Calculation of solubility in titanium alloys from first principles

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Abstract

We present an approach to calculate the atomic bulk solubility in binary alloys based on the statistical-thermodynamic theory of dilute lattice gas. The model considers all the appropriate ground states of the alloy and results in a simple Arrhenius-type temperature dependence determined by a “low-solubility formation enthalpy”. This quantity, directly obtainable from first principles, is defined as the composition derivative of the compound formation enthalpy with respect to nearby ground states. We apply the framework and calculate the solubility of the A solutes in A–Ti alloys (A = Ag, Au, Cd, Co, Cr, Ir, W, Zn). In addition to determination of unknown low-temperature ground states for the eight alloys, we find qualitative agreements with solubility experimental results. The presented formalism, correct in the low-solubility limit, should be considered as an appropriate starting point for estimation of whether a more computationally expensive formalism is needed.

Keywords: Phase separation; Precipitation; Solubility

1. Introduction

High-throughput ab initio methods are capable of predicting materials’ properties and searching for better systems. They are becoming important tools for scientists working on rational materials development. These methods allow researchers to exploit property correlations between different systems and to guide the prediction of new materials [1–6]. The main difference between the “several-calculations” and the “high-throughput” philosophies is that the former concentrates on the calculation of a particular property, while the latter focuses on the extraction of property correlations in the search for systems with target characteristics. Several applications of high-throughput ab initio approaches have been proposed in recent years. Examples are the “data-mining of quantum calculations” method leading to the principle-component analysis of the formation energies of many alloys in several configurations [4,5,7,8], the evolutionary approach for determining lattice Hamiltonians [9], the “Pareto-optimal” search for alloys and catalysts [10,11], the prediction of the lithium–boron superconductor [12], the “high-throughput Kohn-anomalies” search in ternary lithium-borides [13,14], and the “multi-optimization” techniques used for the study of high-temperature reactions in multicomponent hydrides [15–17].

To overcome the immense quantity of information necessary to build correlations, the high-throughput approach requires a rapid yet approximate estimation of the material’s properties. For example, the “Automatic-Flow” (AFlow) Consortium Project, aimed to the parameterization of all the binary intermetallic alloys, contains data for more than 120,000 ab initio calculations [18]. In addition, ad hoc algorithms and appropriate computer software must be developed to analyze and to conclude about correlations. Finally, once the search space has been narrowed, a detailed study is employed to pinpoint the feasible candidate systems.

This manuscript focuses on one of the requirements for high-throughput approaches: we present an ad hoc algorithm to calculate rapidly the solubility in binary alloys.
The knowledge of solubility is crucial for designing new alloys with particular physical, chemical and mechanical properties. For example, if we have to enhance an alloy property by adding extra species as solutes, it is necessary to know the equilibrium solubility, to avoid supersaturation-precipitation and subsequent modification of the target property (aging). In superconducting materials research, the problem emerges frequently: often expensive and difficult experiments are undertaken to enhance the critical temperature [19,20]. In catalysis research, experiments and modeling have shown that size-dependent carbon solubility is responsible for thermodynamic instabilities hindering the catalytic activity of very small Fe and Fe:Mo clusters [21,22]. The solubility of Zr in Al has already been addressed with success within the regular solution model [21,22]. The solubility of Zr in Al has already been addressed with success within the regular solution model [21,22].

In the present paper we devised a statistical-thermodynamic approach to tackle the task. Our approach considers all available binary ground states rather than just pure solids. To test the method, we present calculations for a number of binary titanium systems. The paper is organized as follows. In Section 2 we write the equations governing solubility of vacancies and substitutional impurities in binary alloys. Section 3 is devoted to the discussion of capabilities and limits of the formalism. In Section 4, the phase diagrams and solubilities are addressed for A–Ti systems (A = Ag, Au, Cd, Co, Cr, Ir, W, Zn). Conclusions are given in Section 5.

2. Solubility formalism

2.1. Enthalpy

Let us consider a disordered dilute solution of A atoms and vacancies (V) in a pure B solid with a given Bravais crystal lattice (labeled with “dis”). Neglecting A–A, A–V and V–V interactions and assuming small A and V concentrations, the approximate enthalpy can be written as:

\[ H_{\text{dis}} = E_{\text{dis}} + pV_{\text{dis}} = H_{\text{B}}^\text{at} N + H_{\text{A}} N_A + H_{\text{V}} N_V, \]  

(1)

where \( H_{\text{B}}^\text{at} \) is the enthalpy of the pure B solid per atom, \( H_{\text{A}} \) is the change in enthalpy of the solid upon substitution of one B atom with an A atom, and \( H_{\text{V}} \) is the change in enthalpy upon removal of one B atom and the introduction of a vacancy. In addition, \( N \) is the total numbers of crystal lattice sites, \( N_x \) (\( x = \text{A, B, V} \)) is the number of \( x \)-type atoms:

\[ N = N_A + N_B + N_V, \quad H_{\text{A}} = E_{\text{A}}^{\text{at}} + pE_{\text{A}}^0, \quad H_{\text{B}} = E_{\text{B}}^{\text{at}} + pE_{\text{B}}^0, \quad H_{\text{V}} = E_{\text{V}}^{\text{at}} + pE_{\text{V}}^0, \]  

(2)

\( E_x^\text{at} \) and \( E_x^0 \) (\( x = \text{A, B} \)) are the energy and volume per atom of the \( x \)-pure solid, \( E_{\text{A}}^0 \) and \( E_{\text{V}}^0 \) represent the change of volume of the B-pure solid upon introduction of one A atom or one vacancy, and \( p \) is the pressure. The framework introduced by Eq. (1) is similar to Wagner–Schottky model of a system of non-interacting particles [29]. The quantities with superscript “0” are considered to be temperature, pressure and composition independent being calculated at zero temperature and pressure. Hence, the accuracy of the approximation is higher in the case of limited pressures or for systems with very high bulk modulus, where the elastic energy fraction of \( E_x^\text{at} \) is negligible.

The quantities in Eq. (2) can be easily approximated as differences of first-principles energies \((E)\) and volumes \((v)\) of large supercell (sc) with and without a defect (substitutional A atom or vacancy):

\[ E_{\text{A}}^0 \simeq E_{\text{sc}}[B_n-1A] - E_{\text{sc}}[B_{n}], \quad E_{\text{B}}^0 \simeq E_{\text{sc}}[B_{n+1}] - E_{\text{sc}}[B_{n}], \quad E_{\text{V}}^0 \simeq E_{\text{sc}}[B_{n+1}]-E_{\text{sc}}[B_{n}]. \]  

(3)

As the size of the supercell increases, the approximate quantities in Eq. (3) approach their exact values. In literature [30] and in this paper, \( E_{\text{A}}^0 \), \( E_{\text{B}}^0 \) and \( H_{\text{A}} \) \((x = \text{A, V})\) are called the “raw” (composition unpreserving) \( x \)-defect formation energy, volume and enthalpy, respectively.

The enthalpy per atom is obtained from Eq. (1) as:

\[ H_{\text{at}}^\text{dis} = H_{\text{at}}^\text{dis}/(N_A + N_B) = H_{\text{B}}^\text{at} + H_{\text{A}} x_A + (H_{\text{V}} + H_{\text{V}}^\text{at}) x_V, \]  

(4)

where \( x_x \) \((x = \text{A, B, V})\) are the atomic concentrations \( x_x = N_x/(N_A + N_B) \).

(5)

Then, we follow the conventional use of the formation enthalpy \( \Delta H_{\text{at}}^\text{dis} \) calculated with respect to the pure A and B solids [31]:

\[ \Delta H_{\text{at}}^\text{dis} = H_{\text{B}}^\text{at} - x_A H_{\text{A}}^\text{at} - (1-x_A) H_{\text{B}}^\text{at}, \]  

(6)

where \( H_{\text{A}}^\text{at} = E_{\text{A}}^\text{at} + pE_{\text{A}}^0 \) and \( H_{\text{B}}^\text{at} \) has been defined in Eq. (2). Combining Eqs. (4) and (6), we get

\[ \Delta H_{\text{at}}^\text{dis} = H_{\text{A}} x_A + H_{\text{V}} x_V, \]  

(7)

where the quantities \( H_{\text{A}} \) and \( H_{\text{V}} \), defined as

\[ H_{\text{A}} = H_{\text{A}}^\text{at} - H_{\text{A}}^{\text{at}} + H_{\text{B}}^{\text{at}}, \quad H_{\text{V}} = H_{\text{V}}^{\text{at}} + H_{\text{B}}^{\text{at}}, \]  

(8)

are usually called A-defect and V-defect “true” (composition preserving) formation enthalpies [30]. They can be obtained from [31]:

\[ H_x = \frac{\partial \Delta H_{\text{at}}^\text{dis}}{\partial x_x} \bigg|_{x_x=0} (x = \text{A, V}). \]  

(9)

2.2. Equilibrium Gibbs free energy

The formation Gibbs free energy, \( \Delta G_{\text{at}}^\text{dis} \), is defined as:

\[ \Delta G_{\text{at}}^\text{dis} = \Delta H_{\text{at}}^\text{dis} - T \Delta S_{\text{at}}^\text{dis}, \]  

(10)
where \( \Delta H_{\text{mix}}^{\text{gs}} \) is described by Eq. (7). The formation entropy \( \Delta S_{\text{at}}^{\text{dis}} = \Delta S_{\text{at}}^{\text{eq}} \) can be obtained within the mean-field approximation as:

\[
\Delta S_{\text{at}}^{\text{dis}} = -\frac{k_{\text{B}}N}{N_{\text{A}} + N_{\text{B}}} \sum_{z=A,B,V} c_z \ln c_z, 
\]

(11)

where \( T, k_{\text{B}}, c_z (z = A, B, V) \) are the temperature, the Boltzmann constant and the site concentrations of atoms:

\[
c_z = N_z/N.
\]

(12)

By changing variables from site concentrations \( c_z \) to atomic concentrations \( x_z \):

\[
x_z = N_z/(N_{\text{A}} + N_{\text{B}}), \quad c_z = x_z/(1 + x_V),
\]

(13)

we rewrite Eq. (10) as

\[
\Delta G_{\text{at}}^{\text{dis}} = \Delta G_{\text{at}}^{\text{dis}, A} + \Delta G_{\text{at}}^{\text{dis}, V},
\]

\[
\Delta G_{\text{at}}^{\text{dis}, A} = H_A x_A + k_{\text{B}} T [x_A \ln x_A + (1-x_A) \ln(1-x_A)],
\]

\[
\Delta G_{\text{at}}^{\text{dis}, V} = H_V x_V + k_{\text{B}} T [x_V \ln x_V - (1+x_V) \ln(1+x_V)].
\]

(14)

In an alloy with fixed atomic composition \( x_A \), the equilibrium concentration of vacancies \( x_{\text{eq}}^V \) is determined by minimizing the formation Gibbs free energy:

\[
\frac{\partial \Delta G_{\text{at}}^{\text{dis}}}{\partial x_V} = \frac{\partial \Delta G_{\text{at}}^{\text{dis}, V}}{\partial x_V} = 0.
\]

(15)

The manipulation of Eqs. (14) and (15) leads to:

\[
x_{\text{eq}}^V = \left[ \exp \left( \frac{H_V}{k_{\text{B}} T} \right) - 1 \right]^{-1},
\]

\[
x_{\text{eq}}^V|_{k_{\text{B}} T \in \text{Ev}} \approx \exp \left( -\frac{H_V}{k_{\text{B}} T} \right),
\]

\[
\Delta G_{\text{at}}^{\text{dis}, V}(x_{\text{eq}}^V) = k_{\text{B}} T \ln \left[ 1 - \exp \left( -\frac{H_V}{k_{\text{B}} T} \right) \right],
\]

\[
\Delta G_{\text{at}}^{\text{dis}, V}(x_{\text{eq}}^V)|_{k_{\text{B}} T \in \text{Ev}} \approx -k_{\text{B}} T \exp \left( -\frac{H_V}{k_{\text{B}} T} \right).
\]

(16)

To conclude, the “true” vacancy formation enthalpy \( H_V \) determines the equilibrium concentration of vacancies within an Arrhenius-type formalism (see also Ref. [31]). In the next section, we show that \( H_A \) resolves the solubility in the case of a phase-separating alloy without intermediate ground states.

2.3. Solubility

At a given temperature, the solubility of A atoms in a B solid phase, \( x_{\text{sol}}^{\text{A}} \), is defined as the maximum homogeneously achievable concentration of A without precipitation of a new phase (Fig. 1a). The accurate calculation of \( x_{\text{sol}}^{\text{A}} \) requires the knowledge of the “closest” ground state (labeled as “gs”). It is followed by the minimization of the formation Gibbs free energy \( \Delta G_{\text{at}}^{\text{mix}}(x) \) for the mixture of (i) the disordered dilute solution of A atoms and vacancies in a B-rich solid phase at composition \( x_{\text{B}} \) (the

"dis"-phase of the previous section), and (ii) the on- or off-stoichiometric “gs”-phase at composition \( x_{\text{gs}} \). The lever rule gives the fractions of the two phases:

\[
\Delta G_{\text{at}}^{\text{mix}}(x) = \frac{x_{\text{gs}}}{x_{\text{B}} - x} \Delta G_{\text{at}}^{\text{dis}}(x_{\text{B}}) + \frac{x - x_{\text{gs}}}{x_{\text{B}} - x_{\text{gs}}} \Delta G_{\text{at}}^{\text{gs}}(x_{\text{gs}}).
\]

(17)

The minimization is performed with respect to \( x_{\text{gs}} \) and \( x_{\text{B}} \) (x is the overall composition of A in the two-phase mixture, \( x_{\text{B}} < x < x_{\text{gs}} \):

\[
\frac{\partial \Delta G_{\text{at}}^{\text{mix}}}{\partial x_{\text{B}}} = 0 \quad \frac{\partial \Delta G_{\text{at}}^{\text{mix}}}{\partial x_{\text{gs}}} = 0.
\]

(18)

Combination of Eqs. (17) and (18) leads to the usual common-tangent rule ("red line" in Fig. 1b):

\[
\frac{\partial \Delta G_{\text{at}}^{\text{mix}}(x_{\text{B}})}{\partial x_{\text{B}}} = \frac{\partial \Delta G_{\text{at}}^{\text{mix}}(x_{\text{gs}})}{\partial x_{\text{gs}}} = \frac{\Delta G_{\text{at}}^{\text{dis}}(x_{\text{B}}) - \Delta G_{\text{at}}^{\text{gs}}(x_{\text{gs}})}{x_{\text{B}} - x_{\text{gs}}}.
\]

(19)

Substituting Eq. (14) into Eq. (19), we obtain

\[
x_{\text{gs}}^{\text{A}} = [ \exp(H_{\text{gs}}/k_{\text{B}} T) + 1 ]^{-1},
\]

(20)

which approximates in an Arrhenius-type relation at low temperature:

\[
x_{\text{gs}}^{\text{A}}|_{k_{\text{B}} T \in H_{\text{gs}}} \approx \exp(-H_{\text{gs}}/k_{\text{B}} T).
\]

(21)
The quantity \( H_{\text{sol}} \) is defined as
\[
H_{\text{sol}} \equiv H_A - \frac{\Delta G_{\text{at}}^{\text{dis}}(x_\text{At}^{\text{sol}}) - \Delta G_{\text{at}}^{\text{dis}}(x_\text{At}^{\text{nv}})}{x_\text{At}^{\text{sol}} - x_\text{At}^{\text{nv}}}.
\] (22)

The non-linear problem described by Eqs. (20)–(22) can be linearized within the low-solubility limit (labeled by “ls”):
\[
\begin{cases}
  x_\text{At}^{\text{sol}} \approx x_\text{At}^0, & \Delta G_{\text{at}}^{\text{dis}}(x_\text{At}^{\text{sol}}) \approx \Delta G_{\text{at}}^{\text{dis}}(x_\text{At}^0), \\
  x_\text{At}^{\text{nv}} \approx x_\text{At}^0, & \Delta G_{\text{at}}^{\text{dis}}(x_\text{At}^{\text{nv}}) \approx \Delta H_{\text{gs}}^{\text{sol}}.
\end{cases}
\] (23)

where \( \Delta H_{\text{gs}}^{\text{sol}} \) is the formation enthalpy of the ground state “gs”. In the low-solubility limit, \( H_{\text{sol}} \) becomes:
\[
H_{\text{sol}}^\text{ls} = H_{\text{sol}}^{\text{nv}} + \Delta G_{\text{at}}^{\text{dis}}(x_\text{eq}^\text{sc})/x_\text{At}^0,
\] (24)

where \( H_{\text{sol}}^{\text{nv}} \) is the non-vacancy contribution (labeled as “nv”):
\[
H_{\text{sol}}^{\text{nv}} = H_A - \Delta H_{\text{at}}^{\text{ls}}/x_\text{At}^0.
\] (25)

From the equilibrium vacancy concentration, Eq. (16), the exponential part of Eqs. (20) and (21) becomes:
\[
\exp(-H_{\text{sol}}^\text{ls}/k_B T) = \exp(-H_{\text{sol}}^{\text{nv}}/k_B T) \times \left[ 1 - \exp\left(-\frac{H_A}{k_B T}\right)^{-1/x_\text{At}^0}, \right.
\] (26)

where the two contributions, non-vacancy and vacancy, are factorized. The last expression indicates that the presence of vacancies increases the solubility by decreasing the number of host B atoms in the solution.

3. Interpretation of \( H_{\text{sol}}^{\text{ls}} \)

The calculation of low-solubility of non-interacting defects can be implemented through the first-principles calculation of \( H_{\text{sol}}^{\text{ls}} \) (Eq. (24)). It requires the knowledge of the enthalpy \( \Delta H_{\text{at}}^{\text{dis}} \) and composition \( x_\text{At}^0 \) of the ground-state “gs”, as well as the “true” defect formation enthalpies \( H_A \) and \( H_{\text{gs}} \) (Eq. (8)).

To capture the physical meaning of \( H_{\text{sol}}^{\text{ls}} \), let us consider an arbitrary dilute solution “sc” at composition \( x_\text{At}^\text{sc} \) (see Fig. 2). The label “sc” indicates that the solution is generated as a supercell of the B solid upon insertion of defects randomly distributed. The first part of Eq. (25) can be rewritten (according to Eq. (9)) as:
\[
H_A = \frac{\partial \Delta H_{\text{at}}^{\text{gs}}(x_\text{At}^\text{sc})}{\partial x_\text{At}^\text{sc}}.
\] (27)

The second part of Eq. (25) becomes:
\[
\frac{\Delta H_{\text{at}}^{\text{gs}}}{x_\text{At}^{\text{gs}}} = \frac{\partial H_{\text{at}}^{\text{B+gs}}(x_\text{sc}^\text{B}, x_\text{At}^\text{bsc})}{\partial x_\text{At}^\text{sc}}.
\] (28)

where \( \Delta H_{\text{at}}^{\text{B+gs}} \) is the formation enthalpy of the mixture of the pure B solid with the ground state “gs” with overall composition \( x_\text{sc}^\text{B} \) (point (B+ “gs”) in Fig. 2). Thus, we obtain:

\[
\frac{\Delta H_{\text{at}}^{\text{B+gs}}}{x_\text{At}^{\text{gs}}} = \frac{\partial H_{\text{at}}^{\text{B+gs}}(x_\text{sc}^\text{B}, x_\text{At}^\text{bsc})}{\partial x_\text{At}^\text{sc}}.
\] (28)

The comparison of Eq. (27) with Eq. (29) leads to the conclusion that both \( H_A \) and \( H_{\text{sol}}^{\text{ls}} \) are derivatives of supercell formation energies with respect to A-composition. For \( H_A \), the supercell formation enthalpy is determined with respect to pure A and B phases (the distance between points “sc” and (B + A) in Fig. 2). For \( H_{\text{sol}}^{\text{ls}} \), the supercell formation enthalpy is determined with respect to B pure and the ground state “gs” (the distance between points “sc” and (B + gs) in Fig. 2). To conclude, \( H_A \) and \( H_{\text{sol}}^{\text{ls}} \) are characterized by the angles \( \alpha \) and \( \beta \) between the B--“sc”/B–A and B--“sc”/B--“gs” lines, respectively. In analogy with the \( H_A \) definition in Eq. (8), \( H_{\text{sol}}^{\text{ls}} \) can be considered as the “low-solubility formation enthalpy”.

The quantities \( H_A \) and \( H_{\text{sol}}^{\text{ls}} \) are identical only for phase-separating alloys without intermediate ground states (i.e. when “gs” \( \equiv A \)). In this case, the low-solubility can be formally determined by minimizing \( \Delta G_{\text{dis}}^{\text{At}} \) (Eq. (14)) with respect to \( x_A \) (e.g. Ref. [32]). However, in the general case, the existence of ordered ground states must be verified so the appropriate formalism is used. Generally, in ordering alloys, \( H_A \) and \( H_{\text{sol}}^{\text{ls}} \) differ and could even have different signs.

Note that if the “sc” point is below (B + gs) in Fig. 2 (\( H_{\text{sol}}^{\text{ls}} < 0 \)), the solubility expressions (20) and (21) are not valid and there must exist an undetected ground state (it might be “sc” itself) with concentration lower than \( x_\text{At}^{\text{nv}} \). In this case, such undetected ground state should be used for the calculation of solubility [33].

The expression for non-binary low-solubility within the regular solution model derived in Refs. [23,24] coincides with our derivation in the case of binary alloys without vacancies and high-temperature contributions. This is because the regular solution model corresponds to our model for the free energy in case of dilute solution.
4. Ground states of selected titanium alloys

As an example of our formalism application, we calculate the solubility of a set of metals in titanium. First, we explore the possible ground states of the A–Ti systems (A = Ag, Au, Cd, Co, Cr, Ir, W, Zn) and then we apply the construction described in the previous section.

The low-temperature stability of A–Ti is studied by using our high-throughput quantum calculations framework [5, 4, 12, 14] based on first-principles energies obtained with the VASP software [34]. We use projector-augmented waves (PAW) pseudopotentials [35] and exchange-correlation functionals as parameterized by Perdew–Burke–Ernzerhof [36] for the generalized gradient approximation (GGA). Simulations are carried out without spin polarization except Ti–Co, at zero temperature and pressure [37], and without zero-point motion. All structures are fully relaxed (shape and volume of the cell and internal positions of the atoms). The effect of lattice vibrations is omitted. Numerical convergence to within about 1 meV atom\(^{-1}\) is ensured by enforcing a high energy cut-off (357 eV) and dense 6000 \(k\)-point meshes.

For each system, the energies of 200 crystal structures were calculated. In addition to the 176 configurations described in Ref. [5], the structures included all the symmetrically distinct hexagonal-close packed (hcp), body-centered cubic (bcc) and face-centered cubic (fcc) based superstructures with up to four atoms per cell, and the prototypes A5, A6, A7, A8, A9, A11, B20, C36, D519, Al2Zr4, Al2Zr2, Cu7, Ge, CdTi, Cu3Ti2, Ga2Hf, Ga4Ni, Ga4Pt5, Ga4Ti5, Hg2Pt, ITl, InTh, LiB-MS1/2, Al2Zr4, NbNi8, NiTi2, SeTI, and V2Zn5. The prototypes were considered because they are common or related to Ti alloys [40, 39]. This protocol gives reasonable results. In Ref. [5], it was shown that the probability of reproducing the correct ground state, if well defined and not ambiguous, is \(\eta^r \sim 96.7\%\) (“reliability of the method”, Eq. (3)). We did not consider hcp superstructures with more than four atoms per cell due to the fact that their number increases considerably and that many hcp–hcp systems do not form hcp fields but instead fcc or bcc (i.e. Co–Ti and Ti–Zn in Figs. 6–10, or off-lattice (i.e. Hf–Ti, Hf–Zr [8]). Therefore, even if it is impossible to rule out the existence of an undetected ground state, the protocol is expected to give a reasonable balance between high-throughput speed and scientific accuracy.

The whole process is performed in an automatic fashion through the software AFLLOW, which generates the prototypes, optimizes the parameters, performs the calculations, corrects possible errors and calculates the phase diagrams [5, 18].

Our results of ground state calculation are presented in Figs. 3–10 and Table 1. The correspondence of ab initio vs. experimental results is very good and typical for this type of calculation [5].

We propose the degenerate results for: (1) Co2Ti: experimentally reported as C14 and C15, respectively; (2) CoTi2: experimentally reported as NiTi2, but with ab initio formation energies of \(-291.2, -287.3\) and \(-285.7\) meV atom\(^{-1}\) for C37, CuZr2, and NiTi2, respectively; (3) TiZn: experimentally reported as B2, but with ab initio formation energies of \(-195.4\) and \(-193.4\) meV atom\(^{-1}\) for L10 and B2, respectively.

We propose novel results for: (1) Ir2Ti: experimentally reported as a two-phase region above 500 °C, but with a pos-

![Fig. 3. Ag–Ti ground state convex hull.](image)

![Fig. 4. Au–Ti ground state convex hull.](image)

![Fig. 5. Cd–Ti ground state convex hull.](image)
possible ab initio low-temperature ground state Ca$_7$Ge with formation energy of $-373.8$ meV atom$^{-1}$. (2) Ir$_2$Ti: experimentally reported as a two-phase region above 500 $^\circ$C, but with a possible ab initio low-temperature ground state C11$_b$, with formation energy of $-716.0$ meV atom$^{-1}$. (3) TiW$_2$: experimentally reported as a two-phase region above 500 $^\circ$C, but with a possible ab initio low-temperature ground state BCC$_{138}$AB$_2$, with formation energy of $-82.7$ meV atom$^{-1}$. (4) TiW$_4$: experimentally reported as a two-phase region above 500 $^\circ$C, but with a possible ab initio low-temperature ground state D1$_a$, with formation energy of $-83.8$ meV atom$^{-1}$. (5) Ti$_3$Zn: experimentally not explored, but with a possible ab initio low-temperature ground state A15, with formation energy of $-120.0$ meV atom$^{-1}$.

In particular, the results indicate that in the Ir–Ti system the low-temperature Ir-rich part of the known phase diagram is not complete, and that the Ti–W alloy has an ordering tendency at low temperature, in contrast to common belief [39,40]. In addition, in Ti–Zn there must exist a Ti-rich compound with Ti composition higher than the reported Ti$_2$Zn [39,40].

5. Results and discussion of solubility in Ti alloys

The “raw” formation enthalpies of a substitutional atom or a vacancy in Ti were obtained through Eq. (3) considering a $3 \times 3 \times 3$ supercell of hcp Ti. The supercell’s dimensions were chosen to limit the defect–defect interactions by having their distance at least three times larger than the nearest neighbor Ti–Ti bond (see also Fig. 13 and the corresponding discussion below). The results are presented in Table 2. The temperature dependency of solubilities is presented in Fig. 11, while Fig. 12 illustrates a
comparison of experimental and theoretical data at $T = 700 \, ^\circ C$.

Table 2 shows negative “true” formation enthalpies $H_A$ for $A = \text{Zn}, \text{Au}, \text{and Ir}$. The data indicates that calculation of Zn, Au and Ir solubilities in Ti is not feasible without considering nearby intermetallic ground states as performed in our model. Figs. 11 and 12 show that the highest theoretical solubility in Ti occurs for Zn, Cd, Ag and Au as a consequence of their low solubility formation enthalpies (see Table 2). The high solubility has also been observed experimentally for Cd, Ag and Au, whereas, to the best of our knowledge, the solubility of Zn has not been studied.

The high solubility of late transition metals Zn, Cd, Ag and Au in the early transition metal Ti is due to the substantial localized stability provided by the filling tendency of the $d$-band of Ti [42]. Because of the very high formation enthalpy of vacancy in Ti (reported in Table 2), the vacancy equilibrium concentration was found to be very low at all considered temperatures (e.g. $x_V^0 < 10^{-6}$ at $T < 1300 \, ^\circ C$). Thus, the effect of vacancies on the solubility in Ti alloys is negligible.

Although theoretical and experimental results follow similar trends, theoretical solubilities are considerably smaller for most of the considered alloys. A similar discrepancy was also observed for Al–Zr in Ref. [24]. The discrepancy could be due to shortcomings of theory and/or experiment. The main approximations of our model consist of (i) neglecting the defect interaction, (ii) neglecting the spatial defect correlation and (iii) assuming a low concentration of defects.

Table 1

<table>
<thead>
<tr>
<th>Experimental (Refs. [40,39])</th>
<th>Ab initio</th>
<th>$\Delta H_{\text{sol}}^\circ$ (meV atom$^{-1}$)</th>
<th>Space group [41]</th>
<th>Pearson symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–Ti</td>
<td>B11</td>
<td>$-67.6$</td>
<td>P4/nmm</td>
<td>tP4</td>
</tr>
<tr>
<td>AgTi–B11</td>
<td>C11$_b$</td>
<td>$-63.3^a$</td>
<td>I4/mmm</td>
<td>t6</td>
</tr>
<tr>
<td>Au–Ti</td>
<td>D1$_a$</td>
<td>$-283.2$</td>
<td>I4/m</td>
<td>t10</td>
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<tr>
<td>Au$_2$Ti–C11$_b$</td>
<td>C11$_b$</td>
<td>$-430.4$</td>
<td>I4/mmm</td>
<td>t6</td>
</tr>
<tr>
<td>Two-phase region above 500 °C</td>
<td>Au$_4$Ti–Cu$_4$Ti$_3$/tie</td>
<td>$-430.6$</td>
<td>I4/mmm</td>
<td>t14</td>
</tr>
<tr>
<td>Au$_2$Ti–B11</td>
<td>B11</td>
<td>$-429.8$</td>
<td>P4/nmm</td>
<td>tP4</td>
</tr>
<tr>
<td>Au$_3$Ti–A15</td>
<td>A15</td>
<td>$-356.1^a$</td>
<td>Pm3n</td>
<td>cP8</td>
</tr>
<tr>
<td>Cd–Ti</td>
<td>B11</td>
<td>$-62.0$</td>
<td>P4/nmm</td>
<td>tP4</td>
</tr>
<tr>
<td>CdTi$_2$–C11$_b$</td>
<td>C11$_b$</td>
<td>$-73.7^a$</td>
<td>I4/mmm</td>
<td>t6</td>
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<tr>
<td>Cr–Ti</td>
<td>C15</td>
<td>$-120.3^a$</td>
<td>Fd3m</td>
<td>cF24</td>
</tr>
<tr>
<td>Co–Ti</td>
<td>L1$_2$</td>
<td>$-254.8$</td>
<td>Pm3m</td>
<td>cP4</td>
</tr>
<tr>
<td>Co$_2$Ti–L1$_2$</td>
<td>C14</td>
<td>$-311.4$</td>
<td>P6$_3$/mm</td>
<td>hP12</td>
</tr>
<tr>
<td>Co$_2$Ti–C15</td>
<td>C15</td>
<td>$-304.0$</td>
<td>Fd3m</td>
<td>cF24</td>
</tr>
<tr>
<td>CoTi–B2</td>
<td>B2</td>
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<td>cP2</td>
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<tr>
<td>CoTi$_2$–NiTi$_2$</td>
<td>C37</td>
<td>$-291.2^a$</td>
<td>Pnma</td>
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<tr>
<td>CuZr$_2$</td>
<td>$-287.3$</td>
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<td>cF96</td>
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<tr>
<td>Ir–Ti</td>
<td>L1$_2$</td>
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<td>cF32</td>
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<tr>
<td>Ir$_2$Ti–C11$_b$</td>
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<td>$-451.8$</td>
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<td>cP4</td>
</tr>
<tr>
<td>IrTi–δ</td>
<td>L1$_0$</td>
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<td>P4/mmm</td>
<td>tP4</td>
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<tr>
<td>Two-phase region above 500 °C</td>
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<td>$-716.0$</td>
<td>I4/mmm</td>
<td>t6</td>
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<tr>
<td>Ir$_3$Ti–A15</td>
<td>A15/tie</td>
<td>$-570.3^a$</td>
<td>Pm3n</td>
<td>cP8</td>
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<tr>
<td>Ti–W</td>
<td>T$<em>{\text{W2}}$–BCC$</em>{\text{[111]}}$</td>
<td>$-82.7^a$</td>
<td>Pm3m</td>
<td>hP3</td>
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<td>Two-phase region above 500 °C</td>
<td>T$_{\text{W4}}$–D1$_a$</td>
<td>$-83.8$</td>
<td>I4/m</td>
<td>t110</td>
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<tr>
<td>Ti–Zn</td>
<td>T$_{\text{Zn–A15}}$</td>
<td>$-120.0^a$</td>
<td>Pm3m</td>
<td>cP8</td>
</tr>
<tr>
<td>Ti$_3$Zn–CuZr$_2$</td>
<td>CuZr$_2$</td>
<td>$-158.0$</td>
<td>I4/mmm</td>
<td>t6</td>
</tr>
<tr>
<td>TiZn$_2$–B2</td>
<td>L1$_0$</td>
<td>$-195.4$</td>
<td>P4/mmm</td>
<td>tP4</td>
</tr>
<tr>
<td>TiZn$_3$–C14</td>
<td>B2</td>
<td>$-193.4$</td>
<td>Pm3m</td>
<td>cP2</td>
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<tr>
<td>TiZn$_3$–L1$_2$</td>
<td>L1$_2$</td>
<td>$-197.2$</td>
<td>P6$_3$/mm</td>
<td>hP12</td>
</tr>
<tr>
<td>TiZn$_3$–L1$_2$</td>
<td>L1$_2$</td>
<td>$-198.0$</td>
<td>Pm3m</td>
<td>cP4</td>
</tr>
</tbody>
</table>

$^a$ The energy values used in solubility calculations.
related, calculations leading to low solubility values validate the assumptions, self-consistently. The mean-field approximation neglects the interatomic positional correlations but it is expected to work well when the deviation from complete stoichiometric (pure Ti solid in our case) is small—and so is the solubility in our case—see Section 19 in Ref. [43].

In order to validate our model of non-interacting solutes, we estimated the convergence of the “raw” formation enthalpies with respect to the size and composition of the supercell (see Fig. 13). The smaller the supercell, the higher the solute composition, the stronger solute–solute interaction, and correspondingly, the larger deviation of the formation enthalpy from the largest supercell (3 x 3 x 3). Fig. 13 illustrates the trend. For a solute compositions up to 16%, there is a 10% maximum deviation in the formation enthalpies, which does not greatly affect the solubilities at high temperatures. Thus, 16% could be considered as a solute composition threshold. Below this composition, our model is valid. If the criterion is violated, a more precise solute interaction and correlation parameterizations are necessary (requiring, for instance, cluster expansion and Monte Carlo simulations for lattice-based alloys). To conclude, our formalism should be considered as an appropriate starting point to determine if more computationally expensive formalisms are needed.

For all the alloys we found that at intermediate temperatures the calculated solubilities are small and within our approximation, but smaller than in experiments, as mentioned before. Ti–Zn has very low formation enthalpy (see Table 2) and, correspondingly, the highest theoretical solubility among the considered alloys (still within the 16% threshold). In Ref. [24], the authors added the defect interactions through the cluster expansion method but did not achieve a significant increase in solubility. In fact, our formalism includes a solute–solvent ordering tendency by considering the real intermetallic ground state other then the pure Ti solid. Thus, we conclude that our approximations

Table 2

“Raw” formation enthalpies \( H_{ATi} \), \( H_{VTi} \) (from Eqs. (2) and (3) at zero pressure), “true” formation enthalpies \( H_A, H_V \) (from Eq. (8) at zero pressure) and low-solubility (non-vacancy) formation enthalpy \( H_{ls}^{sol} \) (from Eq. (25) at zero pressure) of substitutional A defects (A = Ag, Au, Cd, Co, Cr) and vacancies (V) in Ti. The elements are ordered from low to high “low-solubility formation enthalpy”. All quantities are in eV units.

<table>
<thead>
<tr>
<th>A</th>
<th>( H_{ATi} )</th>
<th>( H_A )</th>
<th>( H_{ls}^{sol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>6.405</td>
<td>-0.262</td>
<td>0.218</td>
</tr>
<tr>
<td>Cd</td>
<td>7.267</td>
<td>0.24</td>
<td>0.461</td>
</tr>
<tr>
<td>Ag</td>
<td>5.412</td>
<td>0.304</td>
<td>0.494</td>
</tr>
<tr>
<td>Au</td>
<td>3.882</td>
<td>-0.781</td>
<td>0.643</td>
</tr>
<tr>
<td>W</td>
<td>-4.303</td>
<td>0.714</td>
<td>0.838</td>
</tr>
<tr>
<td>Ir</td>
<td>-2.059</td>
<td>-1.14</td>
<td>1.141</td>
</tr>
<tr>
<td>Co</td>
<td>1.138</td>
<td>0.316</td>
<td>1.19</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.674</td>
<td>1.024</td>
<td>1.205</td>
</tr>
</tbody>
</table>

\( H_{VTi} = 10.002 \) \( H_V = 2.068 \)
The other approximation is the assumed independence of the parameters with respect to temperature. The dependence can be caused by atom vibrations, anharmonicity of the parameters with respect to temperature. The dependence discrepancy is observed even at low temperatures and magnetic ordering. However, theory–experiment solubility discrepancy can be caused by atom vibrations, anharmonicity of the parameters with respect to temperature. The dependence discrepancy for the theory–experiment solubility discrepancy. (or those of the cluster expansion method) are not responsible for the theory–experiment solubility discrepancy.

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6. Conclusions

Based on the statistical-thermodynamic theory of dilute lattice gas, we have developed an approach to calculate the atomic bulk solubility in alloys. The approach considers all available binary ground states rather than just pure solids. It is shown that low-solubility follows simple Arrhenius-type temperature dependence determined by a “low-solubility formation enthalpy”. This quantity is defined as the composition derivative of the compound formation enthalpy with respect to nearby ground states. “Low-solubility formation enthalpy” coincides with the usual defect formation enthalpy only in the case of a phase-separating alloy without intermediate ground states and vacancies. The key quantities of our model can be directly obtained from first principles or by fitting the experimental temperature dependence of solubility. Generalization of our model to intermediate phases and/or to multicomponent, multi-sublattice, interstitial-substitutional alloys is straightforward and it has been performed for the Mg–B–X systems [33].

As example, we applied the developed framework for a set of eight Ti alloys A–Ti (A = Ag, Au, Cd, Co, Cr, Ir, W, Zn). We have found that the highest solubility for Zn, Cd, Ag and Au is in qualitative agreement with available experimental data and band structure considerations. The quantitative differences between the theory and experiment observed in the present and other similar studies are discussed.

The formalism is expected to be valid in the limit of low-solubility, and should be used to estimate if more computationally expensive formalisms are otherwise needed.

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References

[37] So that by calling the enthalpy we actually mean the energy in this section.