Predictions of the Pt$_8$Ti Phase in Unexpected Systems

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Abstract: The binary A$_8$B phase (prototype Pt$_8$Ti) has been experimentally observed in 11 systems. A high-throughput search over all the binary alloy phase diagrams, however, reveals 59 occurrences of the A$_8$B phase: A$_8$B$_3$, Cd$_8$Sc$_3$, Cu$_8$Ni$_8$, Cu$_8$Zn$_8$, Hg$_8$La, Ir$_8$Os$_8$, Ir$_8$Ru$_8$, Ir$_8$Tc, Ir$_8$W$_8$, Nb$_8$Os$_8$, Nb$_8$Rh$_8$, Nb$_8$Ru$_8$, Nb$_8$Ta$_8$, Ni$_8$Fe, Ni$_8$Mo$_8^*$, Ni$_8$Nb$_8^*$, Ni$_8$Ta$_8$, Ni$_8$V$_8$, Ni$_8$W, Pd$_8$Al$_8^*$, Pd$_8$Fe, Pd$_8$Hf, Pd$_8$Mn, Pd$_8$Mo$_8^*$, Pd$_8$Nb, Pd$_8$Sc, Pd$_8$Ta, Pd$_8$Ti$_8^*$, Pd$_8$V$_8^*$, Pd$_8$W$_8^*$, Pd$_8$Zn, Pd$_8$Zr, Pt$_8$Al$_8^*$, Pt$_8$Cr$_8^*$, Pt$_8$Hf, Pt$_8$Mn, Pt$_8$Mo, Pt$_8$Nb, Pt$_8$Rh$_8$, Pt$_8$Sc, Pt$_8$Ta, Pt$_8$Ti$_8^*$, Pt$_8$V$_8^*$, Pt$_8$W$_8$, Pt$_8$Zr$_8$, Rh$_8$Mo, Rh$_8$W, Ta$_8$Pd, Ta$_8$Pt, Ta$_8$Rh, V$_8$Cr$_8^*$, V$_8$Fe$_8^*$, V$_8$Ir$_8^*$, V$_8$Nb$_8^*$, V$_8$Pd, V$_8$Pt, V$_8$Rh, and V$_8$Ru$_8$.$^\dagger$ ( metavarstable, $^*$ = experimentally observed). This is surprising for the wealth of new occurrences that are predicted, especially in well-characterized systems (e.g., Cu–Zn). By verifying all experimental results while offering additional predictions, our study serves as a striking demonstration of the power of the high-throughput approach. The practicality of the method is demonstrated in the Rh–W system. A cluster-expansion-based Monte Carlo model reveals a relatively high order–disorder transition temperature.

I. Introduction

Binary ordered phases with high stoichiometric ratio compositions (7:1 and higher) are rare.$^{1,2}$ Despite the rarity of phases with stoichiometry far from 1:1, however, there is considerable interest in identifying their existence. Beyond the fundamental scientific motivation to characterize the complete ground states of binary systems, it is well known that even small amounts of an alloying agent may result in dramatic material enhancements when ordering occurs (e.g., strength$^{3,4}$. To illustrate this point, consider the case of order-induced hardening in platinum–copper.$^5$ The addition of 14 atom % Cu in Pt can result in the formation of ordered domains of the type A7B,$^6$ increasing the hardness in some instances by more than double that of untreated specimens.

Of the few high-stoichiometry phases, the A8B phase (Pearson symbol t18 and space group I4/mmm,$^7$ Figure 1) is of particular interest—it forms in systems containing elements from the transition metal group and has potential applications in catalysis, high-temperature electrodes, and jewelry. It was first reported by Pietrokowsky in 1965 in Pt–Ti (hence prototype Pt$_8$Ti$^8$) and has since been found in 11 metallic systems. In order of discovery, they are Pt$_8$Ti,$^9$ Pt$_8$Zr,$^{10}$ Ni$_8$Nb,$^{11}$ Ni$_8$Ta,$^{12}$ Ni$_8$V,$^{13}$ Pd$_8$W,$^{14}$ Pd$_8$V,$^{15}$ Pt$_8$V,$^{7}$ Ni$_8$Mo,$^{16}$ Pd$_8$Mo$^{17}$ and Pt$_8$Cr.$^{18}$

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Figure 1. Projections of the A$_8$B phase along (001) and (100). Atoms sit on face-centered cubic lattice sites, with large circles indicating atoms in the plane of the page and small circles suggesting a displacement a/2 perpendicular to the plane. The body-centered tetragonal unit cell is outlined by the dashed lines. A non-primitive face-centered tetragonal cell is outlined by the perimeter.

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In the HT approach, previously unexpected ground states are found by a brute-force search: formation enthalpies are calculated for essentially every crystal structure ever observed in binary metal systems as well as a large number of enumerated derivative superstructures. For this study, the calculations were performed using the AFLOW framework based on ab initio calculations of the energies using the VASP software. We used projector-augmented wave (PAW) pseudopotentials and the exchange-correlation functionals parameterized by Perdew, Burke, and Ernzerhof for the generalized gradient approximation. The energies were calculated at zero temperature and pressure (thus energies and enthalpies coincide), with spin polarization and without zero-point motion or lattice vibrations (zero-point motion is negligible because we do not consider light elements). All crystal structures were fully relaxed (cell volume and shape, and atomic positions). Numerical convergence to about ~1 meV/atom was ensured by a high energy cutoff (30% higher than the highest-energy cutoff for the pseudopotentials of the components) and dense 6000 k-point Monkhorst–Pack meshes.

The HT search included the 435 binary intermetallics that can be made with transition metals (La included). For each system, the energies of 200 crystal structures were calculated. In addition to the 176 configurations described in ref 23, these included all the symmetrically distinct hexagonal close packed (hcp)-, body-centered cubic (bcc)-, and face-centered cubic (fcc)-based superstructures, with up to four atoms per cell, and the prototypes A5, A6, A7, A8, A9, A11, B20, C36, D59, AlZr, AlZr2, CuTi, Cu2Ti6, GaHf, GaNi, GaPt, GaTi5, HgPt, ITI, InTi, LiB-MSi2/3, NbNi4(Pt3Ti), NiTi5, ScTi, and V3Zn5. The additional prototypes were considered because they are common or related to noble metal alloys. We did not consider lattice superstructures with more than four atoms per cell because their number increases enormously. It should also be noted that systems exist which do not conserve the parents’ lattice (i.e., Hf–Ti, Hf–Zr2).

This procedure gives reasonable results, as shown in ref 23. Here it was shown that the probability of reproducing the correct ground state—if well defined, unambiguous, and present in our list of prototypes—is η ≈ 96.7% (“reliability of the method”, eq 3 of ref 23). There is no guarantee that the true ground state of a system will be found among the common experimentally observed structures or among small-unit-cell derivative structures. However, even if it is impossible to rule out the existence of an unexpected ground state, this procedure (searching many enumerated derivative structures and exhaustively exploring experimentally reported structures) is expected to give a reasonable balance between HT speed and scientific accuracy to determine the presence of A8B phases.

III. Results and Discussion

Following the unexpected HT predictions shown in Figure 2b, the search for systems exhibiting A8B was extended to all transition metals, including lanthanum. The results of the HT
Thus, previously unsuspected occurrences of the A8B phase are Pd8Nb, Pd8Sc, Pd8Ta, Pd8Ti, Pd8V*, Pd8W*, Pd8Zn, Pd8Zr, Cu8Ni†, Cu8Zn†, Hg8La, Ir8Os†, Ir8Re, Ir8Ru†, Ir8Tc, Ir8W†, Pt8Ti*, Pt8V*, Pt8W, Pt8Zr*, Rh8Mo, Rh8W, Ta8Pd, Ta8Pt, († described below) A8B phases in 59 systems: Au8Zn†, Cd8Sc†, search indicate thermodynamically stable and metastable (de-

Figure 3. Complete set of A8B phases predicted by HT calculations. Elements are listed according to the Mendeleev number after Pettifor.20 Many previously unsuspected candidate systems are revealed, spanning the transition metals and La and Sc. “W—Co” = W, Mo, Cr, Re, Tc, Mn, Fe, Ru, Os, and Co; no ground states at composition A8B were found in this region.

Systems in which the A8B structure is less than 3 meV above or below the tie line defined by adjacent ground states are labeled metastable (indicated by the blue tiles in Figure 3). A definitive statement regarding the existence of a T = 0 K ground state at 8:1 stoichiometry is difficult to make in these instances. Energies on the order of several millielectronvolts are small in comparison with the formation enthalpies of stable states in the systems studied, and such small fluctuations may be due to systematic error in DFT calculations. Regardless of these considerations, however, metastable states are often realizable at finite temperature because of entropic stabilization. Indeed, certain experimental phases (e.g., Ni8Mo) are found to be metastable by our quantum mechanical calculations.

The case of Pt7Cu was introduced at the beginning as an example of material improvement gained by ordering. More noteworthy, however, is the fact that a well-studied system yielded a previously unobserved ordered phase. Pt—Cu is a common jewelry alloy that has been investigated for decades and has been used for more than a century. Despite this, the ordered phase was only observed recently, after the appropriate sequence of annealing and cold working. Thus, one should not discount predicted phases merely because a system is well studied (e.g., Cu—Zn, Cu—Ni). Phases with finite order—disorder transitions may go unnoticed for many reasons, not the least of which is the real limitation imposed by kinetics. Several observed A8B phases (Pd8W, Pd8V, and Pd8Mo), for example, have only been realized after the introduction of excess vacancies by charged-particle irradiation.15

Even so, since all HT quantum mechanical energy calculations were performed at zero temperature, it is possible that some of the predicted A8B phases will not be observed experimentally. That is, it may be difficult to achieve thermal equilibrium in certain systems. The kinetics will be too slow to observe ordering in reasonable time if the concentration of thermally induced vacancies is too low.

To address this, it is desirable to leverage the synergy of an approach that combines HT with a model that can be extended to finite temperature, such as the cluster expansion (CE). Transition temperatures estimated by CE-based Monte Carlo simulations give an estimate of the likelihood of observing a transition experimentally.

We conducted a CE study, using the UNCLE33,34 code, on the A8B-forming Rh—W system. The CE was constructed using the energies of structures with concentrations in the range 0–25 atom % W (Figure 4). At higher W concentration, HT results indicate that zero temperature ground states will not form fcc CE derivative superstructures. Thus, the range of the CE was kept on the order of several millielectronvolts are small in comparison with the formation enthalpies of stable states in the systems studied, and such small fluctuations may be due to systematic error in DFT calculations. Regardless of these considerations, however, metastable states are often realizable at finite temperature because of entropic stabilization. Indeed, certain experimental phases (e.g., Ni8Mo) are found to be metastable by our quantum mechanical calculations.

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Figure 4. CE input energies calculated from first principles (red, large circles) with cluster expansion predictions (blue, stars). The blue tie line connects the stable structures after a ground state search. For clarity, the ground state search enthalpies are not shown except for the stable states, the vertices of the convex hull (blue line). The stable state at x = 11 atom % W is the 8:1 structure. Input structures with concentrations between 0 and 25 atom % W were selected because the applicability of an fcc CE approach was established by HT within this range.

Quantum mechanical energies used in the construction of the CE were computed on an equivalent k-point scheme to reduce systematic error. Rh and W pseudopotentials incorporating the semi-core p electrons with an energy cutoff of approximately 271 eV were used. Input energies, CE predictions, and lowest-energy predictions of the ground state search (including fcc superstructures with up to 10 atoms per unit cell) are shown in Figure 4. A canonical Monte Carlo simulation using the Metropolis algorithm was performed on a 20 x 20 x 20 unit cell with periodic boundary conditions. The results, including the specific heat determined using the familiar statistical relation $\sigma_k^2 = \langle E^2 \rangle - \langle E \rangle^2$, are shown in Figure 5.

CE-based MC modeling revealed an order–disorder transition temperature between 900 and 1000 K in the Rh–W system at 8:1 stoichiometry. Experimental Rh–W phase diagrams show the liquidus line near 2200 K at 11 atom % W. It is then conceivable that the A8B phase could be produced after the introduction of excess vacancies (via charged particle irradiation15 or cold working5), if not by spontaneous ordering alone.

IV. Conclusions

In conclusion, using the high-throughput method, the A8B phase was found in 59 systems, 48 of which are yet unobserved. By verifying experiment and previous predictions while also offering additional predictions, our results demonstrate the power of the HT approach in a dramatic fashion. Although it is possible that some of the predicted phases may not be observed experimentally due to kinetic limitations, a CE extension to finite temperatures illustrates that the investigation is not merely academic. In the system Rh–W, the transition was predicted high enough to be realized experimentally. Further investigation is required to determine the extent to which the remaining predicted phases may be seen experimentally.

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