Accuracy of ab initio methods in predicting the crystal structures of metals: review of 80 binary alloys.

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Predicting and characterizing the crystal structure of materials is a key problem in materials research and development. We report the results of ab initio LDA/GGA computations for the following systems: AgAu, AgCd, AgMo∗, AgNa, AgNb*, AgPd, AgRh*, AgRu*, AgTc*, AgTi, AgY, AgZr, AlSc, AuCd, AuMo∗, AuNb, AuPd, AuPt*, AuRh*, AuRu*, AuSc, AuTc*, AuTi, AuY, AuZr, CdMo*, CdNb*, CdPd, CdPt, CdRh, CdRu*, CdTc*, CdTi, CdY, CdZr, CrMg*, MoNb, MoPd, MoPt, MoRh, MoRu, MoTc*, MoTi, MoY*, MoZr, NbPd, NbPt, NbRh, NbRu, NbTc, NbY*, NbZr*, PdTc, PdRh*, PdRu*, PdTa, PdTc, PdTi, PdY, PdZr, PtRh, PtRu, PtY, PtTc, PtTi, PtZr, RhRu, RhTc, RhTi, RhY, RhZr, RuTi, RuTc, RuY, RuZr, TcTi, TcY, TcZr, TizR*, YZr* (* = systems in which the ab initio method predicts that no compounds are stable). A detailed comparison to experimental data confirms the high accuracy with which ab initio methods can predict ground states.

Keywords: Binary Alloys, Ab initio, Intermetallics, Transition Metals, Structure Prediction, Phase Stability, Aluminum, Cadmium, Gold, Magnesium, Molybdenum, Niobium, Palladium, Platinum, Rhodium, Ruthenium, Scandium, Silver, Sodium, Titanium, Technetium, Yttrium, Zirconium.

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I. INTRODUCTION

First principles computation, whereby the properties of materials are predicted starting from the principles of quantum mechanics, is becoming well integrated with more traditional materials research. A list of ab initio studies on binary and ternary alloy phase stability up to 1994 can be found in reference [1]. Since the earliest, completely ab initio computation of a binary phase diagram [2], the approaches to compute the total energy of a solid have significantly improved, and computing resources have continued to become faster and less expensive. We believe that a point has been reached where, with a reasonable amount of resources, high throughput first principles studies of a large number of alloys can be performed [3–8]. In this paper we present the results of a first principles study of 14080 computed total energies on 176 crystal structures in 80 binary alloys. To our knowledge this is the largest first principles study of its kind on alloys. As we have compared the results in every system to experimental compilations, this study also offers a statistical test on the accuracy of some current ab initio approaches in correctly predicting the structure of materials.

For 89 compounds we find unambiguous agreement between experiment and the ab initio computation (Table 5), giving some indication of the predictive power of modern ab initio electronic structure methods. For many systems, verification of the ab initio results is difficult, as the systems have been poorly or incompletely characterized,
or only high-temperature information is available experimentally. For most of these system, we make predictions that are consistent with the limited available information. Even though our library of 176 crystal structures is, to our knowledge, the largest library of \textit{ab initio} energies ever produced, there are still 27 compounds for which we cannot verify the experimental structures as they are not in our library. We have not included such prototypes because they are extremely rare and complicated (many atoms per unit cell) (Table 8).

Overall, we find remarkably few significant discrepancies between the \textit{ab initio} predictions and the experimental observations (Table 9). Based on the experimental data in references [9,10], we find only nine compounds for which LDA/GGA seems to predict the ground state incorrectly. For four of these nine systems, the experimental ground state is within less than 10meV/atom of the \textit{ab initio} ground state. For the remaining five systems, there are at least two in which further investigation indicates that the experimental structure assignment is poorly justified, leaving three compounds in which a significant disagreement between experiment and \textit{ab initio} LDA/GGA is likely. Such disagreements are addressed in Section (IV).

We believe that the low ratio of unambiguous correct predictions (89) is encouraging, and establishes clearly the potential of predicting crystal structure correctly with \textit{ab initio} methods.

We also predict the stability of five new crystal structures, to the best of our knowledge, have not yet been observed in any system. An AB$_3$ superstructure of the fcc lattice, stable for CdPt$_3$, PdPt$_3$ and Pd$_3$Pt, an AB bcc superstructure for MoTi$_3$, an AB$_3$ bcc superstructure for MoTi$_3$, Mo$_7$Ti, Nb$_3$Tc, Ru$_3$Ti$_3$ and Tc$_3$Ti$_3$, an A$_2$B$_2$ hcp superstructure for RhRu$_2$, and an A$_2$B$_4$ hcp superstructure for RhRu$_2$ (Appendix (XI)). In addition, we find two new crystal structures which are not superstructures of fcc, bcc or hcp: MoZr$_3$ and Mo$_5$Ti$_3$ (for Mo$_5$Ti, MoZr$_5$, and Nb$_5$Ru) (Appendix (XII)).

II. THE LIBRARY: ALLOYS AND STRUCTURES

**Binary alloys.** Our calculated library contains 80 binary intermetallic alloys. The alloys include the binaries that can be made from row 5 transition metals, as well as some systems with Aluminum, Gold, Magnesium, Platinum, Scandium, Sodium, Titanium, and Technetium. The alloys are: AgAu, AgCd, AgMg, AgMo*, AgNa, AgNb*, AgPd, AgRh*, AgRu*, AgTc*, AgTi, AgY, AgZr, AuCd, AuMo*, AuNb, AuPd, AuPt*, AuRh*, AuRu*, AuSc, AuTc*, AuTi, AuY, AuZr, AlSc, CdMo*, CdNb*, CdPd, CdPt, CdRh, CdRu*, CdTc*, CdTi, CdY, CdZr, CrMg*, MoNb, MoPd, MoPt, MoRh, MoRu, MoTc*, MoTi, MoY*, MoZr, NbPd, NbPt, NbRh, NbRu, NbTc, NbY*, NbZr*, PdPt, PdRh*, PdRu*, PdTc, PdTi, PdY, PtRh, PtRu, PtY, PtTc, PtZr, PtZr, PtZr, RhRu, RhTc, RhTc, RhY, RhZr, RuTi, RuTc, RuY, RuZr, TcTi, TcY, TcZr, TlZr*, YZr*, where the superscript * indicates the systems in which the \textit{high throughput ab initio} method predicts that no compounds are stable: 57 alloys form compounds and 23 are non compound forming.

**Structures and their prototypes.** The library contains 176 crystal structures. Many of these have the same structure type but with different compositions of occupancies, for example, AB$_3$ and A$_3$B (also AB and BA if the point groups of atomic positions of A and B are different), so the number of distinct prototypes is 101. The various concentrations are listed in the table below.

| Compounds composition | Conc. of B | number of prototypes |
|-----------------------|-----------|----------------------|
| A & B                 | 0%        | 4                    |
| A$_2$B & AB$_3$       | 16.66%    | 3                    |
| A$_4$B & AB$_4$       | 20%       | 2                    |
| A$_3$B & AB$_3$       | 25%       | 27                   |
| A$_2$B & AB$_2$       | 33.33%    | 32                   |
| A$_2$B$_3$ & AB$_5$   | 37.5%     | 2                    |
| A$_2$B$_2$ & AB$_4$   | 40%       | 1                    |
| A$_2$B$_4$ & AB$_3$   | 42.85%    | 1                    |
| (AB & (BA)*)          | 50%       | 29 i(0)              |

**Table 1.** Compositions, concentrations and number of prototypes inside the library. The library has 176 structures, and 101 distinct prototypes (* at composition AB, 3 prototypes have different point groups in atomic positions A and B, therefore they represent distinct structure types). Of such prototypes, 65 are chosen from the most common intermetallic binary structures in the CRYSTMET database [11] and in the Pauling File [10]. Such prototypes can be described by their Strukturbericht designation and/or natural prototypes [9,10]: A1, A2, A3, A4, A15, B1, B2, B3, B4, B81, B82, B10, B11, B19, B27, B32, B33 (Bf$_2$), Cc, C2, C6, C11$_b$, C14, C15, C15$_b$, C16, C18, C22, C32, C33, C37, C38, C49, D0$_5$, D1$_5$, D0$_9$, D0$_{11}$, D0$_{19}$, D0$_{22}$, D0$_{23}$, D0$_{24}$, D1$_{3}$, D1$_{4}$, D2$_{d}$, D7$_{3}$, D8$_{5}$, L1$_{0}$, L1$_{1}$, L1$_{2}$, L6$_{0}$, CaH$_2$, CuTe, CuZr$_2$, GdSi$_2$ (1.4), MoPt$_2$, NbAs (NbP), NbPd$_3$, Ni$_2$Si, Ω (with z=1/4), Pu$_3$Al (Co$_3$V), Tl$_3$Cu$_4$, W$_5$Si$_3$, YCd$_3$, ZrSi$_2$, γ-Ir. The rest of the structures (36) are fcc, bcc or hcp superstructures. Twelve of these superstructures consist of stacking of pure A and B planes along some direction. Of such prototypes, 12 contain a stacking direction, therefore we can name them following the parent lattice and the stacking direction:

\[ \text{LATTICE}^{[direction]}_{\text{stacking}} \]

For example the designation \textit{FCC}$_{\text{[A2B2]}}$ indicates a structure prototype with FCC parent lattice and A2B2...
stacking along direction $[001]$. The 12 prototypes of the library that can be labeled in this manner are: \( \text{BCC}_{[100]} \), \( \text{BCC}_{[211]} \), \( \text{FCC}_{[001]} \), \( \text{FCC}_{[011]} \), \( \text{FCC}_{[111]} \), \( \text{FCC}_{[101]} \), \( \text{FCC}_{[210]} \), \( \text{FCC}_{[311]} \), \( \text{FCC}_{[321]} \), \( \text{FCC}_{[111]} \), \( \text{FCC}_{[211]} \), \( \text{FCC}_{[311]} \), \( \text{FCC}_{[321]} \). For the FCC superstructures, a conversion table between the lattice-stacking-direction, the Sanchez - de Fontaine notation [12], and the Lu et al. designations [13,14] is included below.

| Space Group | Sanchez - de Fontaine [12] | Lu et al. [13,14] | Here and [15] |
|-------------|--------------------------|-----------------|--------------|
| \( \text{AB}_2 \) | 14/mmm #139 | \( \text{AB}_2 \) | 14/mmm #139 |
| \( \text{AB}_2 \) | P3m1 #164 | \( \text{AB}_2 \) | P3m1 #164 |
| \( \text{AB}_3 \) | P4/mmm #123 | Z1/Z3 | Z1/Z3 |
| \( \text{A}_2 \text{B}_2 \) | P4/mmm #129 | \( \text{A}_2 \text{B}_2 \) | P4/mmm #129 |
| \( \text{A}_2 \text{B}_2 \) | C2/m #12 | W2 | W2 |
| \( \text{A}_2 \text{B}_2 \) | Pmmn #47 | Y1/Y3 | Y1/Y3 |
| \( \text{A}_2 \text{B}_2 \) | Pnnm #50 | AB(e) | V2 |
| \( \text{A}_2 \text{B}_2 \) | I4/mamd #141 | CH or “40” | CH or “40” |
| \( \text{AB}_3 \) | R3m #166 | V1/V3 | V1/V3 |
| \( \text{AB}_2 \) | R3m #166 | V2 | V2 |

TABLE 2. Conversion table between the lattice-stacking-direction, the Sanchez - de Fontaine notation [12], and the Lu et al. designations [13,14].

The prototypes of stable structures, that cannot be described by Strukturbericht designation, natural prototypes or lattice-stacking-direction convention, are described in Appendix XI. The complete geometrical description of all the fcc, bcc, and hcp superstructures of the library can be found in reference [15].

III. HIGH-THROUGHPUT FIRST PRINCIPLES CALCULATIONS

Ultra Soft Pseudopotentials LDA calculations (US-LDA). Most of the energy calculations of the library were performed using Density Functional Theory in the Local Density Approximation (LDA), with the Ceperley-Alder form for the correlation energy as parameterized by Perdew-Zunger [18] with ultra soft Vanderbilt type pseudopotentials [19], as implemented in VASP [20]. Calculations are at zero temperature and pressure, and without zero-point motion. The energy cutoff in each calculation was set to 1.75 times the larger of the suggested energy cutoffs of the pseudopotentials of the elements of the alloy. Brillouin zone integrations were done using at least \( \sim 3500/(\text{number of atoms in unit cell}) \) \( k \)-points distributed as uniformly as possible on a Monkhorst-Pack mesh [21,22]. Spin polarization was used in all calculations. We expect such calculations to be able to distinguish energies of structures previously degenerate. This is because the increased density of the \( k \)-points mesh, the reduced radial cutoff of the PAW potentials versus the ultrasoft pseudopotentials, and the GGA correlation energy implementation. With such methodology, we consider degenerate structures the ones that have energies closer than \( \lesssim 1 \text{meV/atom} \).

One would expect the PAW-GGA approach to be somewhat more accurate than the US-LDA. For the GGA correlation energy, we used the Perdew-Wang parameterization (GGA-PW91) [25]. Similar to the US-LDA case, all PAW-GGA calculations are performed at zero temperature and pressure, and without zero-point motion. The energy cutoff in each calculation was set to 1.75 times the larger of the suggested energy cutoffs of the pseudopotentials of the elements of the alloy. Brillouin zone integrations were done using at least \( \sim 3500/(\text{number of atoms in unit cell}) \) \( k \)-points distributed as uniformly as possible on a Monkhorst-Pack mesh [21,22]. Spin polarization was used in all calculations. We expect such calculations to be able to distinguish energies of structures previously degenerate. This is because the increased density of the \( k \)-points mesh, the reduced radial cutoff of the PAW potentials versus the ultrasoft pseudopotentials, and the GGA correlation energy implementation. With such methodology, we consider degenerate structures the ones that have energies closer than \( \lesssim 1 \text{meV/atom} \).

For some structures both the US-LDA and PAW-GGA calculations are presented. To avoid confusion, we specify the type of calculation in brackets: \((\text{us-lda})\) or \((\text{paw-gga})\). In addition, all the results of the PAW-GGA calculations are described in italics.

Symmetries of the pure elements. Both the US-LDA and PAW-GGA calculations reproduce the correct experimental crystal structures of the pure elements at room temperature. The only exception is Sodium. In the two formalisms, Na-hcp is very slightly favored over Na-bcc and Na-fcc, in agreement with other first principle calculations [26–30]. At room temperature Sodium has the bcc structure, and undergoes a martensitic transformation below 35K, to a closed packed structure [31–38]. Therefore our results, Na-hcp stable and the very small energy differences with Na-bcc and Na-fcc, are consistent with the behavior at low temperature only.
**High-throughput computing.** To perform the high number of calculations, we have implemented a set of automatic tools to prepare initial data, perform calculations and analyze results.

**Preparation of input files.** All input files are prepared by starting from the templates based on the prototype chemistry. The volume of the unit cells is determined as a linear combination of atomic volumes of pure elements with Vegard’s law [39]. The internal position of the atoms have been taken from geometrical configurations (for fcc, bcc, hcp superstructures) or have been extracted from the CRYSTMET and the Pauling File databases [11,10].

**Ab initio Calculations.** The calculations are performed by a high-throughput tool, called AFLOW (automatic flow), which searches inside the library for potential input files and performs the proper ab initio calculations. AFLOW is able to balance the CPU loads in a multi-processor and cluster environment, maximizing the total throughput of the process [15]. AFLOW extracts the energy and initiates further relaxations with the atomic positions and unit cell geometries obtained from VASP. Therefore, all the structures are relaxed at least twice, and many (∼10% of the total) are relaxed three or more times, until proper geometrical and energetic convergence is obtained. To conclude, for a library of 176 crystal structures in 80 binary alloys, with a total of 14080 structures, AFLOW performed 32,402 VASP calculations. The total computing time used for this project was ∼ 9.05·10⁸ CPU seconds (∼ 28.7 CPU years), which was spread over a large set of computers [40]. Given the different types of CPUs used, we can only estimate the total amount of computation for the project at roughly ∼ 1.2 · 10⁹ TER-AFLOP.

**Collection and error check of the results.** Once each structure has been calculated, space group symmetry, bond distances, coordination numbers and unit volumes are compared for all the structures of that alloy with the same concentration in the library. Frequently, several structures, starting from different prototypes, relax to the same final structure with the same energy. Therefore, to identify the correct stable phase, it is mandatory to be able to determine the final relaxed structure with the highest possible reliability. Details of the high-throughput error checking tool can be found in reference [15]. A few stable structures remain unidentified. For those we report the unit cell and atomic positions in Appendix XI. Such prototypes might be new phases to be checked experimentally.

**Calculation of the formation energies and the convex hull.** The formation energy for each structure is determined with respect to the most stable structure of the pure elements. To determine the ground states of a system one needs to find, as a function of composition, the ordered compounds that have an energy lower than any other structure or any linear combination of structures that gives the proper composition. This set of ground state structures forms a convex hull, as all other structures have an energy that falls above the set of tie lines that connects the energy of the ground states. In thermodynamical terms, the convex hull represents the Gibbs free energy of the alloy at zero temperature.

**Comparison with experiments.** To compare the ab initio results to experimental information, we relied on the information and references in the Binary Alloy Phase Diagrams (Massalski [9]) and in the Pauling File [10]. Though in some cases references not included in these were also used, no systematic approach to go beyond information in the Pauling File or Binary Alloy Phase Diagrams was used.

**IV. DISCUSSION AND SUMMARY OF RESULTS**

In comparing the stable structures predicted by the ab initio computations with available experimental information, we have attempted to classify the results in a few distinct categories. Table 5 gives the compounds where the ab initio result and experiments are in unambiguous agreement. The fact that there are a large number of compounds (89) in Table 5 is a positive statement about the accuracy of LDA/GGA in capturing the close energetic competition between the 176 structures in our library. For one of the systems in Table 5 (PdTi₃) we took the liberty of modifying the experimental result [9] which shows the A15 structure (stoichiometry AB₃) as a line compound at composition PdTi₃. While off-stoichiometric compounds are obviously possible, this usually goes together with significant width of the single-phase field. Hence, we concluded (maybe erroneously) that the placement of A15 at composition PdTi₄ in reference [9] is likely a typographical error.

Table 6 shows compositions which are experimentally known to form compounds, but lack a complete identification of the structure type. Hence, the ab initio prediction should be seen as a likely crystal structure for the compound. In most cases, the ab initio structure is consistent with the conditions imposed by the limited experimental data (e.g. bcc-ordering is seen for Ag-Cd, and we predict B19; or C37 is speculated for Au-Sc, in agreement with what we predict). Hence, it is likely that with further experimental characterization, many of these systems would move to Table 5.

Table 7a-b contains compositions which are experimentally characterized as solid solutions, high-temperature two-phase regions, or have not been studied at all in a particular composition range. Because of the lack of low-temperature information in these systems, an unambiguous statement about the accuracy of the LDA/GGA prediction cannot be made. For some systems, the ab initio
result is very consistent with the experimentally observed behavior. For example, in Ag-Au we find many fcc ordered superstructures with low formation energies, indicating a weak ordering interaction. So it is likely that the ab initio predicted structures are stable at low temperature, but disorder into a solid solution at elevated temperature, a rather common occurrence for noble-metal alloys. For other systems in this table the comparison between experiments and ab initio is more troubling. For example, while Mo-Ti is experimentally described as a two-phase system with no known compounds down to 400°C, we find very strong compound formation. While it is possible that these compounds disappear through peritectoid reactions below 400°C, the large negative formation energies make this unlikely. It is more likely that either the experimental characterization of this system, or the ab initio result is significantly in error. A system such as Mo-Nb, on the other hand, is not at all studied experimentally, and no statement about the accuracy of our prediction in this system can be made.

Table 8 contains the compounds whose crystal structure is not present in the library, and hence, it is not possible to make a comparison with the ab initio data. In some cases (e.g. Au10Zr7), this is because the crystal structure is uncommon and has a large unit cell, making it less worthwhile to include it in the library. In other cases (e.g. Rh2-Ti) the structure is simply unknown. Table 8 also includes structures that are only stable at off-stoichiometric compositions (e.g. B19 in Au-Ti), as we did not include disorder in the library prototypes. Finally, Table 9 contains the compositions for which there seems to be a clear disagreement between the experimental data in references [9,10] and the ab initio results. Because these systems can point at either experimental errors, or shortcomings of the ab initio method, we discuss them here in more detail. Note that ab initio errors are most likely due to the LDA or GGA approximations or the pseudopotentials being used. In general, one should consider that our calculations only produce the zero-K energy, whereas all the experimental results are at non-zero temperature. Given that entropic differences between structures can be of the order 0.1 ∼ 1.0k_B per atom [381], very small energy differences between the experimentally observed structure and our ab initio results, could be reversed at elevated temperature. In particular, AuNb3-A15, NbRh3-L12, NbRu3-L12 and NbRu'-L12 may be in this category. This phenomenon is quite common. As an example, Wolverton and Ozilins have shown that, in the case of the aluminum-copper system, the vibrational entropy difference is responsible for stabilizing the θ phase Al2Cu (tetragonal C16) over the competing Al2Cu-θ' phase (distortion of θ-C1, the cubic fluorite phase with CaF2 prototype), which has the lowest energy, and, therefore, is the stable structure at zero Kelvin [382]. At temperatures higher than T∼ 150 – 200°C, Al2Cu-θ is more favorable.

A. Discussion of disagreement between experimental and ab initio results

AuNb3. The structure AuNb3-A15 has been reported a number of times [9,10,127–141]. In particular, Röschel et al. [132] observed the A15 structure to grow in quenched samples. Ball-milling samples of the material to form disordered bcc, revert upon heat treatment in an exothermic reaction to A15, suggesting that A15 could be the ground state for this composition at low temperature. The relatively small energy difference between A15 and the AuNb3↔Nb tie-line in our calculation could lead to finite temperature stability of A15. Alternatively, the ∼7meV/atom energy difference (US-LDA and PAW-GGA) could simply be an error of the ab initio approach.

AuY. While we predict the B33 structure to be stable by 26meV/atom below the B2 structure, this system is experimentally listed as having a B2 structure. This experimental classification is based on a paper by Chao et al. [170,10]. Chao’s work mentioned that they only see B2 when performing a rapid quench. Further work by Kusma [172] and Dwight [158] did not observe the B2 structure. The experimental results in this system are therefore somewhat suspect. It is possible that B2 is a high temperature structure while B33 is the low temperature form. However, it should also be pointed out that the mixing energies in this system are very large (∼1eV), and that the potential error of ∼25meV/atom (US-LDA and PAW-GGA) is a small fraction of this.

Cd3Nb. The structure of this compound is one of the more interesting discrepancies between ab initio and experiments to emerge from our study. Based on experimental work of Von Holleck [178], a single L12 compound is claimed to be stable in this system. Computationally, no compounds are stable at all, and we find this system to be immiscible. The compound with lowest energy is a bcc superstructure at composition CdNb, and energy ∼55meV/atom above the Cd↔Nb tie-line (∼62meV/atom with PAW-GGA). The Cd3Nb-L12 is 70meV/atom above that same tie-line (>100meV/atom with PAW-GGA). It is not common for LDA/GGA to make such large and qualitative errors in metals, and further investigation of this system is suggested, as it will likely lead to a reconsideration of the experimental classification, or to some novel understanding of the errors that ab initio methods can produce in metals.

CdPt3. Experimentally this compound is claimed to form in the L12 structure, while we predict it to form in a new structure for which no prototype yet exists.
(CdPt$^{\text{prot}}_{3}$ in Appendix VIII). We believe the experimental assignment to be uncertain. It is based on a single paper by Nowotny [181] which actually does not observe the L1$_2$ structure in this system, but assigns it by chemical similarity with the Pt$_3$Zn system.

**NbRh$_3$.** This compound is characterized as an L1$_2$ structure, whereas our *ab initio* results find the A1$_5$Pu prototype to be 8meV/atom lower in energy (5.3meV/atom with PAW-GGA). This small energy difference could very well be an LDA/GGA error, or could be reversed at elevated temperature by entropic effects.

**NbRu$_3$.** NbRu$_3$ is similar to the discrepancy of compound NbRh$_3$. Experimentally it is found to be an L1$_2$ structure, whereas we find a D0$_{24}$ structure that is 8meV/atom below the L1$_2$. With PAW pseudopotentials and the GGA exchange correlation corrections the D0$_{24}$-L1$_2$ energy difference reduces to 2.5meV/atom. Because this number is so small, extremely large k-points sets and high energy cutoff were used to converge it. The results indicate that L1$_2$ and D0$_{24}$ are all but degenerate in this system. Since D0$_{24}$ and L1$_2$ are very similar (D0$_{24}$ is a periodically anti-phased version of L1$_2$) subtle entropic effects can easily reverse the stability between these two.

**NbRu.** Experimentally this system is classified to have the L1$_0$ structure, whereas the *ab initio* results indicate an unusual two-phase region between Nb$_3$Ru (D0$_3$) and NbRu$_2$ (C37) covering this composition [9,10,233,237]. The most recent experimental result is based on the assignment by Chen [237] who observes a disordered bcc solution at high temperature and a transformation to a tetragonal structure near 1000°C. Between 720–920°C they see a further symmetry reduction to an orthorhombic phase. Hence, even if the tetragonal structure below 1000°C would be L1$_0$ (which is only speculated by Chen) its further transformation to an orthorhombic structure indicates that L1$_0$ is not the ground state structure. Based on a diffusion couple study, Hurley [235] believes that a two-phase region exists near 50% Ru, though the results seem to be irreproducible. Besides the difficulty with interpreting the experimental data, significant problems also exists on the *ab initio* side with this compound. The PAW-GGA result is substantially different from the US-LDA result. GGA gives L1$_0$ only 4meV/atom above the tie-line (versus 20meV/atom in LDA), whereas B19 seems to be >100meV/atom above the tie-line (versus 13meV/atom with LDA).

**PtY.** Experimental assignment of the structure of this compound as B27 is based on two papers [277,316]. The *ab initio* work finds B33 to be lowest in energy with B27 higher by 50meV/atom (60meV/atom with PAW-GGA). Given that the experimental results seem sound, this is probably a true *ab initio* error.

**Pt$_3$Zr$_5$.** The work of Schubert *et al.* [323] establishes Pt$_3$Zr$_5$ as a D8$_8$ structure, whereas our *ab initio* (LDA) results put the D8$_8$ structure 36meV/atom above the tie-line formed by PtZr$_2$-C16 and PtZr-B33. The GGA result is 26meV/atom above the tie-line. In each case the W$_3$Si$_3$ structure is lower in energy than the D8$_8$. Given the large mixing energies in this system (of the order of 1 eV/atom), these *ab initio* errors seem plausible.

**V. CONCLUSIONS**

Overall, the comparison between experimental data and *ab initio* results is encouraging. A large number of the ground states are predicted correctly, even though significant competition exists between various structures, indicating that relative energy differences are well reproduced by LDA/GGA. In many cases, the direct comparison between *ab initio* and experiments is difficult, as systems have often not been studied completely, or have not been studied to low enough temperature to make a reliable statement about the ground state structures. For only a small number of cases, there is a clear discrepancy between *ab initio* and experiments (Table 9). On further investigations, we find that some of the experimental assignments are poorly justified (e.g. CdPt$_3$). In a few of the "error systems", the energy difference between the observed structure and the *ab initio* structure is small, which makes it fall within the uncertainty one would expect from LDA/GGA or from a lack of entropic considerations.

A few systems display, in our opinion, such a significant discrepancy between available experimental data and *ab initio* results as to make them worthwhile for further study. These include Cd$_3$Nb (L1$_2$ observed, but no compounds from *ab initio*), Nb-Ru and Pt$_3$Zr$_5$ (respectively L1$_0$ and D8$_8$ observed, but no stable compounds at that composition in *ab initio*), PtY (significant energy error between B33 and B27) and the complete Mo-Ti system (which from experiments appears to be a miscibility gap, but in the *ab initio* results display a number of novel and strongly stabilized compounds). These systems should be investigated further, either to find experimental errors, or to shed new light on *ab initio* problems.

Our findings are summarized in Table 3. By comparing all the available *ab initio* calculations with the experimental results [9,10], we obtain 284 potential structure comparisons. A subset of these, (48), are not available due to the lack of the proper prototype or the unknown experimental compound. The rest of the structure comparisons, (236), can be divided in 89 agreements in ordered systems ($N_{ac}$), 21 agreements in immiscible systems ($N_{ai}$), 9 disagreements ($N_{d}$), 21 good predictions ($N_{gp}$), and 96 possible predictions ($N_{pp}$). This division is summarized in the following table.
TABLE 3. Summary of the 284 structure comparisons between experimental and \textit{ab initio} calculations. When available, we use the PAW-GGA calculations, otherwise we use the US-LDA ones. If only US-LDA calculations were used, we would obtain $N_{ac}^{LDA}=84$ agreements and $N_{d}^{LDA}=14$ disagreements.

The reliability of our \textit{ab initio} method can be defined as the fraction of correct compounds (agreements) over the number of accessible compounds (agreements and disagreements):

$$\eta_c \equiv \frac{N_{ac}}{N_{ac} + N_d} \approx 90.8\%.$$  \hfill (2)

Such quantity, $\eta_c$, contains the reliability of the experimental results, which can be removed by considering only the \textit{true unambiguous disagreements} of Table 9 ($N_d = 3$). Hence the reliability of the method becomes:

$$\eta^*_c \equiv \frac{N_{ac}}{N_{ac} + N_d^*} \approx 96.7\%.$$  \hfill (3)

Such quantities, $\eta_c$ and $\eta^*_c$, can be considered as the probabilities that the most stable \textit{ab initio} compounds reproduce the correct experimental compound. The quantity $\eta^*_c$ should be used if the experimental compound is certain.

If we extend the argument to the agreements with experimental compounds and immiscible systems, then the reliabilities become:

$$\eta \equiv \frac{N_{ac} + N_{ai}}{N_{ac} + N_{ai} + N_{d}} \approx 92.4\%,$$  \hfill (4)

$$\eta^* \equiv \frac{N_{ac} + N_{ai}}{N_{ac} + N_{ai} + N_{d}^*} \approx 97.3\%$$  \hfill (5)

where the quantity $\eta^*_c$ should be used if the experimental compound or immiscibility is certain. Such quantities, $\eta$ and $\eta^*$, can be considered as the probabilities that \textit{ab initio} results reproduce the correct experimental compounds or immiscibilities.

Given the large number of calculations of this project, we believe $\eta$, $\eta^*$, $\eta_c$, and $\eta^*_c$ to be good estimations of state of the art pseudopotential \textit{ab initio} accuracies in phase stability prediction.
VI. ALLOYS WITHOUT AB INITIO COMPOUNDS

Table 4 gives the alloys for which we find no compounds with negative formation energy, and the structure with lowest formation energy in the system. All of these agree with experiments except for the ones described below.

| System | Structure | \( E_f \) (us-lda) meV/atom | References |
|--------|-----------|-----------------------------|------------|
| Ag-Mo  | AgMo\(_3\)-BCC proto. #72 in [16] | 208 | [9,11] and |
| Ag-Nb  | AgNb\(_3\)-BCC proto. #72 in [16] | 62 | (86,87) |
| Ag-Rh  | AgRh\(_3\)-FCC\([\text{111}]_{\text{A62}}\) | 116 | [50,94–96] |
| Ag-Ru  | AgRu\(_3\)-HEX proto. #127 in [16] | 199 | [41,43,96–98] |
| Ag-Tc  | AgTc-HEX proto. #126 in [16] | 147 | [99] |
| Au-Mo  | AuMo\(_2\)-D0\(_1\) | 75 | [41,46,118–127] |
| Au-Pt  | Au\(_2\)-FCC\([\text{111}]_{\text{A62}}\) | 9 | [41,117,119,146–148] |
| Au-Rh  | AuRh\(_3\)-FCC\([001]_{\text{A62}}\) | 91 | [116,119,149,150] |
| Au-Ru  | AuRu\(_3\)-HEX proto. #125 in [16] | 165 | [116,119,151,152] |
| Au-Tc  | AuTc-HEX proto. #126 in [16] | 74 | [116,159] |
| Cd-Mo  | Cd\(_3\)Mo-HEX proto. #128 in [16] | 173 | [9] |
| Cd-Nb  | CdNb\(_5\)-BCC proto. #71 in [16] | 55 (us-lda) | [178] |
| Cd-Ru  | CdRu\(_3\)-FCC\([001]_{\text{A62}}\) | 88 | see note “Cd-Ru” |
| Cd-Tc  | CdTc-B11 | 92 | [182] |
| Cr-Mg  | CrMg\(_2\)-B11 | 251 | [45,191] |
| Mo-Tc  | Mo\(_2\)Tc-A15 | 53 | [44,217] see note “Mo-Tc” |
| Mo-Y   | Mo\(_2\)Y-C15 | 40 | [222,223] |
| Nb-Y   | Nb\(_2\)Y-C49 | 132 | [244–245] |
| Nb-Zr  | NbZr\(_2\)-HEX proto. #129 in [16] | 22 | [238–245] |
| Pd-Rh  | PdRh\(_3\)-FCC\([001]_{\text{A62}}\) | 35 | [13,263–270] |
| Pd-Ru  | PdRu-HEX proto. #126 in [16] | 44 | [217–218] |
| Ti-Zr  | TiZr\(_2\)-B2 | 18 | [48,49,371–374] |
| V-Zr   | VZr\(_2\)-HEX proto. #141 in [16] | 35 | [49,375–380] |

**TABLE 4.** Systems without intermetallic compounds. The second and third columns give, for each system, the structure with the lowest formation energy \( E_f \) (US-LDA calculations). The table contains 23 entries. 21 of these are in agreement with experiments. References include both experimental and \textit{ab initio} studies.

**Cd-Nb.** One compound, Cd\(_3\)Nb-L1\(_2\), has been reported for the system Cd-Nb [9,178]. However, we did not find any stable phase (Cd\(_3\)Nb-L1\(_2\) has formation energy of \( \sim 70 \text{meV/atom} \)). The disagreement of compound Cd\(_3\)Nb-L1\(_2\) is further discussed in the Section (IV).

**Cd-Ru.** The authors are not aware of any experimental result for the Cd-Ru system.

**Mo-Tc.** Two compounds have been suggested based on thermodynamic models: \( \beta \text{Mo}_{2}\text{Tc}_{3}\)-A15 and \( \sigma \text{Mo}_{3}\text{Tc}_{7}\)-D8\(_b\) [9,44]. However, we did not find any stable phase for the system, nor can we check the suggested compounds, since our library does not have the \( \sigma \) phase or the off-stoichiometry A15.
VII. ALLOYS WITH AB INITIO COMPOUNDS

Ag-Au (Silver - Gold). The system Ag-Au has not been studied in great detail at low temperatures, and no intermetallic compounds have been reported [9,10,52–55,119]. The solid is reported to be short-range ordered fcc, though it is suggested that long-order might exist at low temperature. At low temperature we find several stable compounds: Ag$_4$Au, Ag$_3$Au, Ag$_2$Au, AgAu-L$_1^0$, AgAu$_2$ and AgAu$_3$. In our electronic structure approach, the ground states are degenerate for Ag$_4$Au, Ag$_3$Au, Ag$_2$Au, AgAu$_2$ and AgAu$_3$. Our best candidates are L$_1^2$, D$_{023}$, Al$_3$Pu, NbPd$_3$, D$_{022}$ and D$_{024}$ for Ag$_3$Au, C37 and MoPt$_2$ for Ag$_2$Au and AgAu$_2$, and L$_{12}$, D$_{022}$ and D$_{023}$ for AgAu$_3$, as shown in figure (1). The considerable degeneracy of the ground states indicates that only very small effective interactions exist between Ag and Ag, consistent with the experimentally observed complete solid solubility. For composition Ag$_4$Au, the structure L$_1^a$ is degenerate with the tie-line of the two-phase region Ag$_4$$\leftrightarrow$Ag$_3$Au. We conclude that further experimental and theoretical investigations are necessary to determine the behavior of AgAu.

To address the degenerate structures, we further investigate Ag$_3$Au, Ag$_2$Au, AgAu$_2$ and AgAu$_3$ with PAW-GGA potentials, as described in Section (III). With PAW, for composition Ag$_3$Au, L$_{12}$ is the most stable compound and D$_{022}$, D$_{023}$, Al$_3$Pu, NbPd$_3$, D$_{024}$ are higher by 0.9, 1.6, 2.2, 2.4, and 3.0meV/atom, respectively. For both composition Ag$_2$Au and AgAu$_2$, C37 is the most stable compound and MoPt$_2$ is higher by 1.9meV/atom and 4.3meV/atom, respectively. For composition AgAu$_3$, L$_{12}$ is the most stable compound and D$_{023}$ and D$_{024}$ are higher by 3.4meV/atom and 3.9meV/atom, respectively.

Other ab initio studies, relevant for this system, can be found in references [56–66].

| Composition % Au | Experimental (Massalski [9]) | Ab initio result |
|------------------|-----------------------------|------------------|
| 20               | short-range order $\geq 950^\circ$C | Ag$_4$Au-D$_1^a$/tie-line |
| 25               | short-range order $\geq 950^\circ$C | Ag$_3$Au/L$_1^2$/D$_{023}$/Al$_3$Pu/ (us-lda) |
|                  |                             | NbPd$_3$/D$_{022}$/D$_{024}$ (us-lda) |
|                  |                             | L$_{12}$ stable (paw-gga) |
|                  |                             | D$_{022}$~0.9meV/at. |
|                  |                             | D$_{023}$~1.6meV/at. |
|                  |                             | Al$_3$Pu~2.2meV/at. |
|                  |                             | NbPd$_3$~2.4meV/at. |
|                  |                             | D$_{024}$~3.0meV/at. |
|                  |                             | above L$_1^2$ (paw-gga). |
| 33.3             | short-range order $\geq 950^\circ$C | Ag$_3$Au-C37/MoPt$_2$ (us-lda) |
|                  |                             | C37 stable (paw-gga) |
|                  |                             | MoPt$_2$~1.9meV/at. |
|                  |                             | above C37 (paw-gga). |
| 50               | short-range order $\geq 950^\circ$C | AgAu-L$_1^0$ |
| 66.6             | short-range order $\geq 950^\circ$C | AgAu$_2$-C37/MoPt$_2$ (us-lda) |
|                  |                             | C37 stable (paw-gga) |
|                  |                             | MoPt$_2$~4.3meV/at. |
|                  |                             | above C37 (paw-gga). |
| 75.0             | short-range order $\geq 950^\circ$C | AgAu$_3$ |
|                  |                             | L$_{12}$/D$_{022}$/D$_{023}$ (us-lda) |
|                  |                             | L$_{12}$ stable (paw-gga) |
|                  |                             | D$_{022}$~3.4meV/at. |
|                  |                             | D$_{023}$~3.9meV/at. |
|                  |                             | above L$_1^2$ (paw-gga). |

FIG. 1. AgAu (Silver - Gold) ground state convex hull.
**Ag-Cd (Silver - Cadmium).** At composition AgCd₃ we find D₀₁₉ stable, while only disordered hcp solid solution has been reported at this composition. Hence, D₀₁₉, an ordered hcp superstructure, probably is stable at low temperature in this system. At composition AgCd₂ we find a previously unknown compound AgCd₂-ZrSi₂. The low temperature β', near AgCd stoichiometry, is reported to be ordered bcc in Massalski [9]. In particular, the Pauling File reports AgCd-B₂ [10,67–70]. We find B₂, B₁₉ and B₂₇ to have degenerate energies (B₁₉ is quite common for Cd alloys). The experimental phase diagram only displays solid solution on the Ag-rich side [9,10]. We find C₃⁷ at Ag₃Cd and a stable phase with stoichiometry Ag₃Cd. The ground state of Ag₃Cd is degenerate: three distinct structure (D₀₁ₙ, D₀₂₂, D₀₂₄) have similar energy. To address the degenerate structures, we further investigate AgCd and Ag₃Cd with PAW-GGA potentials, as described in Section (III). With PAW, for compound AgCd, B₁₉ is the most stable structure, and B₂⁷ and B₂ are higher by 2.8meV/atom and 3.4meV/atom, respectively. For compound Ag₃Cd, D₀₂₂ and D₀₂₄ are still degenerate ground states and D₀₁₉ is higher by only 2.2meV/atom. It is possible that these compounds have not yet been observed, or that they have low ordering temperatures.

| Ag-Cd system | Low Temperature Phases comparison chart |
|--------------|------------------------------------------|
| Composition | % Cd | Experimental (Massalski [9]) | Ab initio result |
| 25.0 | fcc solid solution | Ag₃Cd | D₀₁₉/D₀₂₂/D₀₂₄ (us-lda) D₀₂₃/D₀₂₄ (paw-gga) D₀₂₅=2.2meV/atom above D₀₂₃/D₀₂₄ (paw-gga) |
| 33.3 | fcc solid solution | Ag₃Cd-C₃⁷ |
| 48.0 to 50 | β'-bcc | AgCd-B₂/B₁₉/B₂₇ (us-lda) B₁₉ stable (paw-gga) B₂₇=2.8meV/atom B₂=3.4meV/atom above B₁₉ (paw-gga) |
| 66.6 | none | AgCd₂-ZrSi₂ |
| 64.5 to 81 | hcp solid solution | AgCd₃-D₀₁₉ |

**Ag-Mg (Silver - Magnesium).** The phase diagram of the system Ag-Mg is known with reasonable accuracy [9,10,71,72,75,77]. Our ab initio method confirms the stability of AgMg-B₂. In the Ag-rich side of the phase diagram, at stoichiometry Ag₃Mg, we find D₀₂₃ and D₀₂₄ to be degenerate. While Massalski [9] indicates Ag₃Mg to be L₁₂, it is known from detailed High Resolution Electronic Microscopy (HREM) that Ag₃Mg forms Long Period Superstructure (LPS) modifications of L₁₂ [73,74] (LPS D₀₂₃ is present in our library). For a detailed discussion of this system see Kulik et-al. [76]. L₁₂ is 15.2meV/atom above D₀₂₃/D₀₂₄. On the Mg-rich side, our library does not have prototypes at 80% Mg concentration, so we are not able to find any hexagonal AgMg₃ (with unknown prototype [75,77]). However we find a stable compound AgMg₃. Two phases, AgMg₃-D₀₈ and AgMg₃-D₀₁₉, have degenerate energies. This is important, since experiments suggest that AgMg₄ was probably identified as hexagonal AgMg₃ in early studies. Unfortunately, we cannot determine the correct ab initio solution since we lack the hexagonal AgMg₄ prototypes in our library. To address the degenerate structures, we further investigate Ag₃Mg and AgMg₃ with PAW-GGA potentials, as described in Section (III). For compound Ag₃Mg, with PAW, D₀₂₃ is the most stable compound (in agreement with [73,74,76]). D₀₂₄ and L₁₂ are 11.3meV/atom higher than D₀₂₃, respectively. In addition, for compound AgMg₃, D₀₁₉ is the most stable structure and D₀₈ is ~6.8meV/atom higher than D₀₁₉.

Other ab initio studies, relevant for this system, can be found in references [78–80].

| Ag-Mg system | Low Temperature Phases comparison chart |
|--------------|------------------------------------------|
| Composition | % Mg | Experimental (Massalski [9]) | Ab initio result |
| 25.0 | L₁₂ | Ag₃Mg-D₀₂₃/D₀₂₄ (us-lda) L₁₂=15meV/atom above D₀₂₃ stable (paw-gga) D₀₂₄~1.1meV/atom L₁₂~11.3meV/atom above D₀₂₃ (paw-gga) |
| 35.5 to 65.4 | B₂ | AgMg₃-B₂ |
| 75.8 to 78.2 | cF₈ (unknown) | AgMg₃ |
| 80.0 | hP₈ (unknown) | unavailable (see text) |

**FIG. 2.** AgCd (Silver - Cadmium) ground state convex hull.
Ag-Na (Silver - Sodium). The phase diagram of the system Ag-Na is known with reasonable accuracy and has only one intermetallic compound [9,10,83–85]. We confirm the stability of Ag$_2$Na-C15 and find almost all the other compounds to have positive formation energies. Both with US-LDA and PAW-GGA, Na-hcp is very slightly favored over Na-bcc and Na-fcc, in agreement with other first principle calculations [26–30]. At room temperature Sodium has the bcc structure, and undergoes a martensitic transformation below 35K, to a closed packed structure [31–38]. Therefore our results, Na-hcp stable and the very small energy differences with Na-bcc and Na-fcc, are consistent with the behaviour at low temperature.

| Composition | Experimental | Ab initio |
|-------------|--------------|-----------|
| % Na        | Massalski [9]| Ag$_2$Na-C15 |
| 33.0        | C15          |           |
**Ag-Pd (Silver - Palladium).** The system Ag-Pd has not been studied in great detail and no intermetallic compounds have been reported [9,10,41,88]. The solid is reported to be disordered fcc. At low temperature we find three stable compounds: AgPd-L1\(_1\), Ag\(_2\)Pd and Ag\(_3\)Pd. In our computations, for Ag\(_2\)Pd and Ag\(_3\)Pd, the ground states are degenerate: our best candidates are C49 or C37 for Ag\(_2\)Pd, and L1\(_2\) or D0\(_{22}\) for Ag\(_3\)Pd, as shown in figure (5). To address the degenerate structures, we further investigate Ag\(_2\)Pd and Ag\(_3\)Pd with PAW-GGA potentials, as described in Section (III). With PAW, for composition Ag\(_2\)Pd, C37 is the most stable compound and C49 is higher by 4meV/atom. For composition Ag\(_3\)Pd, L1\(_2\) and D0\(_{22}\) remain degenerate. In fact, D0\(_{22}\) has an energy 0.4meV/atom greater than L1\(_2\), too small compared to the numerical accuracy of the ab initio calculation.

Other ab initio studies, relevant for this system, can be found in references [89–93].

**Ag-Pd system**

| Composition \(\%\) Ag | Experimental (Massalski [9]) | Ab initio result |
|---------------------|---------------------------|-----------------|
| 50                  | solid solution            | AgPd-L1\(_1\)   |
| 66.6                | solid solution            | Ag\(_2\)Pd      |
|                     |                           | C37/C49 (us-lda) |
|                     |                           | C\(_{49}\) ~4meV/atom. |
|                     |                           | above C37 (paw-gga) |
| 75.0                | solid solution            | Ag\(_3\)Pd      |
|                     |                           | L1\(_2\)/D0\(_{22}\) (us & paw-gga) |

**Ag-Ti (Silver - Titanium).** The stability of AgTi\(_2\)-C11\(_b\) and AgTi-B11 is confirmed [9,10,100,101], and no other stable phases are found computationally. Hence, we conclude that the low temperature part of the phase diagram of AgTi is probably accurate.

**Ag-Ti system**

| Composition \(\%\) Ag | Experimental (Massalski [9]) | Ab initio result |
|---------------------|---------------------------|-----------------|
| 33.3                | C11\(_b\)                 | AgTi\(_2\)-C11\(_b\) |
| 50                  | B11                       | AgTi-B11 (\(\gamma\)CuTi) |

**FIG. 5.** AgPd (Silver - Palladium) ground state convex hull.

**FIG. 6.** AgTi (Silver - Titanium) ground state convex hull.
Ag-Y (Silver - Yttrium). The stability of AgY-B2 and Ag2Y-C11b is confirmed [9,10,102]. In the Ag-rich region, we do not determine the stability of Ag51Y14, since we do not have the prototype in our library [103,104]. Instead, we find Ag3Y with D0a structure stable with an energy ∼22meV/atom below the energy of a two-phase region Ag++Ag2Y. In the real system, the presence of Ag51Y14 probably makes structure D0a metastable.

In the Y-rich region we find AgY2-C37 degenerate with the two-phase region Y↔AgY (within ∼1.7meV/atom) as shown in figure (7).

| Ag-Y system | Low Temperature Phases comparison chart |
|-------------|-----------------------------------------|
| Composition | Experimental % Ag (Massalski [9]) result |
| 33.3        | two-phase region above 200°CAgY2-C37/tie-line |
| 50          | B2                                      |
| 66.6        | C11b                                    |
| 75          | two-phase region above 200°CAg3Y-D0a (uncertain) |
| 78.5        | Ag51Gd14 unavailable                     |

Ag-Zr (Silver - Zirconium). The phase diagram of Ag-Zr is known partially, and it has been estimated from thermodynamic properties [9,10,105,106]. The stability of the two known phases AgZr-B11 (γ-CuTi prototype) and AgZr2-C11b is confirmed by our calculation. In addition to the known intermetallic compounds, we find a stable phase Ag2Zr, which is not present in Massalski [9]: the C6 and C32 structures are degenerate. To conclude, we find AgZr3-FCC[001]AB3 degenerate with the two-phase region Zr↔AgZr2 (within ∼1.3meV/atom). To address the degenerate structures, we further investigate Ag2Zr with PAW-GGA potentials, as described in Section (III). With PAW, C32 is the most stable compound and C6 is 2meV/atom above C32.

| Ag-Zr system | Low Temperature Phases comparison chart |
|--------------|-----------------------------------------|
| Composition  | Experimental % Ag (Massalski [9]) result |
| 25.0         | two-phase region estimated above 700°CAgZr3 FCC[001]AB3/tie-line |
| 33.3         | C11b                                    |
| 50           | B11                                      |
| 66.6         | AgZr-B11 (γ-CuTi)                        |
|              | two-phase region estimated above 700°CAg2Zr C6/C32 (us-lda) |
|              | C32 stable (paw-gga)                     |
|              | C6~2meV/at. above C32 (paw-gga)          |

FIG. 7. AgY (Silver - Yttrium) ground state convex hull.

FIG. 8. AgZr (Silver - Zirconium) ground state convex hull.
Al-Sc (Aluminum - Scandium). The experimental phase diagram has compounds at compositions: Al₃Sc, Al₃Sc, AlSc, and AlSc₂ [9,10,107–109]. The ab initio technique confirms the stability of Al₃Sc-L1₂, Al₂Sc-C15, AlSc-B2, and AlSc₂-B8₂. In the Sc-rich region of the phase diagram, we find a new hexagonal stable phase AlSc₃-D₀₁₉, which is not present in Massalski [9]. Only very limited experimental data is available for this side of the phase diagram.

Other ab initio studies, relevant for this system, can be found in references [110–115].

Au-Cd (Gold - Cadmium). Several compounds have been reported for the system Au-Cd, and the phase diagram is known with reasonable accuracy [9,10,41,117,119,123–126]. We confirm β'-AuCd-B19 and the high-temperature phase β'-AuCd-B2 (with energy ∼6meV/atom higher than B19). At 25% Cd composition, we do not find the compound α₂Au₃Cd-Ag₃Mg because we do not have the proper prototype in our library. Instead, we find structures D₀₂₄, D₀₁₉, and Al₃Pu (Co₃V) with degenerate energies. Such structures have hexagonal lattices and they are candidates for the phase field α₂ which has been reported to be a long-period superstructure with hP lattice [9]. At 33% Cd composition, we find three phases Au₂Cd-C37, Au₂Cd-MoPt₂, and Au₄Cd-C₄₉ with energies 4meV/atom, 14meV/atom and 16meV/atom above the tie-line Au₃Cd ↔ AuCd, respectively. At 50% Cd composition, the prototype of the phase β''-AuCd is not known, but it is reported to have a hexagonal structure. For β'', we suggest two candidates: AuCd-L₁₀ and AuCd-FCC [201] (CH “40” in reference [262]), which have energies higher by 5.4meV/atom and 5.5meV/atom with respect to B19. None of these structures has hexagonal lattice type, and all our hexagonal prototypes have much higher energies.

At concentration ∼75% Cd, a stable phase ϵ', with unknown structure, is believed to exist [9]. We confirm the existence of a stable compound and our best prediction is AuCd₃-L₆₀. At concentration ∼82% Cd another stable phase η' is believed to exist. We are not able to confirm η'. In fact at 83.3% Cd, the phase with lowest energy is ∼60meV/atom higher than the two tie-line AuCd₄ ↔ Cd. To address the degenerate structures, we further investigate Au₃Cd with PAW-GGA potentials, as described in Section (III). Also with PAW, D₀₂₄, Al₃Pu and D₀₁₉ remain degenerate.
Au-Nb (Gold - Niobium). The phase diagram of the system Au-Nb is based on three known compounds (Au$_2$Nb, Au$_2$Nb$_3$, AuNb$_3$) [9,10,47,117,119,127–141]. We do not confirm the stability of phase Au$_2$Nb-C32 [9,10,47]. Instead of C32, we find a stable compound Au$_2$Nb-C6 and C32 with energy higher by ∼12 meV/atom with respect to C6. We can not conclude anything about stability of Au$_2$Nb$_3$ since our library does not contain any A$_2$B$_3$ prototype. The Nb-rich side of the experimental phase diagram is drawn with the assumption that AuNb$_3$-A15 is stable at low temperature (∼500°C) [9]. Our calculations suggest that AuNb$_3$-A15 might not be stable at low-temperature as it is ∼7 meV/atom above the two phase field AuNb$_2$+Nb. In addition, we find a stable phase AuNb$_2$ at 66.6% Nb composition, with bcc parent lattice, and space group Fmmm #69. The compound, labeled as BCC$_{AB}^{[011]}$, has AB$_2$ stacking along [011] direction. If the prototype BCC$_{AB}^{[011]}$ were not included in the calculation, the phase AuNb$_3$-A15 would be stable, as shown in figure (11). To conclude, we think it might be worthwhile to reconsider the thermodynamic modeling of the Nb-rich side of the phase diagram with the inclusion of AuNb$_2$-BCC$_{AB}^{[011]}$, to obtain the proper temperature and concentration ranges of phase A15. To address the disagreements with the experimental results, we further investigate Au$_2$Nb and AuNb$_3$ with PAW-GGA potentials, as described in Section (III). For the compound Au$_2$Nb C32 is the most stable compound and C6 is higher by 3.2 meV/atom. For composition AuNb$_3$, A15 is still unstable, being ∼6.5 meV/atom above the tie-line AuNb$_2$+Nb. The disagreement at composition AuNb$_3$ is further discussed in Section (IV).

**Au-Nb system**

| Composition % Nb | Experimental result (Massalski [9]) | Ab initio result |
|-----------------|-----------------------------------|-----------------|
| 33.3            | Au$_2$Nb-C6 (us-lda). C32 ∼12 meV/atom above C6 (us-lda). C32 stable (paw-gga). C6 ∼3.2 meV/atom above C32 (paw-gga). |     |
| 60              | Au$_2$Nb$_3$ (unknown) tH10 14/mmm unavailable |     |
| 66.6            | two-phase region (calculated) AuNb$_2$-BCC$_{AB}^{[011]}$ |     |
| 73 to 83        | A15 two-phase region AuNb$_2$+Nb. AuNb$_2$+Nb at ∼6.5 meV/atom above tie-line (us-lda). A15 is ∼6.5 meV/atom above tie-line (paw-gga). See Section (IV). |   |
Au-Pd (Gold - Palladium). Two ordered compounds have been suggested for the system Au-Pd in the fcc solid solution (Au,Pd): Au$_3$Pd and AuPd$_3$ [142–145]. The low-temperature part of the phase diagram has been constructed with the addition of a phase field AuPd that is believed to exist below $\sim 100^\circ$C [9,10,117,119]. In the Au-rich part of the phase diagram, we confirm the stability of a compound Au$_3$Pd, but we find three structures, D0$_{23}$, D0$_{22}$ and L1$_2$, with degenerate energy. At composition Au$_4$Pd, we find the structure D1$_a$ to be degenerate with the tie-line Au$+$Au$_3$Pd. At composition 33.3% Pd, we find a stable compound Au$_2$Pd, but again, two structures C49 and C37 are degenerate. At composition 50%, we confirm the existence of a stable phase AuPd. The prototype is not known. Our best guess is AuPd-FCC$_{[201]}^{[201]}$ (CH “40” in reference [262]), and L1$_0$ with an energy higher by 8meV/atom with respect to FCC$_{[201]}^{[201]}$. Finally, in the Pd-rich part of the phase diagram, we find a compound AuPd$_3$ to be degenerate with the tie-line of the two-phase region AuPd$+$Pd. For this compound, three structures, D0$_{23}$, D0$_{22}$ and L1$_2$, have degenerate energies. The considerable degeneracy of the ground states is indicative of week effective interactions and consistent with the significant miscibility of the two elements inside each other. The near degeneracy of structures such as D0$_{23}$, D0$_{22}$ and L1$_2$, which are related to each other by periodic antiphase boundaries, indicates that more complicated Long Period Superstructures (LPS) might be present. To address the small energy differences between structures, we further investigate Au$_3$Pd, Au$_2$Pd, AuPd, and AuPd$_3$ with PAW-GGA potentials, as described in Section (III). For the compound Au$_3$Pd, D0$_{23}$ is the most stable compound and D0$_{22}$ and L1$_2$ are higher by 9.4meV/atom and 12.7meV/atom, respectively. For the compound AuPd$_3$, D0$_{23}$ is the most stable compound and L1$_2$ and D0$_{22}$ are higher by 1.8meV/atom and 4.8meV/atom, respectively. Also with PAW, for the compound Au$_2$Pd, C37 and C49 remain degenerate. For the compound AuPd, FCC$_{[201]}^{[201]}$ is the most stable compound and L1$_0$ is higher by 10.8meV/atom.

Another ab initio study, relevant for this system, can be found in reference [60].
Au-Sc (Gold - Scandium). The phase diagram of the system Au-Sc is known only in the Au-rich region, and a total of three intermetallic compounds have been reported: Au₄Sc, Au₃Sc, and AuSc [9,10,119,153–158]. At 20% Sc, we confirm Au₄Sc-D₁₄. At 25% Sc, we find a two-phase region, in agreement with experiments. In fact, Au₃Sc-D₀ₐ, the structure with lowest energy, is higher by ∼7meV/atom with respect to the tie-line Au₄Sc-D₁₄ ↔ Au₂Sc-C₁₁₆. At 33% and at 50% concentrations of Sc, we find two stable phases Au₃Sc and AuSc, but in both cases two structures are degenerate C₁₁₆ and MoPt₂ for Au₂Sc, and B₂ and B₁₉ for AuSc. The experimental results indicate Au₂Sc-C₁₁₆ and AuSc-B₂. The AuSc-C₃₇ (Co₂Si prototype) compound has been speculated to exist by similarity with other Au-(Rare Earth)₂ systems [153]. Our ab initio method confirms AuSc-C₃₇. To address the degenerate structures, we further investigate Au₂Sc and AuSc with PAW-GGA potentials, as described in Section (III). For compound Au₂Sc, with PAW, Au₂Sc-C₁₁₆ is the most stable compound and Au₂Sc-MoPt₂ is higher by 1.0meV/atom. In addition, for compound AuSc, Au₂Sc-B₂ is the most stable compound and Au₂Sc-B₁₉ is higher by 2.2meV/atom. While these energy differences are very small, both calculations are in agreement with experiments.

FIG. 12. AuPd (Gold - Palladium) ground state convex hull.
Au-Ti (Gold - Titanium). Five ordered compounds have been reported for the system Au-Ti at low temperature: Au₄Ti, Au₂Ti, αAuTi, βAuTi, and AuT₃ [9,10,48,101,160–169,311,283,321,298]. We confirm the stability of αAuTi-B₁₁, Au₄Ti-D₁₉ and AuT₃-A₁₅. At 25% Ti, we find a two-phase region, in agreement with experiments. In fact, Au₄Ti-D₀₆, the structure with lowest energy, is higher by ~11meV/atom with respect to the tie-line Au₄Ti↔Au₂Ti. For compound Au₂Ti, the experimental phase is C₁₁₆. At such composition we find two structures with degenerate energies: Au₂Ti-C₁₁₆ and Au₂Ti-MoPt₂. We do not confirm an off-stoichiometry stable phase βAuTi-B₁₉, because we do not have such prototype in our library. The stoichiometric B₁₉ has an energy ∼50meV/atom above αAuTi-B₁₁. At 42.8% concentration of Ti, we find a previously unknown compound Au₄T₃-Cu₄T₃. This compound is degenerate with the tie-line of the two-phase field Au₂Ti↔AuTi, therefore its existence is uncertain. To address the degenerate structures Au₂Ti-C₁₁₆/MoPt₂ and the energy difference between αAuTi-B₁₁ and βAuTi-B₁₉ phases, we further investigate Au₂Ti and AuTi with PAW-GGA potentials, as described in Section (III). With PAW, Au₂Ti-C₁₁₆ is the most stable compound and Au₂Ti-MoPt₂ is higher by 3.7meV/atom. For phase AuTi, AuTi-B₁₁ is the most stable compound (as in the ultrasoft pseudopotential case), and AuTi-B₁₉ is higher by 53.6meV/atom.

Au-Ti system

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|-------------------------------|------------------|
| 18-21       | D₁₉                           | Au₄Ti-D₁₉         |
| 25          | two-phase region above 500°C  | two-phase region |
|             | Au₄Ti-D₀₆, ~11meV/atom above Au₄Ti↔Au₂Ti. |        |
| 33.3        | C₁₁₆                          | Au₂Ti            |
|             | C₁₁₆/MoPt₂ (us-lda)           | C₁₁₆, stable (paw-gga) |
|             | MoPt₂~3.7meV/atom above C₁₁₆, (paw-gga). |                  |
| 42.8        | two-phase region above 500°C  | Au₄T₃            |
|             | Cu₄T₃/tie                      |                  |
| 50          | αAuTi-B₁₁                     | AuTi-B₁₁         |
| 50-51       | βAuTi-B₁₉                     | B₁₉~50meV/atom, B₁₉~53.6meV/atom (us-lda) above B₁₁ (paw-gga). |
| 38-52       | γAuTi-B₂                     | B₂~135meV/atom, above B₁₁ (us-lda). |
| 75          | A₁₅                           | AuT₃-A₁₅         |
Au-Y (Gold - Yttrium). Four intermetallic compounds have been reported for the system Au-Y: Au$_3$Y, Au$_2$Y, AuY, and AuY$_3$ [9,10,119,155–158,170–173]. With our ab initio method, we confirm stability of Au$_3$Y-D0$_a$ and Au$_2$Y-C11$_b$. At equal composition, AuY, we do not confirm B2: we find a stable B33 and phase B2 higher by $\sim$26meV/atom. No experimental compound is reported for composition AuY$_2$, though we obtain AuY$_2$-C37. At 75% composition of Y, we do not find a stable AuY$_3$ compound reported experimentally [10,156]: the structure with lowest energy is AuY$_3$-D0$_{11}$ with an energy higher by $\sim$30meV/atom with respect to the tie-line. We further investigate AuY with PAW-GGA potentials, as described in Section (III). With PAW, B33 is the most stable compound and B2 is $\sim$25meV/atom higher than B33. The disagreement at composition AuY is further discussed in Section (IV).

Au-Y system

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|-----------------------------|------------------|
| % Y | | |
| 25 | D0$_a$ | Au$_3$Y-D0$_a$ |
| 34.3 | C11$_b$ | Au$_2$Y-C11$_b$ |
| 50 | B2 | Au$_3$Y-B33 (us-lda) B2$\sim$26meV/atom. above B33 (us-lda). B33 stable (paw-gga) B2$\sim$25meV/atom. above B33 (paw-gga). See Section (IV). |
| 66.6 | not studied | AuY$_2$-C37 |
| 75 | hyp (uncertain prototype) | nothing stable D0$_{11}$ $\sim$30meV/atom. above tie-line |

FIG. 14. AuTi (Gold - Titanium) ground state convex hull.

FIG. 15. AuY (Gold - Yttrium) ground state convex hull.
Au-Zr (Gold - Zirconium). Several ordered compounds have been reported for the system Au-Zr: Au₄Zr, Au₅Zr, Au₆Zr, Au₁₀Zr₇, Au₄Zr₅, Au₂Zr₂, and AuZr₃ [9,10,163,174–177]. Our ab initio method confirms the stability of Au₃Zr-D0ₐ, Au₂Zr-C11ₖ and AuZr₃-A15. At composition AuZr₂, Massalski and the Pauling file report C11ₖ and CuZr₂ type compounds, respectively [9,10]. C11ₖ (MoSi₂ prototype) and CuZr₂ are very similar structures, both tetragonal (tI₆) and with the same space group #139. C11ₖ belongs to the bcc superstructure family while CuZr₂, a slightly distorted version of C11ₖ, is a closed packed structure [10], therefore, within the formalism of the atomic environments, they represent two different prototypes [10]. Our library contains both prototypes. However, in our calculations, AuZr₂-C11ₖ and AuZr₂-CuZr₂ are both unstable with degenerate energies higher by ∼20meV/atom with respect to the tie-line AuZr↔AuZr₃. We can not say anything about Au₄Zr, Au₁₀Zr₇ and Au₄Zr₅, because our library lacks prototypes at the proper concentrations. At AuZr composition we find two structures with degenerate energies: B11 and FCC[001] A₂B₂[001] [001]. This prediction is unreliable because such compounds appear in the two-phase region Au₁₀Zr₇↔Au₄Zr₅, that we are not able to describe properly. At 42.8% concentration of Zr, we find Au₄Zr₃-Cu₄Ti₃. As before, this prediction is unreliable because it appears in the two-phase region Au₂Zr↔Au₁₀Zr₇, that we are not able to describe. To conclude, the inclusion of prototypes of Au₁₀Zr₇ and Au₄Zr₅ in our calculations, might change the stability of the predicted AuZr and AuZr₃ phases. To address the degenerate structures, we further investigate AuZr₂ with PAW-GGA potentials, as described in Section (III). With PAW, AuZr₂-CuZr₂ and AuZr₂-C11ₖ are still degenerate, but become stable with an energy 6.6meV/atom lower than the tie-line AuZr↔AuZr₃.

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|-------------------------------|-----------------|
| 20          | Au₄Zr                         | unavailable     |
| 25          | Au₂Zr                         | AuZr-D0ₐ        |
| 33.3        | C11ₖ                          | AuZr-C11ₖ       |
| 42.8        | two-phase region               | Au₂Zr↔Au₁₀Zr₇   |
|             |                                | unreliable, see text. |
| 45          | Au₁₀Zr₇                        | unavailable     |
| 50          | two-phase region               | AuZr-B11/FCC[001] |
|             |                                | unreliable, see text. |
| 66.6        | CuZr₂ [10]                    | two-phase region (us-lda) |
|             |                                | AuZr₂-CuZr₂/C11ₖ |
|             |                                | ∼20meV/atom above tie-line |
|             |                                | AuZr↔AuZr₃ (us-lda). CuZr₂/C11ₖ stable |
|             |                                | ∼6.6meV/atom below |
|             | AuZr↔AuZr₃ (paw-gga).          |                 |
| 75          | A15                           | AuZr₃-A15       |

FIG. 16. AuZr (Gold - Zirconium) ground state convex hull.
Cd-Nb (Cadmium - Niobium). The phase diagram for the system Cd-Nb is not known [9]. It has been reported that Cd$_3$Nb has L1$_2$ prototype [178]. However, we are not able to find any stable compound, so we propose that the system is not compound-forming, but will display low-temperature immiscibility. In our calculations, Cd$_3$Nb-L1$_2$ is $\sim$70meV/atom higher in energy than the phase separation of Cd$\leftrightarrow$Nb. In addition, the structure with the lowest formation energy is a bcc superstructure at composition CdNb and energy $\sim$55meV/atom higher than Cd$\leftrightarrow$Nb. To address the disagreement with the experimental result, we further investigate the relevant compounds with PAW-GGA potentials, as described in Section (III). With PAW, Cd$_3$Nb-L1$_2$ is $>100$meV/atom higher in energy than the tie-line Cd$\leftrightarrow$Nb. The structure with the lowest formation energy is a bcc superstructure at composition CdNb, and energy $\sim$58meV/atom above Cd$\leftrightarrow$Nb. It is unlikely that the ab initio calculations have such a large errors. The disagreement at composition Cd$_3$Nb is further discussed in Section (IV).

Cd-Pd (Cadmium - Palladium). Four Cd-Pd compounds have been identified experimentally at low-temperature ($\gamma, \gamma_1, \gamma'$ and $\beta_1$ [179,180,9]). However, the phase boundaries are unknown. We confirm $\beta_1$-CdPd-L1$_0$. In the Cd-rich part of the phase diagram, we find Cd$_3$Pd (near $\gamma'$ at 74%E). We are not able to determine the exact structure of Cd$_3$Pd but our best candidates are D0$_{19}$, D0$_{24}$, NbPd$_3$-type, and Al$_3$Pu-type (Co$_3$V). In the Pd-rich part of the phase diagram, we find a stable phase CdPd$_3$. As before, we cannot determine its structure, precisely. Our guesses are D0$_{22}$ and NbPd$_3$-type, which have degenerate energies. At concentration 33.3% Cd, we find a new compound CdPd$_2$-C37 which is not present in Massalski [9]. To address the degenerate structures, we further investigate the relevant compounds with PAW-GGA potentials, as described in Section (III). Compounds CdPd$_3$, D0$_{22}$ and CdPd$_3$-NbPd$_3$ remain degenerate with PAW (the energy difference is 1.1meV/atom). In addition, for Cd$_3$Pd composition, NbPd$_3$/Al$_3$Pu remain degenerate compounds, and D0$_{22}$, D0$_{19}$, D0$_{24}$ are higher by 4.7meV/atom, 5.6meV/atom, 6.7meV/atom, respectively.
Cd-Pt (Cadmium - Platinum). The phase diagram of the system Cd-Pt is partially known [181,9], with several compounds of unknown structure. We confirm the stability of phase $\alpha'$-CdPt-L1$_0$. In the Cd-rich part of the phase diagram, the prototypes of Cd$_2$Pt and $\gamma_1$ are unknown. For Cd$_2$Pt, our best guess are two degenerate structures, Cd$_2$Pt-C37 and Cd$_2$Pt-C16, which are also degenerate with the hull. For $\gamma_1$, at stoichiometry Cd$_3$Pt, we find two degenerate structures D0$_{11}$, D0$_a$ and D0$_{22}$. In the Pt-rich part of the phase diagram, we do not find a stable compound $\alpha'$-CdPt$_3$-L1$_2$. Instead, we find a stable orthorhombic CdPt$_3$ with fcc superstructure and Cmmm #65 space group. The prototype, labeled as CdPt$_3$$_{\text{proto}}$, is described in Appendix (XI). In addition, CdPt$_3$-L1$_2$ is found with an energy $\sim$25meV/atom above CdPt$_3$$_{\text{proto}}$. To address the degenerate structures and the disagreement with experimental results for compound CdPt$_3$, we further investigate CdPt$_3$, Cd$_2$Pt and Cd$_3$Pt with PAW-GGA potentials, as described in Section (III). With PAW, CdPt$_3$-CdPt$_3$$_{\text{proto}}$ is the most stable structure and CdPt$_3$-L1$_2$ higher by $\sim$10.4meV/atom. For compound Cd$_2$Pt, C16 is the most stable compound and C37 is $\sim$33meV/atom higher than C16. For compound Cd$_3$Pt, D0$_{11}$ is the most stable compound and D0$_a$ and D0$_{22}$ are higher by $\sim$52meV/atom and $\sim$60meV/atom, respectively. The disagreement at composition CdPt$_3$ is further discussed in Section (IV).

### Cd-Pt system

| Composition | Experimental | Ab initio |
|-------------|--------------|-----------|
| % Pt (Massalski [9]) | result | |
| ~13 to 17 | $\gamma$-(unknown) | two-phase region |
| 24 to 26 | $\gamma_1$-(unknown) | Cd$_3$Pt |
| | | D0$_{11}$/D0$_{a}$/D0$_{22}$ (us-lda) |
| | | D0$_{11}$ stable (paw-gga) |
| | | D0$_a$ $\sim$53meV/atom |
| | | D0$_{22}$ $\sim$66meV/atom |
| | | above D0$_{11}$ (paw-gga) |
| ~26 to 28 | $\gamma_2$-(unknown) | unavailable |
| ~31 to 38 | Cd$_2$Pt-(unknown) | Cd$_3$Pt |
| | | C37/C16/tie-line (us-lda) |
| | | C16 stable (paw-gga) |
| | | C37 $\sim$33meV/atom |
| | | above C16 (paw-gga) |
| ~49 to 51 | $\alpha'$-L1$_0$ | CdPt-L1$_0$ |
| ~75 | $\alpha'$-L1$_2$ | Appendix (XI) |
| | | L1$_2$ $\sim$25meV/atom |
| | | above CdPt$_3$$_{\text{proto}}$ |
| | | CdPt$_3$$_{\text{proto}}$ stable (paw-gga) |
| | | L1$_2$ $\sim$10.4meV/atom above CdPt$_3$$_{\text{proto}}$ (paw-gga) |
| | | See Section (IV). |
Cd-Rh (Cadmium - Rhodium). No experimental phase diagram is available [9]. With our ab initio technique we find two stable compounds, Cd$_2$Rh-C$_{37}$, and Cd$_3$Rh. Our best guesses for Cd$_3$Rh are Cd$_3$Rh-D$_{0_{24}}$ and Cd$_3$Rh-Al$_3$Pu-type (Co$_3$V), which have degenerate energies ($2\text{meV/atom difference}$). Interesting metastable phases are Cd$_3$Rh-D$_{0_{19}}$, (11 meV/atom above Cd$_3$Rh), and Cd$_3$Rh-C$_{49}$ (8meV/atom above Cd$_3$Rh-C$_{37}$). To address the degenerate structures, we further investigate Cd$_3$Rh with PAW-GGA potentials, as described in Section (III). With PAW, Cd$_3$Rh-Al$_3$Pu is the ground state, and Cd$_3$Rh-D$_{0_{24}}$ has an energy 5meV/atom higher.

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|------------------------------|------------------|
| % Cd        |                               |                  |
| 66.6        | not studied                   | Cd$_2$Rh-C$_{37}$|
|             |                               | C$_{49}$ metastable|
| 75          | not studied                   | Cd$_3$Rh-D$_{0_{24}}$/Al$_3$Pu (us-lda) |
|            |                               | D$_{0_{19}}$/Al$_3$Pu (us-lda) |
|             |                               | above D$_{0_{24}}$/Al$_3$Pu (us-lda) |
|             |                               | Al$_3$Pu stable (paw-gga) |
|             |                               | D$_{0_{24}}$ ~ 5meV/atom. |
|             |                               | above Al$_3$Pu (paw-gga) |

Cd-Ti (Cadmium - Titanium). Little is known for the system Cd-Ti at high-temperature [9,10,183,184]. At low temperature only two stable intermetallic compounds have been reported [184]. We confirm the stability of Ti$_2$Cd-C$_{11_b}$. At composition CdTi, Massalski and the Pauling file, report B11 and CdTi compounds, respectively [9,10]. B11 ($\gamma$CuTi prototype) and CdTi are very similar structures, both tetragonal (tp4) and with the same space group #129. B11 belongs to the bcc superstructure family while CdTi, a slightly distorted version of B11, is a closed packed structure [10]. Therefore, within the formalism of the atomic environments, they represents two different prototypes [10]. The ab initio calculation is able to relax one structure into the other, easily. For CdTi we confirm the experimental results. In addition, at concentration 42.8%Cd, we find a compound Cd$_3$Ti$_4$Cu$_4$Ti$_3$, degenerate with the tie-line of the two-phase region CdTi$_2$↔CdTi. We have not found any other stable or metastable compound: we conclude that the low temperature part of the phase diagram is complete. Note that this system is very similar to Ag-Ti.

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|------------------------------|------------------|
| % Cd        |                               |                  |
| 33.3        | C$_{11_b}$                    | CdTi$_2$-C$_{11_b}$|
| 42.8        | two-phase region              | Cd$_3$Ti$_4$Cu$_4$Ti$_3$/tie-line |
| 50          | B11                          | CdTi-B11 (CdTi) |

FIG. 19. CdRh (Cadmium - Rhodium) ground state convex hull.

FIG. 20. CdTi (Cadmium - Titanium) ground state convex hull.
Cd-Y (Cadmium - Yttrium). The stability of compounds YCd-B2, YCd2-C6 and YCd3 (Cd3Er prototype) [9,10,185–187] is confirmed. The Yttrium-rich side of the phase diagram is poorly known. In that region we find two degenerate phases Y2Cd-C49 and Y2Cd-C37, both of which are close to the energy of the two phase region Y↔CdY (figure (21)). We do not find any other stable or metastable phase. To address the degenerate structures, we further investigate Y2Cd with PAW-GGA potentials, as described in Section (III). With PAW, C37 is the most stable compound and C49 is higher by 7.7meV/atom.

Another ab initio study, relevant for this system, can be found in reference [188].

Cd-Zr (Cadmium - Zirconium). The Cd-Zr system is poorly characterized [49,9,189], and compounds have been identified at four compositions Cd3Zr, Cd3Zr, CdZr, and CdZr2. Massalski [9] reports Cd3Zr-L10-AuCu, which we consider a misprint for Cd3Zr-L12-AuCu3, while CRYSTMET and Pauling File databases [10,11] report Cd3Zr-D01-βCu3Ti from reference [190]. We confirm the stability of Cd3Zr-L12 and CdZr2-C11b. At composition CdZr, Massalski and the Pauling file, report B11 and CdTi compounds, respectively [9,10]. B11 (γCuTi prototype) and CdTi are very similar structures, both tetragonal (tP4) and with the same space group #129. B11 belongs to the bcc superstructure family while CdTi, a slightly distorted version of B11, is a closed packed structure [10]. Therefore, within the formalism of the atomic environments, they represent two different prototypes [10]. The ab initio calculation is able to relax one structure into the other, easily. For CdZr, we find CdZr-L10 instead of CdZr-B11, which has an energy ~18meV/atom higher than L10. The prototype of Cd2Zr is not known: our best guess is Cd2Zr-C11b. In addition, we find a stable compound CdZr3-A15 not present in Massalski [9], and a metastable L12 which is 8.5meV/atom higher than A15. To address the disagreement with the experimental results for compound CdZr, we further investigate L10 and B11 with PAW-GGA potentials, as described in Section (III). With PAW, CdZr-B11 is the most stable compound and CdZr-L10 is higher by 13meV/atom.
Mo-Nb (Molybdenum - Niobium). The system MoNb has not been studied in great detail and no experimental intermetallic compounds have been found [9,10,47,197]. A bcc solid solution is reported from 2400°C up to the melt. We predict four stable compounds at low temperature: MoNb$_2$-C11$_b$, MoNb-B2, Mo$_2$Nb-C11$_b$, and Mo$_3$Nb-D0$_3$, as shown in figure (23).

Other ab initio studies, relevant for this system, can be found in references [90,198–200].

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|-------------------------------|-----------------|
| 33.3% Mo    | not studied                   | MoNb$_2$-C11$_b$|
| 50% Mo      | not studied                   | MoNb-B2         |
| 66.6% Mo    | not studied                   | Mo$_2$Nb-C11$_b$|
| 75% Mo      | not studied                   | Mo$_3$Nb-D0$_3$|

Mo-Nb system

| Low Temperature Phases comparison chart |
|----------------------------------------|
| a | b | c | d |

FIG. 22. CdZr (Cadmium - Zirconium) ground state convex hull.

FIG. 23. MoNb (Molybdenum - Niobium) ground state convex hull.
Mo-Pd (Molybdenum - Palladium). The phase diagram of this alloy is known from experimental investigations and thermodynamic calculations [9,10,46,51,201]. The only compound is at composition MoPd$_2$ and is listed in Massalski as having approximately the MoPt$_2$ structure [9,10,201]. Our \textit{ab initio} method finds that the MoPt$_2$ structure is 8meV/atom higher than MoPd$_2$-ZrSi$_2$. In addition, we find a stable phase MoPd$_4$-D$_{1a}$ (MoNi$_4$ prototype), previously unknown.

| Composition | Experimental (Massalski [9]) | \textit{Ab initio} result |
|-------------|-------------------------------|---------------------------|
| % Pd        |                               |                           |
| 66 to 67    | \textasciitilde MoPt$_2$       | MoPd$_2$-ZrSi$_2$         |
| 80          | disorder fcc Pd-A1            | MoPd$_4$-D$_{1a}$         |

Mo-Pt (Molybdenum - Platinum). The phase diagram of this alloy is known from experimental investigations and thermodynamic modeling [9,10,201–210,277]. We confirm the stability of MoPt-B$_{19}$ and MoPt$_2$ (with MoPt$_2$ prototype). In the Pt-rich part of the phase diagram, we find a compound MoPt$_3$-D$_{1a}$ (MoNi$_3$ prototype), previously unknown. The observed high-temperature phase A$_{15}$, reported as Mo$_6$Pt in Massalski [9] and as Mo$_3$Pt$_{0.8}$ in the Pauling File [10], is off-stoichiometry. Our \textit{ab initio} method finds a stoichiometric Mo$_3$Pt-A$_{15}$ to be \textasciitilde 45meV/atom above the two-phase region Mo$+$MoPt-B$_{19}$. For a detailed experimental study of such A$_{15}$ phase, see reference [210].

| Composition | Experimental (Massalski [9]) | \textit{Ab initio} result |
|-------------|-------------------------------|---------------------------|
| % Pt        |                               |                           |
| 18.5        | Mo$_6$Pt-A$_{15}$ [9]         | Mo$_3$Pt-A$_{15}$         |
| 20          | Mo$_3$Pt$_{0.8}$-A$_{15}$ [10] | \textasciitilde 45meV/atom above \textasciitilde 1200$^\circ$C |
| 31.5 to 45  | \textasciitilde D$_{019}$     | unavailable at such composition |
| 50          | B$_{19}$                      | MoPt-B$_{19}$             |
| 66.6        | MoPt$_2$                      | MoPt$_2$                  |
| 80          | two-phase region              | MoPt$_3$-D$_{1a}$         |

**FIG. 24.** MoPd (Molybdenum - Palladium) ground state convex hull.

**FIG. 25.** MoPt (Molybdenum - Platinum) ground state convex hull.
Mo-Rh (Molybdenum - Rhodium). The phase diagram of the system Mo-Rh is known above \( \sim 900^\circ \text{C} \) and is based on thermodynamic calculations and experimental results [9,10,51,211–214]. We confirm the stability of the two known compounds MoRh-B19 [9] and MoRh\(_3\)-CdMg\(_3\) [10,213]. At concentration 66.6% Rh, we find the stable phase MoRh\(_2\)-C37 (prototype Co\(_2\)Si), previously not identified [9].

| Composition | Experimental (Massalski [9]) | \( \text{Ab initio} \) result |
|-------------|-----------------------------|-----------------------------|
| \( \sim50 \) | B19                         | MoRh-B19                    |
| 66.6        | two-phase region            | Mo\(_2\)Rh-C37              |
| \( \sim75 \) | CdMg\(_3\) [10,213]         | MoRh\(_3\)-CdMg\(_3\)       |

FIG. 26. MoRh (Molybdenum - Rhodium) ground state convex hull.

Mo-Ru (Molybdenum - Ruthenium). The phase diagram of this system is known at medium and high-temperature [9,10,215]. There is a \( \sigma \) phase around 38% Ru, which is quite common when bcc (Mo) and hcp (Ru) elements are mixed. We are not able to confirm the \( \sigma \) phase since we do not have the proper prototype in our library. At concentration 75% Ru, we find the stable phase MoRu\(_3\)-D0\(_{19}\) (formation energy \( \sim 60\text{meV/atom} \)), not present in Massalski [9], indicating that it might be a low-temperature ordered structure.

Another \textit{ab initio} study, relevant for this system, can be found in reference [216].

| Composition | Experimental (Massalski [9]) | \( \text{Ab initio} \) result |
|-------------|-----------------------------|-----------------------------|
| 75          | disorder hcp Mo\(_2\)Ru-A3 above 800\(^\circ\)C | MoRu\(_3\)-D0\(_{19}\) |

FIG. 27. MoRu (Molybdenum - Ruthenium) ground state convex hull.
Mo-Ti (Molybdenum - Titanium). To our knowledge, no intermetallic compounds have been reported for the system Mo-Ti [9,10,48,218–220], and it is considered a non-compound forming system [10,11]. In contrast to the experimental assessment, we find seven stable compounds. Four of these have bcc superstructures: orthorhombic MoTi₃, degenerate with the two-phase region Ti++MoTi₂, with space group Immm #71 and prototype MoTi₃/proto (Appendix (XI)); orthorhombic Mo₅Ti with space group Immm #71 and prototype Mo₅Ti/proto (Appendix (XI)); trigonal MoTi₂-BCC[211]AB₂ and orthorhombic MoTi with space group Imma #74 and prototype MoTi/proto (Appendix (XI)). In addition, we find a stable compound Mo₂Ti-C11b, a compound Mo₅Ti-D1ₐ degenerate with the tie-line, and finally a monoclinic MoTi which has space group C₂/m #12 and prototype Mo₅Ti/proto (Appendix (XII)). Given the relatively large value of the formation energy, the experimental miscibility gap is surprising. This system warrants further study to sort out the apparent discrepancy between experiments and ab initio computation.

Another ab initio study, relevant for this system, can be found in reference [221].

Mo-Zr (Molybdenum - Zirconium). Not much is known of the system Mo-Zr to produce a reliable phase diagram [9,10,49]. We confirm the stability of the only known compound Mo₂Zr-C15. Experimentally, the Zr-rich side of the phase diagram has not been explored in detail at low temperature, and it is reported to have a two-phase region Mo₂Zr-C15+(αZr)-A₃ above 400°C. However, we find two possible new compounds: the orthorhombic phase MoZr₃ with space group Imma #74, prototype MoZr₃/proto (Appendix (XI)), and the monoclinic compound MoZr₂-Mo₅Ti/proto with space group C2/m #12, and prototype Mo₅Ti/proto (Appendix (XII)). Both compounds MoZr₃/proto and MoZr₂-Mo₅Ti/proto are quasi-degenerate with respect to the two-phase region Mo₂Zr+(αZr). Hence, the existence of MoZr₃/proto and MoZr₂-Mo₅Ti/proto is uncertain. It is useful mentioning that we find a metastable orthorhombic phase MoZr with space group Imma #74 and prototype similar to MoTi/proto (Appendix (XI)) only ~2meV/atom above the tie-line Mo₂Zr+(αZr).

Another ab initio study, relevant for this system, can be found in reference [110].
**Nb-Pd (Niobium - Palladium).** The Pd-Nb phase diagram is known with reasonable accuracy in the Pd-rich region \[9,10,47,259\]. The stability of the experimental phase \(\text{NbPd}_2\)-\(\text{MoPt}_2\) and \(\alpha\text{NbPd}_3\)-\(\text{D}0_{22}\) is confirmed. In the Nb-rich region, at concentration 33% Nb, we find an orthorhombic compound \(\text{NbPd}_2\)-\text{BCC}\([011]\) type, \(\text{MoPt}_2\) not present in Massalski [9]. The energy of this phase is \(\sim 11\text{meV/atom}\) below the tie-line of the two-phase region \(\text{Nb} \leftrightarrow \text{NbPd}_2\).

Another *ab initio* study, relevant for this system, can be found in reference [224].

![ Nb-Pd system](image)

### Nb-Pd system

| Composition | Experimental (Massalski [9]) | *Ab initio* result |
|-------------|------------------------------|--------------------|
| 33.3        | two-phase region above 700°C | \(\text{NbPd}_2\)-\text{BCC}\([011]\) |
| 66.6        | \(\text{MoPt}_2\)            | \(\text{NbPd}_2\)-\(\text{MoPt}_2\) |
| 75          | \(\alpha\text{-D}0_{22}\)     | \(\text{NbPd}_3\)-\(\text{D}0_{22}\) |

**FIG. 30.** NbPd (Niobium - Palladium) ground state convex hull.

**Nb-Pt (Niobium - Platinum).** Several intermetallic compounds have been reported for the system Nb-Pt \[9,10,47,225-229\]. We confirm the experimental phases \(\text{Nb}_3\text{Pt}-\text{A}15\) and \(\alpha\text{NbPt}_3\)-\(\text{D}0_{22}\) (\(\beta\text{Cu}_3\text{Ti}\) prototype). The prototype of \(\text{NbPt}_2\) is not reported in Massalski [9] (orthorhombic \(\text{O}1\), with space group \(\text{Immm}\)). We find \(\text{NbPt}_2\)-\(\text{MoPt}_2\), in agreement with references [10,227,228]. At 50% concentration we do not confirm the stability of \(\text{NbPt}-\text{B}19\). Instead of \(\text{B}19\) we find \(\text{NbPt}-\text{L}1_0\), and \(\text{B}19\) to be higher by \(\sim 11\text{meV/atom}\) above \(\text{L}1_0\). It is possible that \(\text{L}1_0\) is a ground state and \(\text{B}19\) a high-temperature state. We can not say anything about the \(\sigma\)-phase \(\text{D}8_b\) since we do not have such prototype in our library. We further investigated \(\text{NbPt}-\text{L}1_0\) and \(\text{NbPt}-\text{B}19\) with PAW-GGA potentials, as described in Section (III). With PAW, \(\text{L}1_0\) is the most stable compound and \(\text{B}19\) is \(\sim 18.5\text{meV/atom}\) higher than \(\text{L}1_0\).

![ Nb-Pt system](image)

### Nb-Pt system

| Composition | Experimental (Massalski [9]) | *Ab initio* result |
|-------------|------------------------------|--------------------|
| 19 to 28    | \(\text{A}15\)              | \(\text{Nb}_3\text{Pt}-\text{A}15\) |
| 31 to 38    | \(\text{D}8_b\)              | unavailable |
| \(\sim 50\) | \(\text{Nb}_{1-x}\text{Pt}_{1+x}\)-\(\text{B}19\) | \(\text{NbPt-L}1_0\) |
| \(\sim 67\) | \(\text{MoPt}_2\)           | \(\text{NbPt}_2\)-\(\text{MoPt}_2\) |
| \(\sim 76\) | \(\text{D}0_{22}\)           | \(\text{NbPt}_2\)-\(\text{D}0_{22}\) |

**FIG. 31.** NbPt (Niobium - Platinum) ground state convex hull.
**Nb-Rh (Niobium - Rhodium).** The system Nb-Rh is poorly characterized in the range of concentration 50∼80% Rh [9,10,47,226,230,231,51]. We confirm the stability of Nb$_3$Rh-A15, NbRh-L1$_0$, NbRh-B19, which is observed as a high-temperature state, is ∼27meV/atom above L1$_0$, and it is possibly stabilized by entropic effects. Note: in Massalski and in the Pauling File [9,10] there is no phase at 50% composition, and Nb$_{0.96}$Rh$_{1.04}$-L1$_0$ appears off-stoichiometry. At concentration 75% Rh, we find the stable phase $\eta$-Al$_3$Pu (Co$_3$V) and $\kappa$NbRh$_3$-L1$_2$ to be higher by 8meV/atom. Hence, we think that $\eta$ prevails at low-temperature over $\kappa$, in contrast with the sketched phase diagram of reference [9]. We can not say anything about D8$_b$ and $\xi$(Nb$_2$Rh$_3$) since we do not have the $\sigma$-phase D8$_b$ and any A$_2$B$_3$ prototypes in our library. To address the structures with similar energy, we further investigate NbRh$_3$ with PAW-GGA potentials, as described in Section (III). With PAW, NbRh$_3$-Al$_3$Pu is the most stable compound and NbRh$_3$-L1$_2$ is higher by 5.3meV/atom. The disagreement at composition NbRh$_3$ is further discussed in Section (IV).

Another *ab initio* study, relevant for this system, can be found in reference [232].

| Nb-Rh system | Low Temperature Phases comparison chart |
|--------------|----------------------------------------|
| **Composition % Rh** | **Experimental (Massalski [9])** | **Ab initio result** |
| 25 | $\alpha$(Nb$_3$Rh)-A15 | Nb$_3$Rh-A15 |
| 28.5 to 39.5 | $\sigma$(Nb$_3$Rh$_7$)-D8$_b$ | unavailable |
| ~51.5 to 52 | Nb$_{0.96}$Rh$_{1.04}$-L1$_0$ ($\leq$ 1337°C) | NbRh-L1$_0$ |
| ~56 to 62 | $\epsilon$(Nb$_2$Rh$_3$)-B19 (high-temperature $\geq$ 1330°C) | NbRh-B19 above L1$_0$ (us-lda) |
| 59 to ~64 | $\xi$(Nb$_2$Rh$_3$)-Nb$_2$Rh$_3$ unavailable | |
| ~67 to 70 | $\eta$(Nb$_{1.13}$Rh$_{2.7}$)-Al$_3$Pu (≡ Co$_3$V in [9]) see below for Al$_3$Pu | |
| ~71 to 79 | $\kappa$(NbRh$_3$)-L1$_2$ NbRh$_3$-Al$_3$Pu (us-lda) above Al$_3$Pu (us-lda) Al$_3$Pu stable (paw-gga) L1$_2$~5.3meV/atom above Al$_3$Pu (paw-gga) See Section (IV) | |

**FIG. 32.** NbRh (Niobium - Rhodium) ground state convex hull.
Nb-Ru (Niobium - Ruthenium). Very little is known for the alloy Nb-Ru, especially at low-temperature [9,10,47,233–237]. We do not confirm the stability of any low-temperature compound at composition NbRu, but instead find a two-phase field between Nb$_3$Ru and NbRu$_2$, even though a high and low-temperature phase of NbRu has been observed [233,237]. In the Ru-rich side of the phase diagram, we find NbRu$_3$-D0$_{24}$ to be 8meV/atom lower than L1$_2$ which is suggested experimentally. At 66% Ru we find NbRu$_2$-C37 (with oP12-Co$_2$Si prototype). With respect to the two-phase field Nb$_3$Ru$\leftrightarrow$NbRu$_2$, the structures closest to the tie-line at NbRu composition are B19 (~13meV/atom), L1$_0$ (~20meV/atom), B27 (~23meV/atom), B33 (~39meV/atom), and B2 (~45meV/atom). Experiments have not found any other stable compound. However, in the Nb-rich side of the phase diagram, we find Nb$_3$Ru-D0$_3$ and a monoclinic Nb$_5$Ru with C2/m #12 space group and prototype Mo$_5$Ti$^{\text{proto}}$. The structure Nb$_5$Ru-Mo$_5$Ti$^{\text{proto}}$ is described in Appendix (XII). To address the disagreements at compositions NbRu and NbRu$_3$ we further investigate the relevant compounds with PAW-GGA potentials, as described in Section (III). For composition NbRu, the PAW-GGA result is substantially different from the US-LDA result. GGA gives L1$_0$ only 4meV/atom above the tie-line (versus 20meV/atom in LDA), whereas B19 was difficult to converge numerically, and seems to be >100meV/atom above the tie-line. For composition NbRu$_3$, also with PAW, D0$_{24}$ is the most stable compound and L1$_2$ is higher by 2.5meV/atom. Because this number is so small, extremely large k-points sets and high energy cutoff were used to converge it. The disagreements at compositions NbRu and NbRu$_3$ are further discussed in Section (IV).

Other ab initio studies, relevant for this system, can be found in references [238–240].

| Nb-Ru system Low Temperature Phases comparison chart |
|---|---|---|
| Composition | Experimental (Massalski [9]) | Ab initio result |
| % Ru | | |
| 16.6 | disorder Nb-A2 | Nb$_5$Ru-Mo$_5$Ti$^{\text{proto}}$ Appendix (XII) |
| 25 | disorder Nb-A2 | Nb$_5$Ru-D0$_3$ |
| ~50 | NbRu’-L1$_0$ (room-temperature) | two-phase region Nb$_3$Ru$\leftrightarrow$NbRu$_2$. |
| | | L1$_0$ =~4meV/atom. (paw-gga) |
| | | B19 >100meV/atom. above tie-line (paw-gga). |
| ~50 | NbRu-B2 (high-temperature) | NbRu$_2$-C37 |
| | | B19=13meV/atom. (us-lda) |
| | | L1$_0$=20meV/atom. |
| | | B2 ~45meV/atom. above the tie-line |
| | | See Section (IV). |
| 66.6 | two-phase region above ~700°C | NbRu$_2$-C37 |
| 75 | L1$_2$ | NbRu$_3$-D0$_{24}$ (us-lda) |
| | | L1$_2$=8meV/atom. above D0$_{24}$ (us-lda) |
| | | D0$_{24}$ stable (paw-gga) |
| | | L1$_2$=2.5meV/atom. above D0$_{24}$ (paw-gga) |
| | | See Section (IV). |

FIG. 33. NbRu (Niobium - Ruthenium) ground state convex hull.
**Nb-Tc (Niobium - Technetium).** The phase diagram of the system Nb-Tc is not known and only one intermetallic compound, NbTc$_3$ (metallic and superconductor) has been reported with $\alpha$Mn structure [9,10,47,241–243,365]. The compound NbTc$_3$ is classified as phase Nb$_{0.15}$Tc$_{0.85}$ in the Pauling File [10]. We do not have $\alpha$Mn in our library of prototypes, and, at such stoichiometry, we do not find any stable compound. In the Tc-rich side of the phase diagram, we find a two-phase field NbTc$\leftrightarrow$Tc, as shown in figure (34). At 50% concentration, we obtain NbTc-B2, and in the Nb-rich side of the diagram, we find Nb$_2$Tc-C11$_b$ and an orthorhombic phase Nb$_3$Tc with space group Immm #71, bcc superstructure, and prototype Nb$_3$Tc$^{\text{proto}}$ described in Appendix (XI). Trends of Tc alloys are further discussed in Section (VIII).

| Nb-Tc system | Low Temperature Phases comparison chart |
|--------------|---------------------------------------|
| Composition  | Experimental (Massalski [9]) | Ab initio result |
| % Tc        |                                     |
| 25          | not studied, NbTc$_3$            | nothing stable   |
| 33.3        | same as above, Nb$_2$Tc-C11$_b$ |                |
| 50          | same as above, NbTc-B2           |                |
| 75          | NbTc$_3$-\(\alpha\)Mn [9]       |                |
| 85          | Nb$_{0.15}$Tc$_{0.85}$-\(\alpha\)Mn [10] |            |

**Pd-Pt (Palladium - Platinum).** The low temperature part of the phase diagram is believed to have a miscibility gap at a temperature of about 770°C. This miscibility gap is predicted on the basis of the difference of melting points between Pd and Pt [9,10,43,260,261]. Instead of such gap, we find three unknown stable compounds with fcc superstructures (Pd and Pt are both fcc). We find PdPt-L1$_1$, and two orthorhombic phases, Pd$_3$Pt and PdPt$_3$, with space group Cmmm #65 and prototypes described in Appendix (XI). The prototypes are labeled as Pd$_3$Pt$^{\text{proto}}$ and PdPt$_3^{\text{proto}}$. The compound Pd$_3$Pt is degenerate with respect the two-phase fields Pd-A1$\leftrightarrow$PdPt-L1$_1$, therefore its existence is uncertain. As shown in figure (35), all the stable phases have small formation energy (< 50meV/atom) making them difficult to determine experimentally. However, we believe the experimental phase diagram to be in error. We further investigate PdPt with PAW-GGA potentials, as described in Section (III). With PAW, PdPt-L1$_1$ is the most stable compound and PdPt-L1$_0$ is higher by 5.5meV/atom. Our results are in disagreement with previous FLAPW-LDA calculations, where L1$_0$ is found to be the most stable compound [262].

Other ab initio studies, relevant for this system, can be found in references [13,62].

| Pd-Pt system | Low Temperature Phases comparison chart |
|--------------|---------------------------------------|
| Composition  | Experimental (Massalski [9]) | Ab initio result |
| % Pt        |                                     |
| 25          | predicted two-phase region Pd-A1$\leftrightarrow$Pt-A1 (uncertain) Appendix (XI) |
| 50          | same as above, PdPt-L1$_1$ L1$_0$~11meV/atom. higher than L1$_1$ (us-lda) L1$_1$ stable L1$_0$~5.5meV/atom. higher than L1$_1$ (paw-gga) Appendix (XI) |
| 75          | same as above, PdPt$_3^{\text{proto}}$ Appendix (XI) |
**Pd-Tc (Palladium - Technetium).** The phase diagram for the system Pd-Tc is sketched based on the solid solubility data [9,10,43,365,368,275,346]. Experimental results report two solid solutions (fcc Pd-rich) and (hcp Tc-rich) with a two-phase region in between. No intermetallic compounds have been reported [9,10]. However, we find one stable phases $\text{PdTc}_3\text{D0}_{19}$. In addition, at 50% concentration, we find a hcp superstructure (trigonal lattice, hP4, space group P$\bar{3}m1$) which has an energy $\sim 3\text{meV/atom}$ higher than the tie-line of the two-phase region $\text{PdTc}_3\leftrightarrow \text{Pd}$. Trends of Tc alloys are further discussed in Section (VIII).

| Pd-Tc system | Low Temperature Phases comparison chart |
|---------------|----------------------------------------|
| Composition | Experimental (Massalski [9]) | Ab initio result |
| 25 | two-phase region above $\sim 1000^\circ\text{C}$ | $\text{PdTc}_3\text{D0}_{19}$ |
| 50 | two-phase region above $\sim 1000^\circ\text{C}$ | $\text{PdTc}_3\leftrightarrow \text{Pd}$ |

**Pd-Ti (Palladium - Titanium).** This system has been subject of conflicting results for several years [9,10,169,276–291]. Our *ab initio* method confirms the stability of the compounds $\text{PdTl}_2\text{C11}_b$, $\text{PdTl}_3\text{A15}$, and $\text{PdTl}_3\text{D0}_{24}$. Near 80% Pd, Long Period Superstructures (LPS) modulations of $\text{L1}_2$ are observed [279]. While we do not have such off-stoichiometric LPS, we find $\text{L1}_2$ to be only $6\text{meV/atom}$ above $\text{D0}_{24}$ at $\text{PdTl}$ composition. The low energy difference between $\text{L1}_2$ and $\text{D0}_{24}$ indicates that it may be easy to form antiphase boundaries and LPS near this composition. We find $\text{PdTl}_2\text{MoPt}_2$ which is an orthorhombic distortion of $\text{C11}_b$ ($\text{MoPt}_2$ is orthorhombic, while $\text{C11}_b$ is tetragonal). We find $\text{PdTl}_2\text{C49}$ and $\text{PdTl}_3\text{C11}_b$ to be higher by $3\text{meV/atom}$ and $14\text{meV/atom}$ above $\text{MoPt}_2$, respectively. At low temperature, at concentration 50%, we find a stable compound $\alpha\text{(TiPd)}$, but two prototypes are degenerate: $\text{L1}_0$ and $\text{B19}$ (which is reported experimentally). We can not find the reported phase $\text{PdTl}_4\text{A15}$ (off-stoichiometry) [9], which we think should appear inside the two-phase region of $\text{Ti} \sim \text{PdTl}_3$, or at composition $\text{PdTl}_3$. While off-stoichiometric compounds are obviously possible, this usually goes together with significant width of the single-phase field. Hence, we concluded (maybe erroneously) that the placement of $\text{A15}$ at composition $\text{PdTl}_4$ in reference [9] is likely a typographical error. To address the degenerate structures, we further investigate $\alpha\text{(TiPd)}$ with PAW-GGA potentials, as described in Section (III). With PAW, $\text{PdTl}-\text{B19}$ is the most stable compound and $\text{PdTl}-\text{L1}_0$ is higher by $10\text{meV/atom}$.

Another *ab initio* study, relevant for this system, can be found in reference [292].

**Pd-Ti system**

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|-------------------------------|-----------------|
| 20 and 25   | $\text{A15}$ at 20% $\rightarrow \text{PDTr}_x\text{A15}$ at 25% |
| 33.3        | $\text{C11}_b$ | $\text{PdTl}_2\text{C11}_b$ |
| 47 to 53    | $\alpha\text{(TiPd)}\text{B19}$ | $\text{PdTlB19/L1}_0$ (us-lda) $\rightarrow 10\text{meV/atom}$ above $\text{B19}$ (paw-gga) |
| 60          | $\text{PdTl}_2\sim \text{Au}_2\text{V}$ | unavailable |
| 62.5        | $\text{Pd}_2\text{Ti}_3\sim \text{C11}_b$ | unavailable |
| 66.6        | orthorhombic distortion of $\text{C11}_b$ | $\text{PdTl}_2\text{MoPt}_2$ (distortion of $\text{C11}_b$) $\rightarrow 3\text{meV/atom}$ above $\text{MoPt}_2$ |
| 75          | $\text{D0}_{24}$ | $\text{PdTl}_2\text{Ti}_2\text{D0}_{24}$ $\rightarrow 6\text{meV/atom}$ above $\text{D0}_{24}$ |
| 80          | $\text{L1}_2$ | $\text{L1}_2$ metastable at 75% (see text) |

FIG. 36. PdTc (Palladium - Technetium) ground state convex hull.
Pd-Y (Palladium - Yttrium). The phase diagram for the system Pd-Y is known with reasonable accuracy. Several intermetallic compounds have been reported, but not all the structures have been determined experimentally [9,10,293–296]. We confirm the stability of the compounds Pd₃Y-L1₂ and PdY₃-D0₁₁. The prototype of αPdY is not known [293]. Our best guesses are PdY-B27 and PdY-B33 (CrB), which are degenerate in the calculation. We also find PdY₂-C37, which occurs in a concentration between two known compounds Pd₂Y₃ and Pd₂Y₅ and is very close to the tie-line of the two-phase field PdY₃↔PdY (5meV/atom). Hence, if Pd₂Y₃ and Pd₂Y₅ were to be included, C37 would likely not be stable. We cannot check this prediction since we do not have Pd₂Y₃ and Pd₂Y₅ prototypes in the set of calculations. To address the degenerate structures, we further investigate PdY with PAW-GGA potentials, as described in Section (III). With PAW, PdY-B27 is the most stable compound and PdY-B33 is higher by 3.1meV/atom.

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|------------------------------|-----------------|
| Pd₂Y₃-D0₁₁  | D₀₁₁                         | PdY₃-D0₁₁       |
| 28.6        | Pd₂Y₅ unknown                | unavailable     |
| 33.3        | two-phase region              | PdY₂-C37 (uncertain) |
| 40          | Pd₂Y₃-hR15 unknown           | unavailable     |
| 50          | αPdY unknown                 | PdY-B27/B33 (us-lda) |
|             |                               | B27 stable (paw-gga) |
|             |                               | B33≈3.1meV/at.   |
|             |                               | above B27 (paw-gga) |
| 57.1        | Pd₄Y₃-hR14 unknown           | unavailable     |
| 60          | αPd₃Y₂ unknown               | unavailable     |
| 66.6        | unknown                      | two phase region |
| 79.5 to 75  | L₁₂                          | Pd₃Y-L₁₂        |
| 87.5        | unknown                      | unavailable     |

FIG. 37. PdTi (Palladium - Titanium) ground state convex hull.

FIG. 38. PdY (Palladium - Yttrium) ground state convex hull.
Pd-Zr (Palladium - Zirconium). The experimental phase diagram for the system Pd-Zr is based on limited information \([9,10,297-299,282,300-304]\). We are able to confirm stability of \(\text{Pd}_3\text{Zr}-\text{D0}_{24}\) and \(\text{PdZr}_2\text{-C11}_b\). The stable phase of PdZr is reported to be CrB (B33) \([10,304]\). At that composition, we find two degenerate structures: \(\text{PdZr}-\text{B27}\) or \(\text{PdZr}-\text{B33}\) (CrB). In the Zr-rich side of the phase diagram, we find \(\text{PdZr}_3\text{-FCC}^{[001]}\). However, the energy difference between \(\text{PdZr}_3\text{-FCC}^{[001]}\) and the two-phase region \(\text{Zr} \leftrightarrow \text{PdZr}_2\text{-C11}_b\), is very small (~6meV/atom). Hence, the existence of compound \(\text{PdZr}_3\text{-FCC}^{[001]}\) remains uncertain. At low-temperature, instead of a stable phase with stoichiometry \(\text{Pd}_2\text{Zr}\), we find the two-phase field \(\text{PdZr} \leftrightarrow \text{Pd}_3\text{Zr}-\text{D0}_{24}\). The least unstable phases are \(\text{Pd}_2\text{Zr}-\text{C49}\), \(\text{Pd}_2\text{Zr}-\text{MoPt}_2\), \(\text{Pd}_2\text{Zr}-\text{C11}_b\), with energies ~18meV/atom, ~24meV/atom, ~26meV/atom above the tie-line of the two-phase region, respectively. To address the degenerate structures and the erroneous two phase region \(\text{PdZr} \leftrightarrow \text{Pd}_2\text{Zr}\), we further investigate \(\text{PdZr}\) and \(\text{Pd}_2\text{Zr}\) with PAW-GGA potentials, as described in Section (III). With PAW, \(\text{PdZr}-\text{B33}\) is the most stable compound and \(\text{PdZr}-\text{B27}\) is higher by 3.2meV/atom. In addition, \(\text{Pd}_2\text{Zr}-\text{C11}_b\) is degenerate with the tie line \(\text{PdZr} \leftrightarrow \text{Pd}_3\text{Zr}\), and MoPt2 and C49 are higher by ~1.3meV/atom and ~7.1meV/atom with respect to C11b (also the tie-line \(\text{PdZr} \leftrightarrow \text{Pd}_3\text{Zr}\) has been recalculated with PAW-GGA potentials).

| Pd-Zr system | Pd-Zr system
| --- | --- |
| **Pd-Zr system** | Pd-Zr system
| **Low Temperature Phases comparison chart** | **Ab initio**
| **Composition** | **Experimental** | **Ab initio** | **Ab initio** |
| % Pd | (Massalski \[9\]) | result | result |
| 25 | two-phase region | \(\text{PdZr}_3\text{-FCC}^{[001]}\) (uncertain) | \(\text{PdZr}_3\text{-FCC}^{[001]}\) (uncertain) |
| 33.3 | \(\text{C11}_b\) | \(\text{PdZr}_2\text{-C11}_b\) | \(\text{PdZr}_2\text{-C11}_b\) |
| 50 | disorder fcc \[9\] | \(\text{PdZr} \leftrightarrow \text{B27/B33} (\text{us-lda})\) | \(\text{PdZr} \leftrightarrow \text{B27/B33} (\text{us-lda})\) |
| | \(\text{CrB(B33-TII)}\) \[10,304\] | \(\text{B33 stable (paw-gga)}\) | \(\text{B33 stable (paw-gga)}\) |
| | | \(\text{B27} \sim 3.2\text{meV/atom above B33 (paw-gga)}\) | \(\text{B27} \sim 3.2\text{meV/atom above B33 (paw-gga)}\) |
| 66.6 | \(\text{C11}_b\) | two-phase region (us-lda). | \(\text{C49} \sim 18\text{meV/atom}\). |
| | | \(\text{MoPt}_2 \sim 24\text{meV/atom}\). | \(\text{C11}_b\text/-tie-line (paw-gga).}\ |
| | | \(\text{C11}_b\text/-tie-line (paw-gga).}\ | \(\text{MoPt}_2 \sim 1.3\text{meV/atom above tie-line (paw-gga)}\). |
| | | \(\text{C49} \sim 7.1\text{meV/atom above tie-line (paw-gga)}\). | \(\text{C49} \sim 7.1\text{meV/atom above tie-line (paw-gga)}\). |
| 75 | \(\text{D0}_{24}\) | \(\text{Pd}_2\text{Zr-D0}_{24}\) | \(\text{Pd}_2\text{Zr-D0}_{24}\) |

**FIG. 39.** PdZr (Palladium - Zirconium) ground state convex hull.
Pt-Rh (Platinum - Rhodium). The experimental phase diagram of the system Pt-Rh is similar to the system Pd-Pt. The low-temperature part of the phase diagram is believed to have a miscibility gap at a temperature of about 760°C \[9,10,43,263,305\]. Instead of the gap, we find several stable phases, all with fcc superstructure (Pt and Rh are both fcc), similar to previous FLAPW-LDA calculations \[262\]. We find Pt\(_4\)Rh-D1\(_a\), Pt\(_3\)Rh-D0\(_{22}\), PtRh\(_2\)-C49, PtRh\(_3\)-D0\(_{22}\), PtRh\(_4\)-D1\(_a\), and, at 50% concentration, PtRh-FCC\(_{A_{2}B_{2}}^{[001]}\) (CH “40” in reference \[262\]). As shown in figure (40), all the stable phases have very small formation energy (<30meV/atom) indicating that they may disorder at relatively low temperature.

Another \textit{ab initio} study, relevant for this system, can be found in reference \[62\].

| Composition % Rh | Experimental (Massalski \[9\]) | Ab initio result |
|------------------|---------------------------------|-----------------|
| 20               | two-phase region [9]            | Pt\(_4\)Rh-D1\(_a\) |
| 25               | two-phase region [9]            | Pt\(_3\)Rh-D0\(_{22}\) |
| 50               | two-phase region [9]            | PtRh-FCC\(_{A_{2}B_{2}}^{[001]}\) |
| 66.6             | two-phase region [9]            | PtRh\(_2\)-C49 |
| 71.4             | two-phase region [9]            | unavailable |
| 80               | two-phase region [9]            | PtRh\(_4\)-D1\(_a\) |

Pt-Ru (Platinum - Ruthenium). Only one compound has been found for the system Pt-Ru \[9,10,306,307\]. At low-temperature, the phase diagram reported in Massalski \[9\] has Platinum-rich and Ruthenium-rich solid solution with large solubilities of the other element, and a two-phase region for concentration between ~70% to ~80% of Ruthenium. However, recent X-ray diffraction experimental work reported the existence of a fcc phase at 50% composition, with unknown prototype \[307\]. For PtRu, our prediction is PtRu-FCC\(_{A_{2}B_{2}}^{[001]}\). At 25% Ru composition, we find a stable phase Pt\(_3\)Ru-FCC\(_{A_{2}B_{2}}^{[001]}\) degenerate with the two-phase field Pt↔PtRu. Hence, the existence of compound Pt\(_3\)Ru-FCC\(_{A_{2}B_{2}}^{[001]}\) remains uncertain. To our knowledge, PtRu is the first known system where the prototype structure FCC\(_{A_{2}B_{2}}^{[001]}\) would be stable.

| Composition % Ru | Experimental (Massalski \[9\]) | Ab initio result |
|------------------|---------------------------------|-----------------|
| 25               | disorder Pt-A1 [9]              | Pt\(_3\)Ru |
| 50               | disorder Pt-A1 [9]              | PtRu-fcc \[307\] |

FIG. 40. PtRh (Platinum - Rhodium) ground state convex hull.

FIG. 41. PtRu (Platinum - Ruthenium) ground state convex hull.
Pt-Tc (Platinum - Technetium). The phase diagram for the system Pt-Tc has been determined from experimental solid solubility data [9,10,43,365,368]. No intermetallic compounds have been reported [9]. However, we find two stable phases: Pt Tc\textsubscript{3}-FCC\textsubscript{[001]}\textsuperscript{\textit{AB}} and Pt Tc\textsubscript{3}-D0\textsubscript{19}. Pt Tc\textsubscript{3}-D0\textsubscript{19} appears in the composition range of a two-phase region Pt-A1 and Tc-A3, that is present at temperatures higher than \sim 1000°C. Trends of Tc alloys are further discussed in Section (VIII).

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|-----------------------------|------------------|
| 25          | disorder Pt-A1               | Pt\textsubscript{Tc}\textsubscript{3}-FCC\textsubscript{[001]}\textsuperscript{\textit{AB}} |
| 75          | two-phase region above \sim 1000°C Pt-A1\leftrightarrow Tc-A3 | Pt Tc\textsubscript{3}-D0\textsubscript{19} |

FIG. 42. PtTc (Platinum - Technetium) ground state convex hull.

Pt-Ti (Platinum - Titanium). Not much is known of Pt-Ti system to produce a precise phase diagram [9,10,48,285,290,308–311,283,312]. Some intermetallic compounds are reported [308–311,283,312,288]. We confirm the stability of phases Pt Ti\textsubscript{3}-A15, αPtTi-B19, Pt Ti\textsubscript{3}-D0\textsubscript{24}. B19 is stable at 50% composition, and L1\textsubscript{0} and B33 are higher by \sim 20meV/atom and \sim 30meV/atom, respectively. At concentration 25%Ti, we confirm the existence of γ-L1\textsubscript{2}, which has an energy that is \sim 5meV/atom higher than Pt Ti\textsubscript{3}-D0\textsubscript{24}. However, L1\textsubscript{2} has been reported to be stable away from stoichiometry < 25% Ti [9]. At composition 33% Ti, Pt\textsubscript{2}Ti, Massalski reports a two-phase region above 600°C [9,10]. Instead of the two-phase field, we find a stable compound Pt\textsubscript{2}Ti: two structures, C49 and C37, are degenerate. We cannot say anything about Pt\textsubscript{8}Ti-D1\textsubscript{a}, because our library does not contain off-stoichiometry D1\textsubscript{a}. To address the degenerate structures, we further investigate Pt\textsubscript{2}Ti with PAW-GGA potentials, as described in Section (III). With PAW, Pt\textsubscript{2}Ti-C49 is the most stable compound and Pt\textsubscript{2}Ti-C37 is higher by 1.9meV/atom.

Another ab initio study, relevant for this system, can be found in reference [292].

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|-----------------------------|------------------|
| 1 to 12     | Pt\textsubscript{8}Ti-D1\textsubscript{a} unavailable |
| 20 to 27    | D0\textsubscript{24} (>25%Ti) Pt\textsubscript{3}Ti-D0\textsubscript{24} γ-L1\textsubscript{2} (<25%Ti) L1\textsubscript{2} \sim 5meV/atom. above D0\textsubscript{24} |
| 33.3        | two-phase region above 600°C [9] Pt\textsubscript{2}Ti-C49/C37 (us-lda) C49 stable C37\sim 1.9meV/atom. above C49 (paw-gga) |
| 46 to 54    | αPtTi-B19 Pt\textsubscript{2}Ti-B19 L1\textsubscript{0} \sim 20meV/atom. above B19 |
| 71 to 78    | A15 PtTi\textsubscript{3}-A15 |

FIG. 43. PtTi (Platinum - Titanium) ground state convex hull.
Pt-Y (Platinum - Yttrium). The experimental phase diagram of the system Pt-Y has been sketched by analogy with other Rare Earth-Platinum diagrams [9]. Several intermetallic compounds have been reported [9,10,43,156,277,285,313-320,324]. The stability of the compounds Pt3Y-L12, Pt2Y-C15, and PtY3-D011 is confirmed. At 50% concentration, we do not find any stable PtY-B27. Instead of B27, we find PtY-B33 (CrB prototype) to have lowest energy with B2 and B27 having energies ∼50meV/atom above B33. At 66.6% Y concentration, we find PtY2-C37 which is the prototype of Co2Si and Ni2Si. Hence our calculations confirm the correct experimental structure. At concentration 62.5% Y, we do not find Pt3Y5-D88, but the two-phase field PtY+PtY2. D88 and W5Si3 are higher by ∼24meV/atom and ∼80meV/atom with respect to the tie-line PtY+PtY2 (this problem is solved with PAW-GGA potentials). As shown in figure (44), at concentration 16.6% Y, we find a two-phase region instead of the reported stable compound Pt3Y with unknown structure [9]. Our best guess is Pt3Y-D2d which is the least-metastable structure we have at such composition (∼18meV/atom above the tie-line Pt+Pt3Y). We conclude that further experimental and theoretical investigations are necessary to determine the behavior of PtY. To address the disagreement with the experimental results for compounds PtY and Pt3Y5, we further investigate the relevant structures with PAW-GGA potentials, as described in Section (III). With PAW, PtY-B33 is stable and PtY-B27 is higher by 60meV/atom. For compound Pt3Y5, D88 is stable with an energy 6.9meV/atom lower than the tie-line PtY+PtY2, which has also been recalculated with PAW-GGA potentials. The disagreement at composition PtY is further discussed in Section (IV).

| Composition % Y | Experimental (Massalski [9]) | Ab initio result |
|-----------------|-------------------------------|------------------|
| 16.6            | unknown                       | Pt5Y-D2d metastable, D2d ~18meV/atom above the tie-line |
| 25              | L12                           | Pt2Y-L12         |
| 33.3            | C15                           | Pt2Y-C15         |
| 42.9            | Pt4Y3-Pd4Pu3                  | unavailable      |
| 50              | B27                           | PtY-B33          |
|                 |                                | B2/B27 ~50meV/atom above B33 |
|                 |                                | B33 stable (paw-gga) |
|                 |                                | B27 ~60meV/atom above B33. (paw-gga) |
| 55.6            | Pt4Y5-Pu5Rh4                  | unavailable      |
| 62.5            | Pt3Y5-D88                     | two-phase region |
|                 |                                | PtY+PtY2. (us-lda) |
|                 |                                | D88 ~24meV/atom above the tie-line (us-lda) |
|                 |                                | D88 stable (paw-gga). |
|                 |                                | ~6.9meV/atom below PtY+PtY2 (paw-gga). |
| 66.6            | PtY2-Ni2Si [9]                | PtY2-C37         |
|                 |                                | (Co2Si)          |
|                 |                                | (Co2Si)          |
| 70              | Pt3Y7-D102                    | unavailable      |
| 75              | L1011                         | PtY4-D011        |

FIG. 44. PtY (Platinum - Yttrium) ground state convex hull.
Pt-Zr (Platinum - Zirconium). The system Pt-Zr is quite interesting. Our *ab initio* method confirms the stability of αPtZr-B33 (CrB prototype). Two crystal structures have been reported for Pt₃Zr: D₀₂₄ and L₁₂ [9,10,321,322,323,285,302]. We confirm the stability of Pt₃Zr-D₀₂₄ and we find L₁₂ to be higher by 10meV/atom with respect to D₀₂₄. In the Zr-rich part of the phase diagram, we find two stable phases PtZr₂-C₁₆ and PtZr₃-A₁₅. At concentration 62.5% Zr, we do not find Pt₃Zr₅-D₈₈, but the two-phase field PtZr→PtZr₂. W₅Si₃ and D₈₈ are higher by ~26meV/atom and ~36meV/atom with respect to the tie-line PtZr→PtZr₂. To address the phase instability at composition Pt₃Zr₅, we further investigate the relevant compounds with PAW-GGA potentials, as described in Section (III). With PAW, at concentration Pt₃Zr₅, there is a two-phase region PtZr→PtZr₂. In addition, Pt₅Zr₅-W₅Si₃ and Pt₅Zr₅-D₈₈ have energies higher by 23meV/atom and 26meV/atoms with respect to the tie-line PtZr→PtZr₂, respectively. The disagreement at composition Pt₃Zr₅ is further discussed in Section (IV).

| Composition | Experimental (Massalski [9]) | *Ab initio* result |
|-------------|-------------------------------|-------------------|
| % Zr        | Pt₃Zr₅-D₈₈                    | PtZr-B33          |
| 62.5        | two-phase region (us-lda)    | two-phase region  |
|             | W₅Si₃~26meV/atom.            | (paw-gga)         |
|             | D₈₈~36meV/atom.              | above tie-line    |
|             | above tie-line (us-lda).     | (paw-gga).        |
| 66.6        | two-phase region             | above 600°C C.    |
|             | above 600°C C.               | (uncertain)       |
| 75          | two-phase region             | PtZr₃-A₁₅         |
|             | above 600°C C.               | (uncertain)       |

FIG. 45. PtZr (Platinum - Zirconium) ground state convex hull.
Rh-Ru (Rhodium - Ruthenium). The phase diagram for the system Rh-Ru is based on the solid solubility data [9,10,43,326]. Experimental results report two solid solutions (fcc Rh-rich) and (hcp Ru-rich) with a two-phase region in between (from 34.5% to 40% atomic percent Ruthenium). No intermetallic compounds have been reported [325–327] and the system is considered to be no compound forming [10]. However, we find two stable phases: an orthorhombic oC12 RhRu$_{2}^{\text{proto}}$, with hcp superstructure and Cmcm #63 space group, and a trigonal hP4 RhRu$_{2}^{\text{proto}}$, with hcp superstructure and P3m1 #164 space group. Both prototypes are described in Appendix (XI). As shown in figure (46), all the stable phases have small formation energy (< 10meV/atom) making them difficult to determine experimentally. To better describe the stability of this system, we further investigate all the structures with negative formation energies with PAW-GGA potentials, as described in Section (III). Also with PAW, RhRu$_{2}^{\text{proto}}$ and RhRu$_{2}^{\text{proto}}$ are the most stable structures, with formation energies of -8.3meV/atom and -8.8meV/atom, respectively.

| Composition (%) | Experimental result | Ab initio result |
|-----------------|---------------------|-----------------|
| 33 Rh-A3 solid solution | RhRu$_{2}^{\text{proto}}$ stable both us-lda and paw-gga, $E_f \sim -8.3\text{meV/atom}$ (paw-gga). | |
| 50 Rh-A3 solid solution | RhRu$_{2}^{\text{proto}}$ stable both us-lda and paw-gga, $E_f \sim -8.8\text{meV/atom}$ (paw-gga). | |

Rh-Tc (Rhodium - Technetium). The phase diagram for the system Rh-Tc is based on the solid solubility data [9,10,43,366,368]. Experimental results report two solid solutions (fcc Rh-rich) and (hcp Tc-rich) with a two-phase region in between. No intermetallic compounds have been reported [366,368]. However, we find three stable phases: RhTc$_{3}$-D0$_{19}$, RhTc-B19, and Ru$_{2}$Tc-ZrSi$_{2}$. Trends of Tc alloys are further discussed in Section (VIII).

| Composition | Experimental | Ab initio |
|-------------|--------------|-----------|
| 25 Rh-A3 solid solution | Tc-A3 | RhTc$_{3}$-D0$_{19}$ |
| 50 Rh-A3 solid solution | Tc-A3 | RhTc-B19 B27~29meV/at. above B19 (us-lda). |
| 66.6 two-phase region above $\sim$1000°C | Pt-A1$\leftrightarrow$Tc-A3 | Rh$_{2}$Tc-ZrSi$_{2}$ |

FIG. 46. RhRu (Rhodium - Ruthenium) ground state convex hull.

FIG. 47. RhTc (Rhodium - Technetium) ground state convex hull.
**Rh-Ti (Rhodium - Titanium).** There are qualitative disagreements about the phase diagram of the Rh-Ti system [9,10,48,322,328-332]. We confirm the stable phases that were found by all investigators [328–331]: RhTi$_2$, αRhTi-L1$_0$, and Rh$_3$Ti-L1$_2$. References [10,322,332] report RhTi$_2$-CuZr$_2$ instead of RhTi$_2$-C11$_b$. The prototype CuZr$_2$ is a distortion of C11$_b$ and has the same lattice type (tetragonal, tI6) and space group (I4/mmm #139) [10]. We find RhTi$_2$-C11$_b$ and RhTi$_2$-CuZr$_2$ to have degenerate energy. In the Rh-rich part of the phase diagram we find a stable phase Rh$_2$Ti-C37. However, we do not have Rh$_5$Ti$_3$ in our library, so C37 might likely be unstable with respect to the two-phase field Rh$_5$Ti$_3$↔L1$_2$. At concentration ≈ 84% Rh, we do not find any stable compound, in agreement with [330] and in contrast with [328]. To address the degeneracy of RhTi$_2$-C11$_b$/CuZr$_2$, we further investigate RhTi$_2$ with PAW-GGA potentials, as described in Section (III). Also with PAW, C11$_b$ and CuZr$_2$ remain degenerate.

Other *ab initio* studies, relevant for this system, can be found in references [232,292].

| Composition % Rh | Experimental (Massalski [9]) | Ab initio result |
|------------------|-----------------------------|-----------------|
| 33.3 C11$_b$ | RhTi$_2$ | |
| ∼38 to 58 | αRhTi-L1$_0$ | RhTi-L1$_0$ |
| 62.5 | Rh$_5$Ti$_3$-Ge$_3$Rh$_5$ | unavailable |
| 66.6 | two-phase region above 600°C | Rh$_2$Ti-C37 |
| 73 to 78 | L1$_2$ | Rh$_3$Ti-L1$_2$ |
| ∼83.8 | Rh$_5$Ti (unknown) | nothing stable |

**Rh-Y (Rhodium - Yttrium).** Several compounds have been reported for the system Rh-Y at low-temperature [9,10,43,277,334,335,337]. The stability of Rh$_2$Y-C15, RhY-B2, Rh$_3$Y-D0$_{11}$ is confirmed. At composition Rh$_5$Y, where a D2$_d$ structure has been seen at high-temperature (but not stable at low-temperature), we find the D2$_d$ to be the lowest energy structure (of all the structures at that composition), even though it is metastable with respect to the phase separation into Rh$_2$Y-C15↔Rh. At composition Rh$_3$Y one compound has been reported to be stable with prototype CeNi$_3$ and space group P6$_3$/mmc #194 [10,336,338]. We do not have such prototype in our library and we do not find any stable phase: Rh$_3$Y-D0$_{11}$ is the least metastable prototype we obtain. Rh$_3$Y-D0$_{11}$ is higher by 130 meV/atom with respect the tie-line, which is at least one order of magnitude bigger than the accuracy of the calculations. We also find Rh$_3$Y-C37, which appears in a concentration between two known compounds, Rh$_3$Y$_5$ and Rh$_3$Y$_7$, that are not present in our set of calculations. Therefore C37 might be unstable with respect to the two-phase region Rh$_3$Y$_5$↔Rh$_3$Y$_7$.

| Composition % Rh | Experimental (Massalski [9]) | Ab initio result |
|------------------|-----------------------------|-----------------|
| 3 | D0$_{11}$ | Rh$_3$Y-D0$_{11}$ |
| 25 | Rh$_3$Y(unknown) | unavailable |
| 33.3 | two-phase region above 0°C | Rh$_2$Y-C37 |
| 37.5 | Rh$_3$Y(unknown) | unavailable |
| 40 | Rh$_3$Y$_5$ (unknown) | t1140-14/mcm |
| 50 | B2 | RhY-B2 |
| 66.6 | C15 | Rh$_3$Y-C15 |
| 75 | Rh$_3$Y(unknown) | D0$_{11}$↔130meV/at. above tie-line |
| 83.5 | Rh$_3$Y-D2$_4$ (high-temperature) | D2$_4$↔110meV/at. above tie-line |

**FIG. 48.** RhTi (Rhodium - Titanium) ground state convex hull.

**FIG. 49.** RhY (Rhodium - Yttrium) ground state convex hull.
Rh-Zr (Rhodium - Zirconium). Although the system Zr-Rh is well known for its superconducting phases [9,10,339,342], further investigations are needed to clarify the stability and presence of intermediate phases [340,341]. Our \textit{ab initio} method confirms the stability of RhZr$_2$-C16 and Rh$_3$Zr-L1$_2$. Massalski does not report the prototype of the low-temperature phase $\alpha$RhZr [9]. References [342–344] report $\alpha$RhZr-B27. We confirm the stability of $\alpha$RhZr-B27 (BFe prototype) with no other metastable compounds with similar energy. In addition, we find three new phases Rh$_2$Zr-C37, RhZr$_4$-D1$_a$ and RhZr$_3$-FCC$_{AB3}$, which are degenerate with the two-phase fields RhZr$\leftrightarrow$Rh$_3$Zr, Zr$\leftrightarrow$RhZr, and Zr$\leftrightarrow$RhZr, respectively.

Other \textit{ab initio} studies, relevant for this system, can be found in references [232,345].

| Composition | Experimental | $Ab \text{ initio}$ |
|-------------|--------------|---------------------|
| % Rh        | (Massalski [9]) | result |
| 20          | two-phase region above 0°C | RhZr$_4$-D1$_a$/tie-line |
| 25          | two-phase region above 0°C | RhZr$_3$-FCC$_{AB3}$/tie-line |
| 33.3        | C16          | RhZr$_2$-C16 |
| 50 to ?     | $\alpha$RhZr | RhZr$_3$-B27 |
| 57.1        | Rh$_2$Zr$_3$ (unknown) | unavailable |
| 62.5        | Rh$_5$Zr$_3$-Pd$_3$Pu$_3$ | unavailable |
| 66.6        | two-phase region above 0°C | Rh$_2$Zr$_3$-C37/tie-line |
| 72 to 82    | L1$_2$       | Rh$_3$Zr-L1$_2$ |

Ru-Tc (Ruthenium - Technetium). The phase diagram for the system Ru-Tc is considered to have a continuous disordered hcp solid solution at low-temperature [9,10,365,368,346]. We find three stable ordered phases Ru$_3$Tc-D0$_{19}$, RuTc-B19, and RuTc$_3$-D0$_{19}$, all of which are hcp superstructures. Hence, it is possible that they are low-temperature phases of the system Ru-Tc. Trends of Tc alloys are further discussed in Section (VIII).

| Composition | Experimental | $Ab \text{ initio}$ |
|-------------|--------------|---------------------|
| % Ru        | (Massalski [9]) | result |
| 25          | disorder solution (Ru,Tc)-A3 | RuTc$_3$-D0$_{19}$ |
| 50          | same as above | RuTc-B19 |
| 75          | same as above | Ru$_3$Tc-D0$_{19}$ |

FIG. 50. RhZr (Rhodium - Zirconium) ground state convex hull.

FIG. 51. RuTc (Ruthenium - Technetium) ground state convex hull.
Ru-Ti (Ruthenium - Titanium). The phase diagram of Ru-Ti is well determined by several investigators. A single low-temperature compound RuTi-B2 has been reported \[9,10,48,285,347,348,350,349,351–354\], and our \textit{ab initio} method confirms its stability. In addition, we find two stable phases: RuTi$_2$-C49, and orthorhombic RuTi$_3$ with space group Immm #71, bcc superstructure, and prototype RuTi$_5^{\text{proto}}$ described in Appendix (XI). Such compounds are close to the tie-line Ti$\leftrightarrow$RuTi. In fact, for C49 and RuTi$_5^{\text{proto}}$, the formation energies are lower by $\sim$34meV/atom and $\sim$37meV/atom with respect to the two-phase field Ti$\leftrightarrow$RuTi.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Composition} & \textbf{Experimental (Massalski [9])} & \textbf{\textit{Ab initio} result} \\
% Ru & & \\
\hline
25 & two-phase region above 600$^\circ$C & RuTi$_2^{\text{proto}}$ Appendix (XI) \\
& & $\sim$37meV/at. below Ti$\leftrightarrow$RuTi \\
33.3 & same as above & RuTi$_2$-C49 \\
& & $\sim$34meV/at. below Ti$\leftrightarrow$RuTi \\
45 to 52 $\pm$ 1 & B2 & RuTi-B2 \\
\hline
\end{tabular}
\caption{Low Temperature Phases comparison chart for Ru-Ti system.}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{RuTi.png}
\caption{RuTi (Ruthenium - Titanium) ground state convex hull.}
\end{figure}

Ru-Y (Ruthenium - Yttrium). Several compounds have been reported for the system Ru-Y \[9,10,43,333,355–359\]. We confirm the stability of RuY$_3$-D0$_{11}$ and Ru$_2$Y-C14. Also, we find Ru$_2$Y$_2$-C16, which appears in a concentration between two known compounds Ru$_{25}$Y$_{44}$ and Ru$_2$Y$_5$ that are not in our library of calculations. Hence, the existence of Ru$_2$Y$_2$-C16 is uncertain. At concentration 50%, we do not find any stable RuY compound, in agreement with \[358\].

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Composition} & \textbf{Experimental (Massalski [9])} & \textbf{\textit{Ab initio} result} \\
% Ru & & \\
\hline
25 & D0$_{11}$ & RuY$_3$-D0$_{11}$ \\
28.6 & Ru$_2$Y$_2$-C$_2$Mn$_5$ mS28 C12/c1 [10,355,356,358] & unavailable \\
33.3 & two-phase region above 0$^\circ$C & RuY$_2$-C16 (uncertain) \\
36.2 & Ru$_{25}$Y$_{44}$ (unknown) oP276 Pnma [10,355,359] & unavailable \\
40 & Ru$_2$Y$_3$-Er$_3$Ru$_2$ hP10 P6$_3$/m [360] & unavailable \\
66.6 & & Ru$_2$Y$_2$-C14 \\
\hline
\end{tabular}
\caption{Low Temperature Phases comparison chart for Ru-Y system.}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{RuY.png}
\caption{RuY (Ruthenium - Yttrium) ground state convex hull.}
\end{figure}
Ru-Zr (Ruthenium - Zirconium). The phase diagram of RuZr is known accurately [9,10,362,361]. Our ab initio method confirms the stability of the low-temperature phase RuZr-B2. In agreement with experiments, we find no ground state at composition Ru$_2$Zr, though the lowest energy structure at that composition in our calculations is C14 which appears in the phase diagram at high-temperature. Ru$_2$Zr-C14 is higher by $\sim$60meV/atom with respect to the two-phase field Ru$\leftrightarrow$RuZr. In the Zr-rich region we find one stable compound, RuZr$_4$-D1$_a$, previously unknown. In addition, we find three metastable phases: RuZr$_5$, RuZr$_3$, and RuZr$_2$-C49, with energies higher by 21meV/atom, 16.6meV/atom, and 14meV/atom, with respect to the two-phase fields RuZr$_4$$\leftrightarrow$Zr, RuZr$\leftrightarrow$RuZr$_4$, and RuZr$\leftrightarrow$RuZr$_4$, respectively. The structure of RuZr$_5$ is similar to MoZr$_5^{\text{proto}}$ (Appendix (XII)), while the structure of RuZr$_3$ is similar to RuTi$_3^{\text{proto}}$ (Appendix (XI)).

Other ab initio studies, relevant for this system, can be found in references [238–240,363].

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|-------------------------------|-----------------|
| 16.6% Ru    | RuZr$\leftrightarrow$Zr at 400°C | RuZr$_5$$\approx$MoZr$_5^{\text{proto}}$ at 21meV/atom above RuZr$_4$$\leftrightarrow$Zr |
| 20% Ru      | same as above                 | RuZr$_4$-D1$_a$ |
| 25% Ru      | same as above                 | RuZr$_3$$\approx$RuTi$_3^{\text{proto}}$ at 16.6meV/atom above RuZr$_2$$\leftrightarrow$RuZr$_4$ |
| 33.3% Ru    | same as above                 | RuZr$_2$-C49 at 14meV/atom above RuZr$_2$$\leftrightarrow$RuZr$_4$ |
| 48 to 52%   | B2                            | RuZr$_2$-B2     |
| 66 to 68%   | C14 (high T)                  | Ru$_2$Zr-C14 at 60meV/atom above Ru$\leftrightarrow$RuZr |

FIG. 54. RuZr (Ruthenium - Zirconium) ground state convex hull.

Tc-Ti (Technetium - Titanium). The phase diagram of the system TcTi has been constructed by analogy with chemically related systems [9,10,48,364,365]. Two intermetallic compound, TcTi-B2 and $\chi$ are reported [364,365]. We confirm the stability of TcTi-B2, but we can not say anything about $\chi$ since we do not have prototypes at composition 85% Ru. In addition, we find Tc$_2$Ti-C11$_b$, TcTi$_2$-C49, and an orthorhombic phase TcTi$_3$ with space group I4mm #71 and prototype TcTi$_3^{\text{proto}}$ described in Appendix (XI). These intermetallics have large negative formation energy, therefore they are expected to be very stable. Trends of Tc alloys are further discussed in Section (VIII).

| Composition | Experimental (Massalski [9]) | Ab initio result |
|-------------|-------------------------------|-----------------|
| 25% Tc      | disorder $\beta$Ti-A2         | TcTi$_2^{\text{proto}}$ in Appendix (XI) |
| 33.3% Tc    | disorder $\beta$Ti-A2         | TcTi$_2$-C49 |
| $\sim$50% Tc| B2                            | TcTi-B2 |
| 66.6% Tc    | two-phase region TcTi$\leftrightarrow$$\chi$ | Tc$_2$Ti-C11$_b$ |
| $\sim$85% Tc| $\chi$-A12                    | unavailable |

FIG. 55. TcTi (Technetium - Titanium) ground state convex hull.


**Tc-Y (Technetium - Yttrium).** Not enough information exists in order to construct a phase diagram for the system Tc-Y [9,10]. Only one intermetallic compound has been reported: Tc$_2$Y-C14 (Friauf-Laves/Frank-Kasper phase) [367,369]. We confirm the stability of Tc$_2$Y-C14. In addition, we find another stable phase TcY$_3$-D0$_{11}$. Trends of Tc alloys are further discussed in Section (VIII).

| Tc-Y system | | | |
|---|---|---|---|
| **Low Temperature Phases comparison chart** | | | |
| Composition | Experimental | Ab initio | |
| % Tc | (Massalski [9]) | result | |
| 25 | no information | | |
| 66.6 | C14 | Tc$_2$Y-C14 | (Laves phase) |

**FIG. 56.** TcY (Technetium - Yttrium) ground state convex hull.

**Tc-Zr (Technetium - Zirconium).** Not enough information exists in order to construct a phase diagram for the system Tc-Zr [9,10]. Only two intermetallic compounds have been reported: Tc$_2$Zr-C14 (Friauf-Laves/Frank-Kasper phase) and Tc$_6$Zr-A12 [9,10,365,370]. We confirm the stability of Tc$_2$Zr-C14, but we cannot determine A12 since we do not have the proper prototype in our library. At 50% composition, Miedema et al. reported the existence of a TcZr compound with unknown structure [10,285]. At such composition we find TcZr-B2. In addition, we find other stable phases: TcZr$_4$-D$_{1a}$ and TcZr$_2$-C$_{49}$. These intermetallics have large negative formation energy, therefore they are expected to be very stable. Trends of Tc alloys are further discussed in Section (VIII).

| Tc-Zr system | | | |
|---|---|---|---|
| **Low Temperature Phases comparison chart** | | | |
| Composition | Experimental | Ab initio | |
| % Tc | (Massalski [9]) | result | |
| 20 | no information | | |
| 33.3 | no information | | |
| 50 | TcZr (unknown) [285] | TcZr-B2 | |
| 66.6 | C14 | TcZr$_2$-C14 | (Laves phase) |
| 85.7 | TcZr-A12 | unavailable | |

**FIG. 57.** TcZr (Technetium - Zirconium) ground state convex hull.

**VIII. TREND FOR TECHNETIUM ALLOYS**

In our set of calculations, we have noticed that the phase D0$_{19}$ appears in systems MTc$_3$ where M is a transition metal in the columns on the right of Tc (Tc is in column 7B) while D0$_{19}$ is not present if M is in the columns on the left of Tc: D0$_{19}$ is stable in PdTc$_3$, PtTc$_3$, RhTc$_3$, RuTc$_3$, and unstable in NbTc, TcTi, TcY, and TcZr.
IX. ACKNOWLEDGMENTS

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X. TABLES OF RESULTS

A. Experimental compounds in agreement with ab initio solutions

| System | Experimental result | Ab initio result | System | Experimental result | Ab initio result |
|--------|---------------------|------------------|--------|---------------------|------------------|
| Ag-Cd  | AgCd-B2 [10.67-70]  |                  | Nb-Pd  | NbPd3-D022          |                  |
| Ag-Mg  | AgMg-D044/390       |                  | Nb-Pt  | NbPt3-A15           |                  |
| Ag-Mg  | AgMg-B2             |                  | Nb-Pt  | NbPt2-MoPt2         |                  |
| Ag-Na  | AgNa-Ci5            |                  | Nb-Pt  | NbPt2-D0a           |                  |
| Ag-Ti  | AgTi-Y-C11b         |                  | Nb-Rh  | Nb3Rh-α′-A15        |                  |
| Ag-Ti  | AgTi-B11            |                  | Nb-Rh  | NbRh-L10            |                  |
| Ag-Y   | AgY-B2              |                  | Nb-Rh  | (Nb2Rh3)-B19 (high T) |                  |
| Ag-Y   | AgY-C11b            |                  | Nb-Rh  | (Nb3Rh27)-Al1Pn     |                  |
| Ag-Zr  | AgZr-C11b           |                  | Pt-Ti  | PtTi3-A15 at 20%    |                  |
| Ag-Zr  | AgZr-B11            |                  | Pt-Ti  | PtTi2-C11b          |                  |
| Al-Sb  | AlSb-B             |                  | Pt-Ti  | PtTi4-B19           |                  |
| Al-Sb  | AlSb-C15           |                  | Pt-Y   | PtY3-D011           |                  |
| Al-Sb  | AlSb-L12          |                  | Pt-Y   | PtY2-Y-L12          |                  |
| Au-Cd  | AuCd-B19           |                  | Pt-Zr  | PtZr2-C11b          |                  |
| Au-Cd  | AuCd-B2            |                  | Pt-Zr  | PtZr3-B33           |                  |
| Au-Nb  | AuNb-C32           |                  | Pt-Zr  | PtZr3-C11b          |                  |
| Au-Nb  | AuNb-D1a           |                  | Pt-Zr  | PtZr3-D024          |                  |
| Au-Sb  | AuSb-C11b          |                  | Pt-Ti  | PtTi3-D024          |                  |
| Au-Sb  | AuSb-C15           |                  | Pt-Ti  | PtTi4-C15           |                  |
| Au-Ti  | AuTi-D1a           |                  | Pt-Ti  | PtTi3-A15           |                  |
| Au-Ti  | AuTi-C11b          |                  | Pt-Y   | PtY3-D011           |                  |
| Au-Ti  | AuTi-B11           |                  | Pt-Y   | PtY2-Y-L12          |                  |
| Au-Y   | AuY-D0a            |                  | Pt-Y   | PtY2-C37            |                  |
| Au-Y   | AuY-Y-C11b         |                  | Pt-Y   | PtY2-Y-L12          |                  |
| Au-Zr  | AuZr-D0a           |                  | Pt-Zr  | PtZr3-D024          |                  |
| Au-Zr  | AuZr-C11b          |                  | Pt-Zr  | PtZr3-B33           |                  |
| Au-Zr  | AuZr2-CuZr2/C11b   |                  | Pt-Zr  | PtZr3-B33           |                  |
| Au-Zr  | AuZr2-CuZr2/C11b   |                  | Pt-Zr  | PtZr3-A15           |                  |
| Cd-Pd  | CdPd3-β-37/L10     |                  | Rh-Ti  | RhTi2-C11b          |                  |
| Cd-Pd  | CdPd3-L10          |                  | Rh-Ti  | RhTi2-C11b          |                  |
| Cd-Pr  | CdPr3-L10          |                  | Rh-Y   | RhY3-D011           |                  |
| Cd-Pr  | CdPr3-C11b         |                  | Rh-Y   | RhY2-B              |                  |
| Cd-Ti  | CdTi2-C11b         |                  | Rh-Y   | RhY2-C15            |                  |
| Cd-Ti  | CdTi2-C11b         |                  | Rh-Zr  | RhZr2-C16           |                  |
| Cd-Ti  | CdTi2-C11b         |                  | Rh-Zr  | RhZr2-C16           |                  |
| Cd-Y   | Cd-Y-C15           |                  | Rh-Zr  | RhZr2-C16           |                  |
| Cd-Y   | Cd-Y-33           |                  | Rh-Zr  | RhZr2-C16           |                  |
| Cd-Y   | Cd-Y-C37Er         |                  | Rh-Zr  | RhZr2-C16           |                  |
| Cd-Zr  | CdZr2-C11b         |                  | Rh-Ti  | RhTi2-B2            |                  |
| Cd-Zr  | CdZr2-B11          |                  | Ru-Y   | RuY2-D011           |                  |
| Cd-Zr  | CdZr2-L12          |                  | Ru-Y   | RuY2-C14            |                  |
| Mo-Pt  | MoPt-B19           |                  | Ru-Zr  | RuZr2-B2            |                  |
| Mo-Pt  | MoPt3-L10          |                  | Ru-Zr  | RuZr2-B2            |                  |
| Mo-Pr  | MoPr2              |                  | Te-Ti  | TeTi2-B2            |                  |
| Mo-Pr  | MoPr2              |                  | Te-Ti  | TeTi2-B2            |                  |
| Mo-Rh  | MoRh-B19           |                  | Te-Y   | TeY2-C14            |                  |
| Mo-Zr  | MoZr-C15           |                  | Te-Zr  | TeZr2-C14           |                  |
| Nb-Pd  | NbPd2-MoPt2        |                  | Te-Zr  | TeZr2-C14           |                  |
| Nb-Pd  | NbPd2-MoPt2        |                  | Nb-Pd  | NbPd3-MoPt2         |                  |

TABLE 5: Experimental compounds in agreement with ab initio solutions (89 entries).
### B. Experimentally unknown, non-identified or speculated compounds and ab initio predictions

| System | Experimental result | Ab initio result |
|--------|---------------------|------------------|
| Ag-Cd  | $\gamma'$-bcc ordered | AgCd-B2/B19/B27  |
| Ag-Mg  | $c\overline{F}^*$ (unknown) | AgMg$_3$-D0$_{19}$ (hP8) / D0$_a$ (oP8) |
| Au-Cd  | Au$_3$Cd-$\alpha_2$-hP? (unknown) | Au$_3$Cd-D0$_{24}$/D0$_{19}$/Al$_3$Pu |
| Au-Cd  | $\alpha''$ ~ AuCd (unknown) | AuCd-L1$_0$/FCC\[201]\ | $\beta$ '-bcc ordered |
| Au-Cd  | Au$_3$Cd (unknown) | AuCd-L6$_0$/fcc |
| Au-Pd  | Au$_3$Pd-L1$_2$ (speculated) | Au$_4$Pd-D0$_{23}$/D0$_{22}$/L1$_2$ (wide concentration range) |
| Au-Pd  | Au$_4$Pd-D1$_a$/tie-line | Au$_4$Pd-D1$_a$/tie-line |
| Au-Pd  | AuPd$_3$L1$_2$ (speculated) | AuPd$_3$-D0$_{23}$/D0$_{22}$/L1$_2$/tie-line |
| Au-Sc  | AuSc$_2$-C37 (speculated) | AuSc$_2$-C37 |
| Cd-Pd  | γ'- (unknown) | Cd$_3$Pd-D0$_{19}$/D0$_{24}$/NbPd$_3$/Al$_3$Pu |
| Cd-Pt  | γ1- (unknown) | Cd$_3$Pt-D0$_{11}$/D0$_a$/D0$_{22}$ |
| Cd-Pt  | $\gamma_2$- (unknown) | Cd$_3$Pt-C37/C16/tie-line |
| Cd-Zr  | cubic (unknown) | Cd$_5$Zr-C11$_b$ |
| Mo-Pd  | MoPd$_2$ ~ MoPt$_2$ | MoPd$_2$-ZrSi$_2$ |
| Mo-Rh  | MoRh$_3$ (unknown) | MoRh$_3$/C16/C11 |
| Nb-Pt  | Nb two-phase region$_{1-x}$ Pt$_{1+x}$-B19 | NbPd-L1$_0$ |
| Pd-Ti  | orthorhombic distortion of Pd$_4$Ti-C11$_b$ | Pd$_4$Ti-MoPt$_2$ (distortion of C11$_b$) |
| Pd-Y   | αPdY (unknown) | PdY-B27 |
| Pt-Ru  | PtRu-FCC (unknown) | PtRu-FCC\[2001]\ |
| Pt-Y   | Pt$_5$Y (unknown) | Pt$_5$Y-D2$_d$ metastable |
| Tc-Zr  | TcZr (unknown) | TcZr-B2 |

**TABLE 6:** Experimentally unknown, non-identified or speculated compounds and *ab initio* predictions (21 entries).
C. Experimental solid solutions, two-phases and “not studied” regions and possible ab initio predictions

| System | Experimental result | Ab initio result |
|--------|---------------------|------------------|
| Ag-Au  | short-range order ≥950°C | Ag$_4$Au-D1$$_{9}$/tie-line |
| Ag-Au  | short-range order ≥950°C | Ag$_3$Au-L1$_2$/D0$_{23}$/Al$_3$Pu/NbPd$_3$/D0$_{22}$/D0$_{24}$ |
| Ag-Au  | short-range order ≥950°C | Ag$_3$Au-C3$$_7$/MoPt$_2$ |
| Ag-Au  | short-range order ≥950°C | AgAu-L1$_0$ |
| Ag-Au  | short-range order ≥950°C | AgAu-C$_3$$_7$/MoPt$_2$ |
| Ag-Au  | short-range order ≥950°C | AgAu-L1$_2$/D0$_{22}$/D0$_{23}$ |
| Ag-Cu  | fcc solid solution | Ag$_3$Cd-D0$_{22}$/D0$_{24}$ |
| Ag-Ni  | fcc solid solution | Ag$_3$Cd-C3$$_7$ |
| Ag-Ti  | none | AgCd$_2$-ZrSi$_2$ |
| Ag-Pd  | hcp solid solution | Ag$_4$Pd-D0$_{19}$ |
| Ag-Pd  | solid solution ≥900°C | Ag$_3$Pd-L1$_4$ |
| Ag-Pd  | solid solution ≥900°C | Ag$_3$Pd-C3$$_7$ |
| Ag-Pd  | solid solution ≥900°C | Ag$_3$Pd-L1$_2$/D0$_{22}$ |
| Ag-Y  | two-phase region above 200°C | Ag$_2$Y-C3$$_7$/tie-line (uncertain) |
| Ag-Y  | two-phase region above 200°C | Ag$_3$Y-D0$_{9}$ (uncertain) |
| Ag-Zr  | two-phase region above 700°C | AgZr$_3$-FCC$^{0011}$ |
| Ag-Zr  | two-phase region above 700°C | AgZr$_3$-FCC$^{0011}$ |
| Al-Sc  | two-phase region above 0°C | AlSc$_3$-D0$_{19}$ |
| Au-Nb  | two-phase region (calculated) | AuNb$_2$-BCC$_{422}$ |
| Au-Pd  | solid solution | Au$_3$Pd-C$_4$/C$_{37}$ |
| Au-Pd  | two-phase region above 500°C | Au$_4$Pd$_3$-Cu$_4$Ti$_3$/tie |
| Au-Pd  | not studied | Au$_2$-C$_3$ |
| Au-Zr  | two-phase region | Au$_2$Zr$_3$-Cu$_4$Ti$_3$ (unreliable) |
| Au-Zr  | two-phase region | Au$_2$Zr$_3$-Cu$_4$Ti$_3$ (unreliable) |
| Cd-Pd  | Pd phase above 100°C | CdPd$_3$-D0$_{22}$/NbPd$_3$ |
| Cd-Pd  | two-phase region above 100°C | CdPd$_2$-C$_{37}$ |
| Cd-Rh  | not studied | Cd$_2$Rh-C$_{37}$ |
| Cd-Rh  | not studied | Cd$_2$Rh-AB$_{1}$ |
| Cd-Ti  | two-phase region above 200°C | Cu$_3$Ti$_3$/tie-line |
| Cd-Ti  | not studied/two-phase region | Cu$_2$Y-C3$$_7$ |
| Cd-Zr  | not studied/two-phase region | Cu$_3$Zr$_2$-A15 |
| Mo-Nb  | not studied | MoNb$_2$-C11$_b$ |
| Mo-Nb  | not studied | MoNb$_2$-D0$_{19}$ |
| Mo-Nb  | not studied | MoNb$_2$-D0$_{19}$ |
| Mo-Nb  | not studied | MoNb$_2$-D0$_{19}$ |
| Mo-Pd  | disorder fcc Pd-A1 | MoPd$_4$-D1$_n$ |
| Mo-Pt  | two-phase region MoPt$_2$ ↔ Pt | MoPt$_4$-D1$_n$ |
| Mo-Rh  | two-phase region above 900°C | Mo$_4$Rh-C$_{37}$ |
| Mo-Rh  | disorder hcp Ru-A3 above 800°C | Mo$_4$Ru$_3$-D0$_{19}$ |
| Mo-Ti  | not studied/two-phase region above 400°C MoTi$_{4}$-tie-line (uncertain), Appendix (XI) | Mo$_4$Ti$_{4}$-tie-line (uncertain), Appendix (XI) |
| Mo-Ti  | not studied/two-phase region above 400°C MoTi$_{4}$-tie-line (uncertain), Appendix (XI) | Mo$_4$Ti$_{4}$-tie-line (uncertain), Appendix (XI) |
| Mo-Ti  | not studied/two-phase region above 400°C MoTi$_{4}$-tie-line (uncertain), Appendix (XI) | Mo$_4$Ti$_{4}$-tie-line (uncertain), Appendix (XI) |
| Mo-Ti  | not studied/two-phase region above 400°C MoTi$_{4}$-tie-line (uncertain), Appendix (XI) | Mo$_4$Ti$_{4}$-tie-line (uncertain), Appendix (XI) |
| Mo-Zr  | two-phase region above 400°C MoZr$_{2}$-tie-line (uncertain), Appendix (XII) (uncertain). | MoZr$_{2}$-tie-line (uncertain), Appendix (XII) (uncertain). |
| Mo-Zr  | two-phase region above 400°C MoZr$_{2}$-tie-line (uncertain), Appendix (XII) (uncertain). | MoZr$_{2}$-tie-line (uncertain), Appendix (XII) (uncertain). |
| Mo-Zr  | two-phase region above 400°C MoZr$_{2}$-tie-line (uncertain), Appendix (XII) (uncertain). | MoZr$_{2}$-tie-line (uncertain), Appendix (XII) (uncertain). |
| Mo-Zr  | two-phase region above 400°C MoZr$_{2}$-tie-line (uncertain), Appendix (XII) (uncertain). | MoZr$_{2}$-tie-line (uncertain), Appendix (XII) (uncertain). |

TABLE 7a: Experimental solid solutions, two-phases and “not studied” regions and possible ab initio predictions. The table continues in the next page.
| System | Experimental result | Ab initio result |
|--------|---------------------|------------------|
| Nb-Pd  | two-phase region above 700°C | Nb$_2$Pd-BCC$^{[011]}$ |
| Nb-Ru  | disorder Nb-A2 | Nb$_5$Ru proto, Appendix (XII) |
| Nb-Ru  | disorder Nb-A2 | Nb$_3$Ru-D0$_1$ |
| Nb-Ru  | two-phase region above 700°C | NbRu$_2$-C37 |
| Nb-Tc  | not studied/unknown | Nb$_3$Tc proto, Appendix (XI) |
| Nb-Tc  | not studied/unknown | Nb$_2$Tc-C11$_b$ |
| Nb-Tc  | not studied/unknown | NbTc-B2 |
| Pd-Pt  | two-phase region Pd↔Pt | Pd$_3$Pt proto/tie-line (uncertain), Appendix (XI) |
| Pd-Tc  | two-phase region Pd↔Pt | Pd$_3$Tc-A1 |
| Pd-Tc  | two-phase region above ~1000°C | Pd$_3$Tc proto$_1$ |
| Pd-Y  | two-phase region | Pd$_3$Y$_2$-C37 (uncertain) |
| Pd-Zr  | two-phase region | PdZr$_2$-FCC$^{[001]}$ (uncertain) |
| Pt-Rh  | two-phase region Pt↔Rh [9], D$_1$a [262] | Pt$_4$Rh-D1$_a$ |
| Pt-Rh  | two-phase region Pt↔Rh | Pt$_3$Rh-D0$_{22}$ |
| Pt-Rh  | two-phase region Pt↔Rh | PtRh-NbP |
| Pt-Rh  | two-phase region Pt↔Rh | PtRh$_2$-C49 |
| Pt-Rh  | two-phase region Pt↔Rh | PtRh$_3$-D0$_{22}$ |
| Pt-Rh  | two-phase region Pt↔Rh [9], D$_1$a [262] | PtRh$_4$-D1$_a$ |
| Pt-Ru  | disorder Pt-A1 | Pt$_3$Ru-FCC$^{[001]}$/tie-line (uncertain) |
| Pt-Tc  | disorder Pt-A1 | Pt$_3$Tc-FCC$^{[001]}$ |
| Pt-Tc  | two-phase region above ~1000°C | Pt$_3$Tc-D0$_{19}$ |
| Pt-Zr  | two-phase region above 600°C | PtZr$_2$-C16 (uncertain) |
| Pt-Zr  | two-phase region above 600°C | PtZr$_3$-A15 (uncertain) |
| Rh-Ru  | solid solution Ru-A3 | RhRu$_2$ proto |
| Rh-Ru  | solid solution Ru-A3 | RhRu$_2$ proto |
| Rh-Tc  | solid solution Tc-A3 | RhTc$_3$-D0$_{19}$ |
| Rh-Tc  | solid solution Tc-A3 | RhTc-B19 |
| Rh-Tc  | two-phase region above 1000°C | Rh$_2$Tc$_2$-ZrSi$_2$ |
| Rh-Ti  | two-phase region above 600°C | Rh$_2$Ti-C37 |
| Rh-Y  | two-phase region above 6°C | RhY$_2$-C37 (uncertain) |
| Rh-Zr  | two-phase region above 0°C | RhZr$_2$-D1$_a$/tie-line |
| Rh-Zr  | two-phase region above 0°C | RhZr$_3$-FCC$^{[001]}$/tie-line |
| Rh-Zr  | two-phase region above 0°C | RhZr$_3$-D0$_{19}$ |
| Ru-Tc  | disorder solution (Ru,Tc)-A3 | RuTc$_3$-D0$_{19}$ |
| Ru-Tc  | disorder solution (Ru,Tc)-A3 | RuTc-B19 |
| Ru-Tc  | disorder solution (Ru,Tc)-A3 | RuTc-D0$_{19}$ |
| Ru-Ti  | two-phase region above 600°C | RuTi$_2$ proto$_1$, Appendix (XI) |
| Ru-Ti  | two-phase region above 600°C | RuTi$_2$-C49 |
| Ru-Y  | two-phase region above 6°C | RuY$_2$-C16 (uncertain) |
| Ru-Zr  | two-phase region above 6°C | RuZr$_2$-D1$_a$ |
| Tc-Ti  | disorder βTi-A2 | TcTi$_2$ proto$_2$, Appendix (XI) |
| Tc-Ti  | disorder βTi-A2 | TcTi$_2$-C49 |
| Tc-Ti  | two-phase region TcTi↔χ | Tc$_2$Ti-C11$_b$ |
| Tc-Y  | no information | TcY$_3$-D0$_{11}$ |
| Tc-Zr  | no information | TcZr$_3$-D1$_a$ |
| Tc-Zr  | no information | TcZr$_3$-D1$_a$ |

**TABLE 7b:** Experimental solid solutions, two-phases and “not studied” regions and possible ab initio predictions (Table 7a + Table 7b = 96 entries). The table starts in the previous page.
D. Experimental compounds that could not be checked by our calculations

| System   | Experimental compound | Ab initio result |
|----------|------------------------|------------------|
| Ag-Mg    | AgMg4-hP* (unknown)    | unknown compound |
| Ag-Y     | Ag51Y4+Ag51Gd14        | unavailable prototype |
| Au-Cd    | η' (unknown)           | unknown compound |
| Au-Cd    | η1Au3Cd-Λ3Mg           | unavailable prototype |
| Au-Cd    | Au3Cd5-D8m             | unknown compound |
| Au-Nb    | Au2Nb3 (unknown)       | unknown compound |
| Au-Ti    | η1AuTi+B19             | unavailable prototype |
| Au-Y     | AuY3 (unknown)         | unknown compound |
| Au-Zr    | AuZr (oP20 - Pnma)     | unavailable prototype |
| Au-Zr    | AuZr (tI14)            | unavailable prototype |
| Au-Zr    | Αu2Zr2 (unknown prototype) | unknown compound |
| Cd-Pd    | η1 (unknown)           | unknown compound |
| Cd-Pd    | η2-D8h                 | unavailable prototype |
| Cd-Pd    | η3 (unknown)           | unknown compound |
| Cd-Pd    | η4 (unknown)           | unknown compound |
| Mg-Pt    | η2-D012 above 1000°C   | unavailable prototype |
| Ni-Pt    | D8h                    | unavailable prototype |
| Ni-Rh    | θ(Nb12Rh7)-D8h         | unavailable prototype |
| Ni-Rh    | ζ(Nb2Rh3)-Nb2Rh3       | unavailable prototype |
| Ni-Pt    | NiPt2NiRh2 (tI85-αMn) | unavailable prototype |
| Pt-Ti    | Pt3Ti2 ~ Αu3V          | unavailable prototype |
| Pt-Ti    | Pt3Ti3 ~ C11b          | unavailable prototype |
| Pd-Y     | unknown at 66.6% Pd    | unknown compound |
| Pd-Y     | unknown at 87.5% Pd    | unknown compound |
| Pd-Y     | Pd4Y5 (unknown)        | unavailable prototype |
| Pd-Y     | Pd4Y12-hR15 (unknown)  | unavailable compound |
| Pd-Y     | Pd4Y14-hR14 (unknown)  | unavailable compound |
| Pd-Y     | αPd3Y2 (unknown)       | unavailable compound |
| Pt-Ti    | Pt3Ti-D1α              | unavailable prototype |
| Pt-Ti    | Pt3Ti-ReSi2            | unavailable prototype |
| Pt-Y     | Pt4Y3-Pt4P3U1          | unavailable prototype |
| Pt-Y     | Pt3Y3-Pt3R3           | unavailable prototype |
| Pt-Y     | Pt3Y3-D10b             | unavailable prototype |
| Rh-Y     | Rh3Y (unknown)         | unknown compound |
| Rh-Y     | Rh3Y2-C14              | unavailable prototype |
| Rh-Y     | Rh3Y5 (unknown)        | unavailable compound |
| Rh-Y     | Rh3Y3 (unknown)        | unknown compound |
| Rh-Zr    | Rh3Zr3 (unknown)       | unknown compound |
| Rh-Zr    | Rh3Zr3-Pd3Pu3          | unavailable prototype |
| Ru-Y     | Ru2Y3-C3M15            | unavailable prototype |
| Ru-Y     | Ru2Y4 (unknown)        | unavailable compound |
| Tc-Ti    | Χ1-A12                 | unavailable prototype |
| Tc-Zr    | Tc3Zr-A12              | unavailable prototype |

**TABLE 8:** Experimental compounds that could not be checked by our calculations, because the proper structure prototype or concentration is not known or not in our library. The table contains 21 “unknown experimental compounds” and 27 “unavailable prototypes” (48 entries total).
E. Experimental compounds in disagreement with other ab initio compounds or two-phase regions

| System | Experimental result | Ab initio result | $\Delta E_f$ (us-LDA) (meV/atom) | $\Delta E_f$ (paw-gga) (meV/atom) | Note |
|--------|---------------------|------------------|----------------------------------|----------------------------------|------|
| Au-Nb  | AuNb$_{3}$-A15      | two-phase region | 7                                | 6.5                              | (a)  |
| Au-Y   | AuY-B2 [170]        | AuY-B33          | 26                               | 25                               | (b)  |
| Cd-Nb  | Cd$_4$Nb-L1$_2$     | immiscible system | 70                               | >100                             | (c)  |
| Cd-Pt  | CdPt$_3$ − α$'$-L1$_2$ [181] | CdPt$_3^{\text{prot}}$-L1$_2$, Appendix (XI) | 25                               | 10.4                             | (b)  |
| Nb-Rh  | α(NbRh$_3$)-L1$_2$  | NbRh$_3$-Al$_2$Pu | 8                                | 5.3                              | (a)  |
| Nb-Ru  | NbRu$_3$L1$_2$      | NbRu$_3$-D0$_2$4 | 8                                | 2.5                              | (a)  |
| Nb-Ru  | NbRu$'$-L1$_0$      | two-phase region | 20                               | 4                                | (a)  |
| Pt-Y   | PtY-B27             | PtY-B33          | 50                               | 60                               | (c)  |
| Pt-Zr  | Pt$_3$Zr$_2$-D8$_8$ | two-phase region | 36                               | 25                               | (c)  |

TABLE 9: Experimental compounds (which we have in the library as prototypes) in disagreement with other ab initio compounds or two-phase regions. We include the differences between the formation energies of the phases in disagreement, both for US-LDA and PAW-GGA potentials. (9 entries). Note (a): the ab initio ground state is within less than 10meV/atom of the experimental ground state (4). Note (b): the assigned experimental structures are poorly justified (2) [170,181]. Note (c): unambiguous significant disagreement (3).
XI. APPENDIX: NEW STRUCTURE PROTOTYPES WHICH ARE SUPERSTRUCTURES OF FCC, BCC, HCP

| System          | CdPt₃, PdPt₃, Pd₃Pt | MoTi₁ | MoTi₃, Mo₅Ti₄, Nb₅Ti₃, RuTi₃, TeTi₃ | RhRu | RhRu₂ |
|-----------------|----------------------|-------|------------------------------------|------|------|
| Superlattice    | FCC AB₁              | BCC A₂B₂ | BCC AB₃                          | HCP A₂B₂ | HCP A₅B₁ |
| Lattice         | Orthorhombic         | Orthorhombic | Orthorhombic   | Trigonal | Orthorhombic |
| Space Group     | Cmmmm #65            | Imma #74 | Immm #71                         | P5₃m1 #164 | Cmcm #63 |
| Pearson symbol  | oC₈                  | o₁₈   | o₁₈                               | hP₄  | oCl₂ |

**Atomic positions (fract.)**

| System          | MoZr₃ (AB₃)       | Mo₅Ti⁺ (AB₂) | MoZr₅⁺ (AB₅) | Nb₅Ru⁺ (AB₅) |
|-----------------|-------------------|--------------|---------------|--------------|
| Lattice         | Orthorhombic      | Monoclinic   | Monoclinic    | Monoclinic   |
| Space Group     | Imma #74          | C₂/m #12     | C₂/m #12      | C₂/m #12     |
| Prototype       | MoZr₃             | Mo₅Ti⁺ see note* | MoZr₅⁺ see note* | Nb₅Ru⁺ see note* |

**Atomic positions (fract.)**

**XII. APPENDIX: RELAXED STRUCTURE PROTOTYPES**

| System          | MoZr₃ (AB₃)       | Mo₅Ti⁺ (AB₂) | MoZr₅⁺ (AB₅) | Nb₅Ru⁺ (AB₅) |
|-----------------|-------------------|--------------|---------------|--------------|
| Lattice         | Orthorhombic      | Monoclinic   | Monoclinic    | Monoclinic   |
| Space Group     | Imma #74          | C₂/m #12     | C₂/m #12      | C₂/m #12     |
| Prototype       | MoZr₃             | Mo₅Ti⁺ see note* | MoZr₅⁺ see note* | Nb₅Ru⁺ see note* |

**Table 11.** Geometry of relaxed structures which appear as new prototypes in our study. Positions are given as unrelaxed positions in the parent lattice.

**Table 12.** Geometry of relaxed structures which appear as new prototypes in our study. Positions are given as fractional positions of the primitive vectors. Note *: Mo₅Ti, MoZr₅, and Nb₅Ru are slight distortions of the prototype Mo₅Tiproto, monoclinic lattice, space group C₂/m #12, with atoms in the following Wyckoff positions: Ti in 2a, Mo(1) in 2c, Mo(2) in 4i (x = 1/3, z = 1/6), Mo(3) in 4i (x = 2/3, z = 1/3), and primitive vectors a₁/a=(3.171, 1, 0), a₂/a= (−0.315, 1, 0), a₃/a= (−0.638, −0.201, 1.987) [17].
REFERENCES

[1] D. de Fontaine, in Solid State Physics, edited by H. Ehrenreich and D. Turnbull (Academic Press 1994), Vol. 47, pp. 33-176.
[2] M. Sluiter, P. Turchi, F. Zezhong, and D. de Fontaine, Tight Binding Calculation of Ti-Rh-Type Phase Diagram, Phys. Rev. Lett. 60, 716 (1988).
[3] S. Curtarolo, D. Morgan, K. Persson, J. Rodgers, and G. Ceder, Phys. Rev. Lett. 91, 135503 (2003).
[4] S. Curtarolo, H. Cocks, and A. N. Kolmogorov, High-Throughput ab initio analysis of the Bi-Mg, Bi-In, In-Mg, Mg-Sb, In-Sb, and Bi-Sb systems, submitted (2005).
[5] S. Curtarolo and A. N. Kolmogorov, Prediction of possible metastable alloy phases in the Mg-Sb system, internal report (2004).
[6] D. Morgan, G. Ceder, and S. Curtarolo, Mat. Res. Soc. Symp. Proc. 804, J39.25 (2004).
[7] D. Morgan, G. Ceder, and S. Curtarolo, J. Measurement Science & Technology, Special Feature Combinatorial and High-Throughput Materials Research, Meas. Sci. Technol. 16, 296-301 (2005).
[8] Y. Wang, S. Curtarolo, C. Jiang, R. Arroyave, T. Wang, G. Ceder, L.-Q. Chen, and Z.-K. Liu, Calphad 28, 79 (2004).
[9] Binary Alloy Phase Diagrams, edited by T. B. Massalski (ASM International, Metals Park, OH, 1992)
[10] P. Villars, K. Cenzual, J. L. C. Daams, F. Hulliger, T. B. Massalski, H. Okamoto, K. Osaki, A. Prince, and S. Iwata, Crystal Impact, Pauling File. Inorganic Materials Database and Design System, Binaries Edition, ASM International, Metal Park, OH (2003)
[11] P. S. White, J. R. Rodgers, and Y. Le Page, CRYSTMET: a database of the structures and powder patterns of intermetallics, Acta Crystal. B 58, 343 (2002).
[12] J. M. Sanchez and D. de Fontaine, Theoretical Prediction of Ordered Superstructures in Metal Alloys, in “Structure and Bonding in Crystals”, Vol. II, Academic Press (1981).
[13] Z. W. Lu, S.-H. Wei, A. Zunger, S. Frota-Pessoa, and L. G. Ferreira, Phys. Rev. B 44, 512 (1991).
[14] C. Wolverton and A. Zunger, Phys. Rev. B 50, 10548 (1994).
[15] S. Curtarolo, Coarse-Graining and Data Mining Approaches to the Prediction of Structures and their Dynamics, Ph.D. Thesis, MIT (2003). Download: burgaz.mit.edu and alpha.mems.duke.edu
[16] Appendix B, pp. 196-210 of reference [15].
[17] International Table of Crystallography, edited by T. Hahn, (Kluwer Academic Publishers, 2002).
[18] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
[19] D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
[20] G. Kresse and J. Furthmuller, Comput. Mater. Sci. 6, 15 (1996).
[21] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[22] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 16, 1748 (1977).
[23] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[24] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[25] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
[26] J. B. Neaton and N. W. Ashcroft, Phys. Rev. Lett. 86, 2830 (2001).
[27] A. K. McMahan and J. A. Moriarty, Phys. Rev. B 27, 3255 (1983).
[28] J. E. Jaffe, Z. Lin, and A. C. Hess, Phys. Rev. B 57, 11834 (1998).
[29] M. M. Dacorogna and M. L. Cohen, Phys. Rev. B 34, 4996 (1986).
[30] M. I. Katsnelson, G. V. Sinko, N. A. Smirnov, A. V. Trefilov, and K. Yu. Khromov, Phys. Rev. B 61, 14420 (2000).
[31] C. S. Barrett and O. R. Trautz, Trans. Am. Inst. Min. Metall. Pet. Eng. 175, 579 (1948).
[32] S. Barrett, Acta Crystallogr. 9, 671 (1956).
[33] A. W. Overhauser, Phys. Rev. Lett. 53, 64 (1984).
[34] G. Ernst, C. Artner, O. Blaschko, and G. Krexner, Phys. Rev. B 33, 6465 (1986).
[35] H. G. Smith, R. Berliner, J. D. Jorgensen, M. Nielsen, and J. Trivisonno, Phys. Rev. B 41, 1231 (1990).
[36] W. Schwarz and O. Blaschko, Phys. Rev. Lett. 65, 3144 (1990).
[37] W. Schwarz, O. Blaschko, and I. Gorgas, Phys. Rev. B 44, 6785 (1991).
[38] O. Blaschko, V. Dmitriev, G. Krexner, P. Toledano, Phys. Rev. B 59, 9095 (1999).
[39] L. Vegard, Z. Phys. 5, 17 (1921).
[40] The reference CPU is Compaq/HP - Alpha 21264 EV67 MHz.
[41] M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, New-York (1958).
[42] W. B. Pearson, Handbook of Lattice Spacings and Structures of Metals and Alloys, Metals Park, Oh: American Society for Metals (1985).
[43] W. G. Moffatt, Ed., Handbook of Binary Phase Diagrams, Business Growth Services, General Electric Co., Schenectady, NY (1976).
[44] F. A. Shunk, Constitution of Binary Alloys, Supplement, McGraw-Hill, New-York; General Electric Co., Business Growth Services, Schenectady, New York (1969).
[45] M. Venkatraman, J. P. Neumann, Phase Diagrams of Binary Titanium Magnesium, ASM International (1988).
[46] L. Brewer, Molybdenum: Physico-Chemical Properties of its Compounds and Alloys, edited by O. Kubaschewski, Atomic Energy Review Special Issue No. 7, International Atomic Energy Agency, Vienna (1980).
[47] V. I. Lavrentev, Ya. I. Gerassimov, P. Fesbotte, D.
and Petroleum Eng. 215, 283-286 (1959).
[349] D. D. Gulamova, M. V. Raevskaya, I. G. Sokolova, F. S. Litvak, and E. M. Sokolovskaya, Moscow Univ. Chem. Bull. 27(4), 96 (1972).
[350] E. Raub and E. Roescher, Z. Metallkd. 54(8) 455 (1963).
[351] Y. Tamminga, B. Barkman, and F. R. De Boer, Solid State Comm. 12, 731-735 (1973).
[352] V. N. Eremenko, T. D. Shtepa, and V. T. Khoruzhaya, Russ. Metall. (2), 155-156 (1973).
[353] N. G. Boriskina and I. I. Kornilov, Russ. Metall. (2), 162 (1976).
[354] J. M. Zhang and G. Y. Guo, J. Phys. Cond. Matt. 7, 6001-6017 (1995).
[355] O. Loebich and E. Raub, J. Less-Common Met. 46, 7 (1976).
[356] K. Cenzual, A. Palenzona, and E. Parthé, Acta Crystallogr. B 36(7), 1631 (1980).
[357] R. Sanjines-Zaballos, B. Chabot, and E. Parthé, J. Less-Common Met. 72, P17 (1980).
[358] P. Sharifi-Razi, R. C. Mohanty, and A. Raman, Z. Metallkd. 75(10), 801 (1984).
[359] M. L. Fornasini, A. Mugnoli, and A. Palenzona, J. Less-Common Met. 154, 149 (1989).
[360] A. Palenzona and E. Canepa, J. Less-Common Met. 162, 267 (1990).
[361] V. N. Eremenko, E. L. Semenova, and T. D. Shtepa, Russ. Metall. (2), 177 (1980).
[362] V. N. Eremenko, V. T. Khoruzhaya, and T. D. Shtepa, Russ. Metall. (1), 194 (1988).
[363] M. J. Mehl, J. E. Osburn, D. A. Papakonstantopoulos, and B. M. Klein, Mat. Res. Soc. Symp. Proc. 186, 277-82 (1991).
[364] C. C. Koch, J. Less-Common Met. 6, 177 (1976).
[365] J. B. Darby, Jr., D. J. Lam, L. J. Norton, and J. W. Downey, J. Less-Common Met. 4, 558 (1962).
[366] J. B. Darby, Jr., L. J. Norton, and J. W. Downey, J. Less-Common Met. 5, 397 (1963).
[367] J. B. Darby, Jr., L. J. Norton, and J. W. Downey, J. Less-Common Met. 6, 165 (1964).
[368] J. Niemiec, Bull. Acad. Pol. Sci. Ser. Sci. Chem. 11, 665 (1963).
[369] E. G. Szklarz and A. L. Giorgi, J. Less-Common Met. 81, 2349 (1981).
[370] A. L. Giorgi and E. G. Szklarz, J. Less-Common Met. 22, 246 (1970).
[371] P. A. Farrar and S. Adler, Trans. AIME 236, 1061 (1966).
[372] D. Chatterji, M. T. Hepworth, and S. J. Hruska, Metall. Trans. 2, 1271 (1971).
[373] J. Etchessahar and J. Debuigne, Mem. Sci. Rev. Metall. 74(3), 195 (1977).
[374] J. P. Auffredic, E. Etchessahar, and J. Debuigne, J. Less-Common Met. 84, 49 (1982).
[375] C. E. Lundin, Rare Earth Symposium, Annual Meeting, Am. Soc. Metals, Chicago (1959).
[376] J. C. Uy, D. J. Lam, L. C. Ianiello, R. A. Proebstle, A. P. Lee, B. T. M. Loh, and A. A. Burr, Final Report AT(30-1)-2159, Rensselaer Polytechnic Institute (1961).
[377] C. E. Lundin, D. T. Klodt, Trans. AIME 224, 367 (1962).
[378] R. Wang, Metall. Trans. 3, 1213 (1972).
[379] R. Wang and Y. B. Kim, Metall. Trans. 5, 1973 (1974).
[380] R. Wang, Mater. Sci. Eng. 23, 135 (1976).
[381] A. van de Walle and G. Ceder, Rev. Mod. Phys. 74(1), 11 (2002).
[382] C. Wolverton and V. Ozolins, Phys. Rev. Lett. 86, 5518 (2001).