2$Pt (hcp-982, mP10, #11) and Li$_3$Pt$_3$ (fcc-625, cF32, #166) were found by CE searches and not considered by HT due to it being unsuspected to occur based on experimental data.

MC simulations performed at composition LiPt$_3$ find the transition temperature for LiPt$_3$ (L1$_3$) to be 1450 °C. This makes this system a good candidate for finding another occurrence of L1$_3$.

### E. Cu-Pt

There are five experimentally reported ground states in this system and one unidentified phase reported$^{2,9,35,36,46-51}$ (see Fig. 5). Experimentally reported Cu-rich phases include Cu$_3$Pt (L1$_2$) and an unknown phase at composition Cu$_3$Pt. The phase with the L1$_2$ structure is reported to have composition range of stability extending from 10 at.% Pt to 25 at.% Pt. However, experimental reports include no x-ray analysis, and therefore

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merely conjecture that the stable phase is the \( L_{12} \) structure. First-principles ground states found in this composition region were \([\text{Cu}_3\text{Pt}] \) (Cas$_7$Ge), \([\text{Cu}_5\text{Pt}_2] \) (bcc-10848, hP12, #164), and \([\text{Cu}_3\text{Pt}] \) (D0$_{22}$). Thus, the experimental phase \([\text{Cu}_3\text{Pt}] \) (\( L_{12} \)) does not continue to be stable down to low temperatures. The unidentified experimental phase reported at composition \([\text{Cu}_3\text{Pt}] \) is not stable at low temperature according to first-principles data, instead we find the two-phase region \([\text{Cu}_3\text{Pt}_5] \leftrightarrow \text{CuPt} \) (\( L_{11} \)).

For Pt-rich compositions, the experimental phases \([\text{Cu}_3\text{Pt}_5] \), \([\text{Cu}_3\text{Pt}_3] \) (\( L_{13} \)), and \([\text{Cu}_5\text{Pt}_7] \) (Cas$_7$Ge) are reported. The experimental phase at composition \([\text{Cu}_3\text{Pt}_3] \) was reported to have rhombohedral symmetry, but the existence of this phase has not been confirmed by additional studies. First-principles calculations confirm the stability of \([\text{Cu}_3\text{Pt}_3] \) (\( L_{13} \)) and \([\text{Cu}_5\text{Pt}_7] \) (Cas$_7$Ge) at low temperature and find \([\text{Cu}_3\text{Pt}_3] \) (bcc-625, cF32, #166), which has trigonal symmetry, to be stable at composition 3:5. A transition from the trigonal phase to the rhombohedral phase may occur at higher temperatures.

The first-principles ground states \([\text{Cu}_3\text{Pt}_5] \) (bcc-625, cF32, #166) and \([\text{Cu}_5\text{Pt}_7] \) (bcc-10848, hP12, #164) are derivative superstructures and were found to be ground states using CE ground-state searches. These crystal structures have not been observed in any binary alloy and were not included in the HT database.

First-principles calculations confirm the stability of \([\text{CuPt}] \) (\( L_{11} \)) down to \( T = 0 \) K. Monte Carlo simulations performed at 1:1 stoichiometry indicate a phase transition occurring at \( \sim 450 \) °C, which is in disagreement with the experimentally reported temperature of \( \sim 800 \) °C.

F. Ag-Pt

Phase diagrams derived from experimental studies indicate three unidentified phases appearing at composition \([\text{Ag}_5\text{Pt}_{15}] \), \([\text{AgPt}] \), and \([\text{AgPt}_3] \). Additionally, the experimental phase \([\text{Ag}_3\text{Pt}] \) (\( L_{12} \)) is reported\(^{55,36,50,52-56}\) (see Fig. 6).

First-principles ground states found for this system differ from the experimental phases mentioned. \([\text{Ag}_5\text{Pt}] \) (fcc-8, hP3, #164) and \([\text{AgPt}] \) (\( L_{12} \)) are found to be stable by first-principles methods. The phase with structure fcc-8 is an AB2 stacking in the [111] direction of a fcc lattice. \([\text{AgPt}] \) (Cas$_7$Ge) was found to be \( \sim 1.3 \) meV/atom above the tie line. This small difference is within numerical accuracy, and thus we report it as a ground state as well.

In 1996, Durussel and Feschotte proposed a new phase diagram, reporting an ordered phase appearing at composition \([\text{Ag}_{15}\text{Pt}_{17}] \) and rejecting all other ordered phases for this system.\(^{56}\) The new phase was reported to be fcc based with a cubic unit cell appearing at \( \sim 800 \) °C. A full crystallographic characterization of this reported phase was not given.

The CE constructed for this system was used in an attempt to find a phase with the reported properties. Instead of enumerating all possible 32-atom unit cells, we used a new enumeration algorithm to only enumerate the ones at 15:17 stoichiometry with cubic unit cells.\(^{35}\) This greatly reduced the time needed to enumerate and the size of the structure list.

Searching the 32 atoms/cell configurations yielded no ground state at 15:17 stoichiometry. However, the 32-atom cell with the lowest formation energy was very \( L_{11} \) like. We assume that the reported phase was in fact \( L_{11} \) with a small number of random defects, or that the experimental determination of the composition was incorrect.

MC simulation performed at composition 1:1 indicates a transition temperature of \( \sim 700 \) °C, which agrees nicely with the experimental transition temperature of the unknown ordered phase reported by Ref. \(^{54}\) as well as the reported transition temperature of the supposed \([\text{Ag}_{15}\text{Pt}_{17}] \) phase reported by Durussel and Feschotte.\(^{56}\)

G. Cd-Pt

Published phase diagrams derived from experiment show several ordered phases, giving information down to \( 100 \) °C on the Cd-rich side of the phase diagram and down to 500 °C on the Pt-rich side\(^{55,36,58}\) (see Fig. 7). On the Cd-rich side, the experimental phase \([\text{Cd}_2\text{Pt}] \) (# 215) and three unknown phases at composition \([\text{Cd}_3\text{Pt}_2] \), \([\text{Cd}_3\text{Pt}_3] \), and \([\text{Cd}_2\text{Pt}_7] \) are reported. First-principles phases \([\text{Cd}_3\text{Pt}_2] \) (D0$_{11}$) and \([\text{Cd}_2\text{Pt}_7] \) (Hg$_2$Pt) are found to be stable in this composition range.

The three first-principles phases at composition \([\text{Cd}_3\text{Pt}_2] \), \([\text{Cd}_3\text{Pt}_3] \), and \([\text{Cd}_1\text{Pt}_3] \) were found by the CE but were removed from the tie line by the presence of the first-principles phases \([\text{Cd}_2\text{Pt}_7] \) (D0$_{11}$) and \([\text{Cd}_2\text{Pt}_7] \) (Hg$_2$Pt) found by HT. These crystal structures were beyond the applicability range of the CE since they are not derivative superstructures.
For Pt-rich compositions, experimental ground states are found at compositions 1:1 and 1:3 with structures L10 and L12, respectively. The stability of CdPt (L10) is verified by first-principles calculations, but the experimental phase CdPt3 (L12) is replaced by the first-principles phase CdPt3 (L12) as a ground state. Additionally, other first-principles phases found to be stable in this region are Cd5Pt11 (fcc-154897, mS32, #12) and CdPt7 (Ca7Ge). The CE identified the first-principles phase Cd5Pt11 (fcc-154897, mS32, #12) as stable.

The characterization of the Cd-rich portion of the phase diagram by HT, together with the identification of Cd5Pt11 (fcc-154897, mS32, #12) as ground states by CE, demonstrates the synergy between these two methods. Either method working alone would not have been able to fully characterize the low-temperature phase diagram for this system.

Two MC simulations were carried out at CdPt3 composition. The first started with perfect L12 at T = 0 and increased the temperature. The other MC simulation started out at high temperature and cooled down to T = 0. The former simulation shows L12 persisting up to ~700 °C followed by a transition to disorder. The latter simulation reveals a transition to L11 at ~700 °C, with no transition to L13 ever being observed. This suggests that a free energy barrier between L12 and L13 is preventing L13 from ordering at low temperature.

H. Pt-Zn

Phase diagrams report two well-known ordered phases in this system and one phase that is lesser known. Additionally, three unidentified phases are reported in this system (see Fig. 8). Experimental ground states include L13 (Cu3Au) and L10 (CuAu), with the composition range of stability for L10 reported to be from 32–47 at.% Zn.

First-principles data confirm the stability of L10 (CuAu) down to the low-temperature regime. At composition Pt3Zn, first-principles calculations indicate L13 (CdPt3) to be stable, indicating that the phase with the L12 structure does not continue to be stable down to low temperatures.

Other first-principles ground states identified at Pt-rich compositions include Pt3Zn (Ca7Ge), Pt10Zn2 (fcc-10775, mS24, #12), and Pt5Zn3 (fcc-630, tI16, #139). The latter two phases were unsuspicious derivative superstructures and were identified as ground states by the CE.

FIG. 8. (Color online) Low-temperature ground states for the binary system Pt-Zn as predicted by the combined effort of HT and CE. The phase with structure L13 (Cu3Au) and L10 (CuAu), with the composition range of stability for L10 reported to be from 32–47 at.% Zn.

First-principles data confirm the stability of L10 (CuAu) down to the low-temperature regime. At composition Pt3Zn, first-principles calculations indicate L13 (CdPt3) to be stable, indicating that the phase with the L12 structure does not continue to be stable down to low temperatures.

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FIG. 7. (Color online) Ground-state crystal structures for the binary system Cd-Pt as determined by the combined effort of HT and CE. HT predictions dominate the Cd-rich portion of the phase diagram, with D011 and Hg2Pt being the only stable Cd-rich phases. This system is predicted to exhibit the rarely seen phase L13 ever being observed. This suggests that a free energy barrier between L12 and L13 is preventing L13 from ordering at low temperature.
For Zn-rich compositions, the experimental ground state \( \text{Pt}_{10} \text{Zn}_{3}\text{6.2} \) (cF392, #216) is reported, as well as three unidentified ground states at compositions \( \text{PtZn}_{3} \), \( \text{PtZn}_{17} \), \( \text{PtZn}_{36} \), and \( \text{PtZn}_{6} \). At composition \( \text{PtZn}_{17} \), first-principles data find the well-known experimental phase \( \text{PtZn}_{3} \) (D0\(_{22}\)) to be stable. The presence of the other two unknown phases in the low-temperature regime is not confirmed by first-principles calculations. Other first-principles ground states with Zn-rich composition include \( \text{PtZn}_{3} \) (fcc-77, oS12, #63), \( \text{PtZn}_{5} \) (hcp-50, hR6, #155), and \( \text{PtZn}_{4} \) (hcp-184, mS16, #5). These three phases are unsuspected, having never been seen in experimental phase diagrams, and were found by the CE.

Two MC simulations were carried out at \( \text{Pt}_{3}\text{Zn} \) composition. The first started with perfect \( L_{13} \) at \( T = 0 \) and increased the temperature. The other MC simulation started out at high temperature and cooled down to \( T = 0 \). The former simulation shows \( L_{13} \) persisting up to \( \sim 1200 \) \( ^{\circ} \)C followed by a transition to disorder. The latter simulation reveals a transition to an unknown ordered phase, perhaps a mix of \( L_{12} \) and \( L_{13} \), at \( \sim 1200 \) \( ^{\circ} \)C, with no transition to \( L_{13} \) ever being observed. This suggests that a free energy barrier is preventing \( L_{13} \) from ordering at low temperature.

V. CONCLUSIONS

A. Summary of \( L_{13}/L_{11} \) predictions

HT and CE techniques have been used to characterize the low-temperature ground states for several binary systems that may exhibit the rarely seen phases \( L_{11} \) and \( L_{13} \). In some cases, these phases were identified as ground states. Specifically, we predict \( L_{11} \) to be stable in Ag-Pt, Cu-Pt, and Li-Pt. We also predict \( L_{13} \) to be stable in Li-Pd, Li-Pt, Cu-Pt, Cd-Pt, and Pt-Zn.

For other systems, cluster-expansion-guided ground-state searches found other low-energy crystal structures, which superseded \( L_{13} \) and/or \( L_{11} \) on the convex hull. This was exemplified in the Pd-Pt and Ag-Pd systems where CE finds a whole host of unsuspected ground states. In these systems, the predicted ground states were unsuspected derivative superstructures, and thus not included in the HT database.

Conversely, HT found ground states that were outside the applicability range of the CE. For example, in the Cd-Pt system HT found D0\(_{11}\) and Hg2Pt, which are not derivative superstructures. The presence of these two ground states lowered the convex hull below all of the CE-predicted Cd-rich ground states. The combined use of HT and CE helps us to characterize the low-temperature ground states of these systems more thoroughly and accurately than we could have done with either method by itself.

B. Summary of differences between experiment and theory

Differences between experimental reports and computational predictions are exhibited in each system. Some systems, such as Ag-Pd and Pd-Pt, are reported to be phase separating or noncompound forming by experiment, but are predicted by computation to have stable ordered phases. These systems are instances where computation can direct future experimental efforts to find new ordered phases.

Other systems, such as Li-Pd, Li-Pt, and Ag-Pt, are reported to exhibit ordered compounds of known or unknown character, but computational predictions differ somewhat. For example, in Li-Pd and Li-Pt, \( L_{13} \) is predicted to be stable by computation for Pt/Pd-rich concentrations. Experimental reports, on the other hand, show a two-phase region at this stoichiometry for both systems. Similar differences occur in Li-rich Li-Pt/Pd and in Ag-Pt.

In Cd-Pt and Cu-Pt, the reported appearance of \( L_{12} \) differs from the first-principles prediction of \( L_{13} \). However, a closer look at the experimental work reveals no convincing evidence for the appearance of the \( L_{12} \) phase. In these systems, experimentalists merely surmise the stability of the \( L_{12} \) structure. On the other hand, the CE-predicted \( L_{13} \) structure does not appear during cool-down MC simulations either, possibly suggesting a free energy barrier between the high-temperature phase and the \( L_{13} \) structure.

Even when convincing crystallographic evidence for a phase’s appearance is given, as in \( \text{Pt}_{3}\text{Zn} \) (\( L_{12} \)), a first-principles-based prediction, which differs from experiment, does not constitute a contradiction with experiment. Metallurgical and kinetic challenges prevent experiments from reporting about phase stability at temperatures lower than a few hundred degrees Celsius at best. This leaves gaps in phase diagrams, gaps which first-principles studies seek to fill.

Any differences between experimental reports and computational predictions are usually attributable to either (1) the addition of entropy at finite temperature, which stabilizes disorder or a phase different from the \( T = 0 \) phase, or (2) slow kinetics, which can prevent the predicted phase from forming below its predicted transition temperature. We hope that our work will serve as motivation for future experimental work to find the predicted phases.

C. Noticeable trends

The results presented here indicate that the phase with structure \( L_{13} \) seems to only appear in Pt/Pd-rich alloys, which could indicate that these elements are important for this crystal structure to form. The unsuspected derivative superstructure (fcc-625, cF32, #166) appeared in three systems: Li-Pd, Li-Pt, and Cu-Pt, possibly indicating that this crystal structure may appear more broadly and thus should be added to the HT database.

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4. Due to atomic and cell relaxation, the atoms may not lie precisely on the lattice sites. However, the experimental structure can be readily associated with the ideal enumerated structure. The energy associated with the relaxation is accounted for implicitly by the CE.
39. A complete description of this crystal structure can be generated using the enumeration code, which is freely available for download via SOURCEFORGE: [http://sourceforge.net/projects/enum/].