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

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## Abstract

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, AgMg, 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*, PdPt, PdRh*, PdRu*, 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

## 1. 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 Ref. [1]. Since the earliest, completely *ab initio* computation of a binary phase diagram [2], the approaches for computing 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 14 080 computed total energies on 176 crystal structures in 80 binary alloys. All energies were computed in the Local Density (LDA) or Generalized Gradient Approximation (GGA) to Density Functional Theory, which are standard approaches for first principles studies on solids. 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

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knowledge, the largest library of *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 *ab initio* predictions and the experimental observations (Table 9). On the basis of the experimental data in Refs. [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 10 meV/atom of the *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 for which a significant disagreement between experiment and *ab initio* LDA/GGA is likely. Such disagreements are addressed in Section 4.

We believe that the low ratio of unambiguous errors (3) to the number of unambiguous correct predictions (89) is encouraging, and establishes clearly the potential of predicting crystal structure correctly with *ab initio* methods.

We also predict the stability of five new crystal structures which, 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 $Pd_3Pt$, an AB bcc superstructure for MoTi, an $AB_3$ bcc superstructure for $MoTi_3$, $Mo_3Ti$, $Nb_3Tc$, $RuTi_3$ and $TcTi_3$, an $A_2B_2$ hcp superstructure for RhRu, and an $A_2B_4$ hcp superstructure for $RhRu_2$ (Appendix A). In addition, we find two new crystal structures which are not superstructures of fcc, bcc or hcp: $Mo_5Ti$ ($Mo_5Ti$ and $Nb_5Ru$) (Appendix B).

## 2. 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, PdZr, PtTi, PtZr, RhRu, RhTc, RhTi, RhY, RhZr, RuTi, RuTc, RuY, RuZr, TcTi, TcY, TcZr, TiZr*, YZr*, where the superscript * indicates the systems in which the *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 $A_3B$ (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 Table 1.

Table 1
Compositions, concentrations and number of prototypes inside the library

| Compounds composition | Concentration of B (%) | Number of prototypes |
|---|---|---|
| A & B | 0 | 4 |
| $A_5B$ & $AB_5$ | 16.66 | 3 |
| $A_4B$ & $AB_4$ | 20 | 2 |
| $A_3B$ & $AB_3$ | 25 | 27 |
| $A_2B$ & $AB_2$ | 33.33 | 32 |
| $A_5B_3$ & $A_3B_5$ | 37.5 | 2 |
| $A_3B_2$ & $A_2B_3$ | 40 | 1 |
| $A_4B_3$ & $A_3B_4$ | 42.85 | 1 |
| AB (& BA*) | 50 | 29 (+3) |

The library has 176 structures, and 101 distinct prototypes (* at composition AB, three 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, $B_h$, B1, B2, B3, B4, $B8_1$, $B8_2$, B10, B11, B19, B27, B32, B33 ($B_f$), $C_c$, C2, C6, $C11_b$, C14, C15, $C15_b$, C16, C18, C22, C32, C33, C37, C38, C49, $D0_a$, $D0_3$, $D0_9$, $D0_{11}$, $D0_{19}$, $D0_{22}$, $D0_{23}$, $D0_{24}$, $D1_3$, $D1_a$, $D2_d$, $D7_3$, $D8_8$, $L1_0$, $L1_1$, $L1_2$, $L6_0$, $CaIn_2$, CuTe, $CuZr_2$, $GdSi_2$ (1.4), $MoPt_2$, NbAs (NbP), $NbPd_3$, $Ni_2Si$, $\Omega$ (with $z = 1/4$), $Pu_3Al$ ($Co_3V$), $Ti_3Cu_4$, $W_5Si_3$, $YCd_3$, $ZrSi_2$, $\gamma$-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:

$$\mathrm{LATTICE}^{[\mathrm{direction}]}_{\mathrm{stacking}}. \tag{1}$$

For example the designation $\mathrm{FCC}^{[001]}_{\mathrm{A2B2}}$ 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: $\mathrm{BCC}^{[011]}_{\mathrm{AB2}}$, $\mathrm{BCC}^{[211]}_{\mathrm{AB2}}$, $\mathrm{FCC}^{[001]}_{\mathrm{A2B2}}$, $\mathrm{FCC}^{[011]}_{\mathrm{A2B2}}$, $\mathrm{FCC}^{[111]}_{\mathrm{A2B2}}$, $\mathrm{FCC}^{[311]}_{\mathrm{A2B2}}$, $\mathrm{FCC}^{[100]}_{\mathrm{AB2}}$, $\mathrm{FCC}^{[111]}_{\mathrm{AB2}}$, $\mathrm{FCC}^{[001]}_{\mathrm{AB3}}$, $\mathrm{FCC}^{[011]}_{\mathrm{AB3}}$, $\mathrm{FCC}^{[011]}_{\mathrm{AB3}}$, $\mathrm{FCC}^{[111]}_{\mathrm{AB3}}$. For the FCC