Energetics of cobalt alloys and compounds and solute–vacancy binding in fcc cobalt: A first-principles database

S. Shahab Naghavi, Vinay I. Hegde, Abhinav Saboo, C. Wolverton*

*Department of Materials Science and Engineering, Northwestern University, Evanston,
Illinois 60208, USA*

Abstract

Using extensive first-principles density functional calculations, we calculate thermodynamic properties of binary fcc cobalt-based alloys with 25 different solute elements. For each solute element X , we calculate its (a) nearest- and next-nearest-neighbor solute–vacancy binding energy, (b) dilute impurity mixing energy with respect to the equilibrium and hypothetical fcc-based reference states of the solute, (c) enthalpy of formation of cobalt-rich binary ordered compounds in the Co– X system, (d) solubility enthalpy, and other derived quantities. We find that the solute–vacancy binding energies of all the studied solutes in fcc cobalt are positive (indicating favorable binding), in contrast to nickel, aluminum, magnesium, and copper-based alloys, where mid $3d$ transition metal solutes have unfavorable solute–vacancy binding. We study the physical and chemical effects influencing solute–vacancy binding energy, and find that (a) it correlates broadly with solute size—larger solute atoms possess stronger binding with vacancies—and this is understood in terms of strain relief and secondary next-nearest-neighbor interactions, and (b) it follows a parabolic trend as a function of d -occupancy across the transition metal series—falling to a minimum at the middle of the series—and this is understood in terms of a d -band filling effect. We also find this d -band filling effect in other calculated quantities

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*Corresponding Author

Email address: c-wolverton@northwestern.edu (C. Wolverton)

such as the dilute impurity volumes and dilute impurity mixing energies. To aid in building thermodynamic databases, we tabulate all the calculated thermodynamic quantities, and compare them with experimental phase diagrams data and previous literature, and find good agreement where such data is available.

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1. Introduction

The field of superalloys (high-performance alloys) has received a spike in interest following the discovery of γ' - $\text{Co}_3(\text{Al,W})$ precipitates with the L1_2 structure [1], promising a new class of Co-based high-temperature materials. These novel superalloys offer better oxidation, corrosion, and wear resistance and potentially higher operation temperatures compared to Ni-based superalloys [2, 3]. Despite having some superior chemical and physical properties [1, 4], alloys based on $\text{Co}_3(\text{Al,W})$ suffer from several problems such as inferior high-temperature strength [5, 6], a narrow $\gamma+\gamma'$ two-phase region, and a low stacking fault energy [6]. Alloying additions are an effective way, at least in part, to overcome these problems and improve the mechanical properties of Co-based superalloys [3, 5–10]. For example, the addition of Ta, Ti, Nb, Hf, or Ni [3, 9–12] increases the stability and the stacking fault energy of γ' - $\text{Co}_3(\text{Al,W})$ simultaneously, thus improving the high-temperature strength of the γ' phase and $\gamma+\gamma'$ two-phase superalloys [12].

To understand the effects of alloying additions on diffusion in fcc cobalt, a detailed knowledge of the interaction between a solute atom and an accompanying vacancy (hereafter, a vacancy is indicated by $\square$) is necessary [13–15]. The solute- $\square$ binding energy directly influences impurity diffusion. In an alloy with dilute solute concentrations, the solute- $\square$ binding energy controls the probability of having a vacancy at a lattice site neighboring a solute atom. Therefore, in a vacancy-mediated diffusion process, energetic binding between a solute atom and a vacancy is a key factor in the quantitative understanding of solute diffusion [13] and as well as other associated kinetic phenomena such as precipitate nucleation. For example, the observed decreased response to natural aging with

microalloying additions (e.g., the behavior of Al-Cu alloys with the microalloying addition of Sn) could be understood in terms of vacancy trapping, due to a strong solute–□ binding energy [13, 14]. Despite its importance, this interaction is notoriously difficult to experimentally measure accurately [16] but can
30 be readily calculated using first-principles electronic structure methods such as density functional theory (DFT) [14, 15, 17, 18]. To our knowledge no such calculations exist for Co-based alloys.

In addition to kinetic phenomena, the thermodynamics of alloying behavior is also critically important in the design of new Co-based alloys. Among the
35 computational tools available today for studying thermodynamic phase stability in alloys, calculation of phase diagrams (CALPHAD) methods are one of the most widely used [19–21]. These methods use databases of thermodynamic functions, and can accurately calculate phase diagrams of multicomponent alloys. While CALPHAD methods have been successfully applied over the years
40 to many commercial alloy systems and databases (e.g., Al-based alloys, Fe-based alloys), mature databases for similar efforts in developing Co-based superalloys are not currently available [22]. In cases where experimental data is unavailable, DFT calculations can provide a wealth of energetic and thermodynamic information (e.g., mixing energies of solid solutions, formation energies of ordered
45 compounds, etc.) [23, 24] that significantly complement CALPHAD approaches. Thus, an extensive first-principles investigation of thermodynamics in cobalt alloys would greatly accelerate the development of CALPHAD databases, and ultimately, the design of new Co-based superalloys.

In the present work, the solute–□ binding energy, dilute mixing energy,
50 dilute volume of mixing, compound formation energy, and solubility enthalpy of 25 substitutional solutes in fcc cobalt are calculated using DFT. We include all of the alloying elements used in Co-based superalloys [6] which consist of almost all 3d, 4d, and 5d transition metal elements — except groups 3 and 12 — together with silicon and aluminum. Some of the alloying elements considered, such as
55 technetium and silver, may have no practical interest but provide useful data that serves to find systematic trends across the periodic table. We analyze the

results of our calculations to search for the key physical effects that influence solute–□ binding, such as d -occupancy, solute size, and second nearest-neighbor interactions. Finally, in an effort to aid in building thermodynamic databases, we tabulate all the calculated thermodynamic properties and compare them with experimental phase diagrams data, where available.

2. Methodology

2.1. Density Functional Theory

For calculations in the present work, we used plane-wave DFT with projector-augmented plane-wave (PAW) method [25, 26] as implemented in Vienna Ab-initio Simulation Package (VASP) [27, 28]. The exchange-correlation energy functional was described with the spin-polarized generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) [29]. We used the PAW potentials recommended by VASP, with a plane wave cutoff energy 1.3 times the maximum energy cutoff (“ENMAX”) listed in the PAW potentials for each system. We verified the convergence of the calculated quantities with respect to the plane wave cutoff energy by calculating all energies at a constant large cutoff of 520 eV — and found that the change in the solute–□ binding energies was negligible ($< 0.2\%$). We relaxed all structures fully, with respect to cell lattice vectors and atomic positions, by minimizing the energy until the Hellmann-Feynman forces on all atoms were less than 0.01 eV/Å, and stresses on the cell were a few kbar or less. We then used this relaxed structure for a final “static” self-consistent run to calculate the total energy. Therefore, all calculations were relaxed under constant zero pressure.

We utilized a periodic supercell in which one host atom is replaced with either a solute or a vacancy to approximate dilute limits. As discussed in Ref. [15], a large size mismatch between the solute/defect and the host atoms can result in elastic strain on nearby atoms, in addition to spurious defect-defect interaction due to periodic boundary conditions, and minimizing this interaction requires very large supercells. Here, we found that a 108-atom supercell consisting of

3×3×3 cubic conventional cells, which separates impurity atoms by ≈ 11 Å, results in solute–□ binding energies converged to within 1 meV/solute atom. We performed integrations over the Brillouin zone of the 108-atom supercell using the first-order Methfessel-Paxton [30] approach with a smearing width of 0.2 eV and a 3×3×3 Monkhorst-Pack [31] k-mesh during structural relaxation, and the tetrahedron method with Blöchl [32] corrections and a 4×4×4 Monkhorst-Pack k-mesh during the final static calculation for accurate total energies.

2.2. Calculation of Energetic Quantities

We calculate the energetics of solute–□ (X –□) binding for various pair spacings (e.g., nearest and second-nearest neighbors). The binding energy E_{bind} is defined as the difference between the energy of “infinite separation” and nearest-neighbor (or second-nearest-neighbor) separation of the solute and the vacancy. We calculated this difference using four independent calculations as follows:

$$-E_{\text{bind}}(X\text{--}\square) = \left(E(\text{Co}_N) - E(\text{Co}_{N-1}\square_1) \right) - \left(E(\text{Co}_{N-1}X_1) - E(\text{Co}_{N-2}X_1\square_1) \right) \quad (1)$$

where X and $\square$ represent a solute and vacancy respectively, embedded in an $N=108$ -atom supercell. The two groups of terms on the right side of Eq. 1 represent the energy required to break a host-host bond (first term) and a host-impurity bond (second term) due to the introduction of a vacancy. Thus, the solute–□ binding energy can be qualitatively understood as the difference between the host-impurity and host-host bond energies. In other words, if the host-impurity (Co- X) interaction is weaker than the host-host (Co-Co) interaction, a favorable solute–□ binding can be expected. The negative sign of E_{bind} in Eq. 1 is included to follow standard convention: a positive value corresponds to a favorable binding between the solute and the vacancy.

By having all the four energy terms on the right side of Eq. 1, one can easily calculate as a “by-product”, the vacancy formation energy in fcc cobalt:

$$E_{\text{vac}}(\square) = E(\text{Co}_{N-1}\square_1) - \frac{N-1}{N}E(\text{Co}_N) \quad (2)$$

Similarly, the dilute impurity mixing energy of a solute X in fcc cobalt is also readily obtained using:

$$E_{\text{imp}}(X) = E(\text{Co}_{N-1}X_1) - \frac{N-1}{N}E(\text{Co}_N) - E(X) \quad (3)$$

where $E_{\text{imp}}(X)$ is calculated for both X in the fcc ($E^{\text{fcc}}(X)$) and its equilibrium
105 crystal structure ($E^{\text{eq}}(X)$).

In order to get a quantitative measure of the atomic size of each solute impurity, X , we also calculate the dilute volume of mixing (hereafter, simply “impurity volume”), V_{imp}^X , which is given by the difference in volume induced by substituting a single fcc cobalt atom with a solute atom:

$$V_{\text{imp}}^X = V(\text{Co}_{N-1}X_1) - V(\text{Co}_N) \quad (4)$$

We note here that after adding a solute atom to the fcc cobalt matrix, we fully relaxed the alloyed structure to its ground state; therefore, this definition of the impurity volume includes all chemical interactions between a solute atom and the nearby cobalt atoms and thus is different from the standard atomic volume
110 of X .

The equilibrium formation enthalpy of a binary ordered compound is the energy of the compound relative to the pure elements, each in their equilibrium crystal structure:

$$\Delta H_{\text{ord}}^{\text{eq}}(\text{Co}_pX_q) = E(\text{Co}_pX_q) - \{(1-x)E^{\text{eq}}(\text{Co}) + xE^{\text{eq}}(X)\} \quad (5)$$

where $E(\text{Co}_pX_q)$ is the ground state energy (per atom) of the ordered Co_pX_q compound and x is the atomic fraction of X , $\frac{q}{p+q}$, in the compound.

Finally, the solubility enthalpy of a solute X is given by the difference (per solute atom) between the equilibrium formation enthalpy of the Co-rich binary ordered compound (from Eq. 5) and the dilute impurity mixing energy (from Eq. 3):

$$\Delta H_{\text{sol}}(X) = \Delta H_{\text{ord}}^{\text{eq}}(\text{Co}_pX_q) - E_{\text{imp}}(X) \quad (6)$$

Using ΔH_{sol} , one can calculate the dilute solubility of a solute X ($x_0(X)$) at a

given temperature T :

$$x_0(X) = \exp(\Delta H_{\text{sol}}/k_{\text{B}}T) \cdot \exp(-\Delta S_{\text{sol}}/k_{\text{B}}) \quad (7)$$

where ΔS_{sol} is the difference in the non-configurational entropy (e.g., vibrational, magnetic, etc.) between the ordered and disordered states (i.e., the non-configurational entropy difference analogous to Eq. 6). The entropic term $\exp(-\Delta S_{\text{sol}}/k_{\text{B}})$ can act as an enhancement factor [33] in solubility calculations. Previous studies [33–35] on the solubility of Sc, Cu, and rare-earth elements in aluminum have demonstrated that an excellent agreement between calculated and experimental solubility can be achieved by calculating and adding vibrational entropy to Eq. 7. Nevertheless, the solubility enthalpy alone can help distinguish between solutes with high and low solubility [36]. We defer the calculation of the nonconfigurational entropy to future work.

3. Results and Discussion

3.1. Solute–Vacancy Binding Energies

To study interactions between a solute and a vacancy in detail, both the nearest-neighbor (NN) and the next-nearest-neighbor (2NN) solute–□ binding energies were calculated. Table 1 lists NN, 2NN solute–□ binding energies for all the 25 solute elements studied (consisting of 23 transition metal and 2 main-group elements). As transition metal solutes are the main focus of this work, we analyze their energetics in great detail, and only briefly comment on the solute–□ binding of the 2 main-group elements, namely aluminum and silicon. Overall, in contrast to Ni, Al, Mg, and Cu alloys in which solute–□ binding energies of mid $3d$ transition metal solutes are negative or nearly zero [14, 17, 18, 37], we calculate all of them to be positive in fcc Co, i.e., indicating favorable binding. We also note that Neumerier et al. [38] recently reported NN and 2NN solute–□ binding energies for Re, Mo, Ta, and W in fcc cobalt—the corresponding binding energies from our calculations are in excellent agreement (within 0.01 eV). We discuss the physical and chemical factors that govern the solute–□ binding energies, namely, solute size and d -occupancy. We focus mainly on the NN

140 binding energies, although our discussion can be easily generalized to the 2NN
solute–□ energies and beyond.

3.1.1. Effect of Solute Size

Main-Group Solutes. The solute–□ binding energies of aluminum and silicon
in fcc cobalt are listed in Table 1. The calculated binding of the solute atom
145 to an accompanying vacancy is positive, and about 0.1 eV, for both Al and
Si. As discussed in Sec. 2.2, such a favorable binding indicates that the $sp-d$
bond formed between the solute and the host is weaker than the $d-d$ bonds
between host atoms, and thus creating a vacancy next to a solute atom is eas-
ier than creating one next to a cobalt atom. But, as seen in Fig. 1, a direct
150 correlation between the (main-group) solute size and its energetic binding to a
vacancy is not apparent—Al is bigger than Co, while Si is smaller, but they
both have similar positive binding energies. As the chemistry of $sp-d$ bonds
is different from that of $d-d$ ones [39, 40], a direct comparison of the change
in volume due to main-group and transition metal solutes cannot be made ei-
155 ther. Further, in main-group element hosts such as Al and Mg, it has been
previously observed [14, 15, 17] that transition metal solutes do not show a
systematic trend in solute–□ binding energies with solute size; and vice versa,
in transition metal hosts such as Cu, binding energies of main-group solutes do
not vary systematically with impurity volume [18]. Since we only consider two
160 main-group elements as solutes, and a detailed analysis of the physics of the
 $sp-d$ interactions is beyond the scope of this work, we will limit the rest of our
discussion to transition metal solutes.

Transition Metal Solutes. Fig. 1 shows the calculated solute–□ binding energies
as a function of the solute volume. We find a fair correlation between the
165 binding energy of a solute and its size. Here we analyze this correlation for all
the transition metal solutes.

To simplify our analysis, we consider a two-dimensional (2D) subspace of a
(100) plane of fcc cobalt, containing a vacancy and a solute atom. As seen in

Table 1: List of elemental solutes considered in this work, their respective dilute impurity volumes (V_{imp}), and NN and 2NN solute–□ binding energies.

	Solute	V_{imp} $(\text{\AA}^3/\text{solute})$	NN (eV)	2NN
3d	Al	1.78	0.10	-0.04
	Si	-1.11	0.13	-0.00
	Ti	3.15	0.16	-0.09
	V	0.75	0.04	-0.03
	Cr	-0.23	0.01	-0.03
	Mn	0.23	0.01	-0.05
	Fe	0.67	0.02	-0.03
	Ni	0.52	0.02	0.00
	Cu	1.44	0.09	-0.02
4d	Zr	9.28	0.46	-0.16
	Nb	4.88	0.24	-0.09
	Mo	3.39	0.10	-0.04
	Tc	4.23	0.03	-0.00
	Ru	4.76	0.05	0.01
	Rh	4.06	0.08	-0.00
	Pd	4.63	0.15	-0.04
	Ag	5.89	0.28	-0.07
5d	Hf	8.07	0.38	-0.15
	Ta	5.40	0.19	-0.09
	W	3.41	0.06	-0.05
	Re	3.77	0.01	0.01
	Os	4.95	0.02	0.04
	Ir	4.90	0.07	0.03
	Pt	5.32	0.13	0.00
	Au	6.76	0.27	-0.04

Figure 1: (Color online) The calculated NN solute–□ binding energies as a function of impurity volume for all the solutes considered in this work. There is a modest correlation between solute–□ binding and the size of the impurity: large solutes bind to vacancies more strongly than small ones, in general.

Figure 2: (Color online) A contour plot of the charge density on a (100) plane of $\text{Co}_{106}\text{X}_1\Box_1$, where the solute X is (a) a Co atom itself (i.e., no solute), (b) a solute atom of size similar to that of Co, such as Ni, and (c) a large solute atom, such as Zr. The dark blue region represents the void due to a vacancy. The length of this void (i.e., Co-Co distance passing directly through the vacant site) in $\text{Co}_{107}\Box_1$ is about 4.90 Å. Large solute atoms such as Zr relax toward the vacancy by up to ≈ 0.45 Å, significantly deforming the geometry of the structure, while solute atoms of the same size as Co, such as Ni, keep the local geometry virtually intact.

Fig. 2, in this (100) plane, we can study the interaction of a vacancy with four
of its nearest-neighbor atoms. In fact, one can easily generalize the following
discussion to the three orthogonal planes that include all 12 nearest-neighbor
atoms of the fcc lattice. The distance between the NN cobalt atoms is 2.48 Å
and twice this distance (the 4NN separation), the face-diagonal of the fcc cube,
is 4.96 Å. The four atoms located at the corners of the 2D body-centered ar-
rangement are 2NN of each other, separated by 3.51 Å. As seen in Fig. 2(a),
once the central cobalt atom is removed, creating a vacancy ($\text{Co}_{N-1}\Box_1$), the
four NN atoms at the corners relax toward the center by ≈ 0.03 Å, reducing
the 4NN distance from 4.96 to 4.90 Å and the 2NN distances (the side of the
square) from 3.51 to 3.47 Å. Here, we address how a solute atom affects the
local environment of a NN vacancy.

A solute atom exerts a strain on all the NN and 2NN host atoms and the
magnitude of this strain depends directly on the solute size and the binding
between the solute and host atoms. To reduce this strain, the NN host atoms

Figure 3: (Color online) The effect of volume and d -occupancy of a substitutional impurity on the atomic relaxation of the (a,b) 12 nearest-neighbor atoms (NN) and (c,d) 6 next-nearest-neighbor atoms (2NN) atoms. The displacements are calculated with respect to fully-relaxed pure fcc cobalt, for which NN and 2NN distances are 2.48 and 3.51 Å respectively. Therefore, here, negative and positive displacements correspond to attractive and repulsive interactions respectively.

tend to relax away from the solute atom. Fig. 3 shows the displacement of the
 185 NN host atoms upon the introduction of a solute atom, relative to pure fcc
 cobalt. Solutes of size similar to Co, such as Ni, apply a negligible strain on the
 adjacent atoms resulting in displacements of only about 0.01 Å, which is in fact
 within the accuracy of DFT [41]. This small strain on the adjacent atoms due
 to the solute atom means that a vacancy next to it does not further reduce the
 190 strain; therefore, based only on strain, we would expect small solute–□ binding
 energies for these solutes. In fact, almost all 3d transition metals, with the
 exception of Ti and to some extent Cu, belong to this category (with binding
 energies less than ≈ 0.05 eV). Not surprisingly, Ti and Cu show larger binding
 energies than the other 3d transition metals (see Fig. 1).

195 Furthermore, substituting a large solute atom in fcc cobalt creates a large
 strain on the NN Co atoms, which relax away with displacements as large as
 0.13 Å for large solute atoms such as Zr (see Fig. 3). Here, creating a vacancy
 in the NN position allows the large solute atom to relax toward the vacancy,
 away from the other 11 NN atoms, reducing the overall strain in the system;
 200 for instance, the Zr solute atom relaxes toward the NN vacancy by 0.45 Å
 (see Fig. 2(b)). Such a large relaxation increases the energetic interaction be-
 tween the solute and an accompanying vacancy. Thus, one can expect stronger
 solute–□ binding energies with increase in the size of the solute/impurity atom.

Thus, solute–□ binding energies seem to broadly correlate with the size of
 205 the transition metal solutes, as seen in Fig. 1. As cobalt is one of the smallest
 transition metals, all other substituted transition metals apply a positive strain
 (repulsive) on the NN Co atoms. Therefore, it is unsurprising that most solutes
 in fcc cobalt favor having a nearest-neighbor vacancy that reduces the strain in
 the lattice.

210 Interestingly, large solute atoms *attract* (i.e., bind weakly) with their 2NN
 host atoms. As seen in Fig. 3(c), large solute atoms such as Hf and Zr attract
 their six 2NN atoms making them relax inward toward the solute by about
 0.03 Å. This inward relaxation of the 2NN host atoms becomes significantly
 larger when the solute atoms neighbor a vacancy. As seen in Fig. 2(b) the

215 Zr-Co 2NN distances in the (100) plane decrease from 3.46 Å in $\text{Co}_{107}\square_1$ to
 3.14 Å in $\text{Co}_{106}\text{Zr}_1\square_1$, approaching the 2.90 Å Zr-Co bondlength in the ordered
 Co_2Zr compound. This weak attraction with the 2NN host atoms leads to
 unfavorable 2NN solute- $\square$ binding energies for large solute atoms, as seen in
 Table 1. Therefore, a NN vacancy not only relaxes the strain associated with
 220 large solutes, but also enhances their bonding interaction with 2NN host atoms.

However, there are exceptions to this size-effect. For instance, Ti has a NN
 solute- $\square$ binding energy (0.16 eV) much larger than that of W (0.06 eV), but
 its impurity volume is around 10% smaller. Though solute size is a large factor
 in controlling the solute- $\square$ binding energy, it is clearly not the only factor, and
 225 there is also an important electronic aspect influencing it. In the next section
 we consider d -band filling model which can serve as a complement to the above
 strain model.

3.1.2. Effect of d -occupancy

Fig. 4 shows that the NN solute- $\square$ binding energy follows a parabolic be-
 havior as a function of the d -occupancy of the solute across the transition metal
 series with a minimum at the middle of the series. A similar parabolic trend is
 known for cohesive energy [42–44], vacancy formation energy [45], and solute- $\square$
 interaction in other hosts [18, 37, 46, 47]. In fact, the parabolic behavior of the
 solute- $\square$ binding energy can be explained as a band-filling effect using Friedel’s
 model [37, 42, 44], and its extension for d -band cohesion in pure transition met-
 als [43]. As discussed in Ref. [44] the bonding energy ($U_{\text{bond}}^{\text{AB}}$) between transition
 metal atoms A and B is defined as:

$$U_{\text{bond}}^{\text{AB}}(\bar{N}) = -\frac{1}{20}\bar{W}_{\text{AB}}\bar{N}(10 - \bar{N}) \quad (8)$$

where $\bar{N} = \frac{1}{2}(N_{\text{d}}^{\text{A}} + N_{\text{d}}^{\text{B}})$ is the average number of d -electrons and $\bar{W}_{\text{AB}} =$
 230 $[\frac{1}{2}(W_{\text{A}}^2 + W_{\text{B}}^2)]^{1/2}$ is the average bandwidth of the d -band. Across a transition
 metal series, from d^1 to d^5 (early d solutes), only the bonding states are filled and
 the bond strength gradually increases. Further, for the later transition metals,
 from d^6 to d^{10} , the anti-bonding states are also filled, thereby lowering the bond

strength (here, between the solute and the host atoms). Therefore, energetics
 235 involving bond breaking (e.g., vacancy formation energy [45], cohesive energy)
 or comparison of bond strengths in transition metals (e.g., solute–□ binding
 energy [37, 48]) always show a band-filling effect. In fact, this d -band filling
 effect is also visible in the effective displacement of host cobalt atoms during
 relaxation upon solute substitution nearest to a vacancy (see Figs. 3(b, d)).
 240 Across a transition metal series, the solute-host bond strength increases toward
 the middle of the series and decreases gradually towards either end (according
 to Eq. 8). This results in the NN host atoms undergoing small, negligible
 displacements away in the case of strongly-binding mid-transition metals, and
 much larger displacements for weakly-binding early- and late-transition metals
 245 (see Fig. 3(b)). Further, the strong solute-NN host bonds in the case of mid-
 transition metals (when compared to early-, late-transition metals) likely result
 in weaker NN-2NN host bonds, thus causing the 2NN host atoms to relax away
 from the solute atom (see the effective repulsive interactions between the solute
 and 2NN host atoms, especially for mid-4d, 5d solutes in Fig. 3(d)). For 3d
 250 transition metal atoms, the solute–□ binding energy parabola is somewhat
 “flattened” (Fig. 4), and a double well is seen (Fig. 3(b, d)) due to the loss of
 their magnetic moments [49], which is absent in the 4d and 5d transition metal
 series.

Further, this d -band filling effect is also observed in the calculated dilute
 255 impurity formation energies ($E_{\text{imp}}^{\text{eq}}$). As seen in Fig. 5, the impurity formation
 energy follows the d -filling across the transition metal series, with the excep-
 tion of group 11 and magnetic 3d transition metals. The flattening of $E_{\text{imp}}^{\text{eq}}$ in
 magnetic transition metals can be attributed to the loss of the atomic magnetic
 moment and the associated exchange energy compared to the free atom [46, 49].

260 3.2. Solubility Enthalpy

For all elemental solutes considered, we calculate their solubility enthalpy
 ΔH_{sol} in fcc cobalt as the difference between the formation enthalpy of the
 respective cobalt-rich ordered compound $\Delta H_{\text{ord}}^{\text{eq}}$ and the impurity formation en-

Figure 4: (Color online) The calculated solute-vacancy binding energies as a function of d -occupancy of the solute — the binding energies follow a parabolic trend across the periodic table, reaching a minimum at d^{4-6} occupancies.

Table 2: For each elemental solute X considered in this paper, we list (a) its elemental equilibrium crystal structure, (b–e) chemical formula, structural prototype, space group, and formation energy of the Co-rich ordered phase reported in the Co- X binary system, (f–g) the dilute impurity formation energy with respect to the X in its equilibrium crystal structure ($E_{\text{imp}}^{\text{eq}}$) and a hypothetical fcc structure ($E_{\text{imp}}^{\text{fcc}}$) respectively, and (h) its solubility enthalpy ΔH_{sol} in fcc cobalt.

	Solute	Crystal structure	Chemical formula [†]	Structural prototype	Space group	$\Delta H_{\text{ord}}^{\text{eq}}$ (eV/atom)	$E_{\text{imp}}^{\text{eq}}$ (eV/solute atom)	$E_{\text{imp}}^{\text{fcc}}$ (eV/solute atom)	ΔH_{sol}
	Al	fcc	CoAl [50]	CsCl	Pm $\bar{3}$ m	-1.22	-0.98	-0.98	-0.24
	Si	diamond	Co ₂ Si [51]	Co ₂ Si	Pnma	-1.39	-1.06	-1.60	-0.33
3d	Ti	hcp	Co ₃ Ti [52]	AuCu ₃	Pm $\bar{3}$ m	-1.09	-0.70	-0.75	-0.39
	V	bcc	Co ₃ V [53]	Al ₃ Pu	Pm $\bar{3}$ m	-0.76	-0.21	-0.46	-0.55
	Cr	bcc	—	—	—	0.00	0.42	0.03	-0.42
	Mn	α -Mn	CoMn [54]	CsCl	Pm $\bar{3}$ m	-0.02	0.30	0.22	-0.32
	Fe	bcc	CoFe [55]	CsCl	Pm $\bar{3}$ m	-0.13	-0.01	-0.16	-0.12
	Ni	fcc	—	—	—	-0.04	-0.04	-0.04	≈ 0.0
	Cu	fcc	—	—	—	0.00	0.35	0.35	-0.35
4d	Zr	hcp	Co ₂ Zr [56]	MgCu ₂	Fd $\bar{3}$ m	-1.01	0.00	-0.20	-1.01
	Nb	bcc	NbCo ₃ [57]	NbCo ₃	P6 ₃ /mm	-0.48	0.12	-0.21	-0.60
	Mo	bcc	Co ₃ Mo [58]	Mg ₃ Cd	P6 ₃ /mm	-0.30	0.70	0.28	-1.00
	Tc	hcp	—	—	—	0.00	0.80	0.73	-0.80
	Ru	hcp	—	—	—	0.00	0.67	0.56	-0.67
	Rh	fcc	—	—	—	0.00	0.18	0.18	-0.18
	Pd	fcc	—	—	—	0.00	0.31	0.31	-0.31
	Ag	fcc	—	—	—	0.00	1.42	1.42	-1.42
5d	Hf	hcp	HfCo ₂ [59]	MgCu ₂	Fd $\bar{3}$ m	-1.15	-0.29	-0.39	-0.86
	Ta	bcc	Co ₃ Ta [60]	AuCu ₃	Pm $\bar{3}$ m	-0.96	-0.10	-0.34	-0.86
	W	bcc	Co ₃ W [58]	Mg ₃ Cd	P6 ₃ /mm	-0.40	0.61	0.12	-1.01
	Re	hcp	—	—	—	0.00	0.79	0.73	-0.79
	Os	hcp	—	—	—	0.00	0.81	0.67	-0.81
	Ir	fcc	—	—	—	0.00	0.13	0.13	-0.13
	Pt	fcc	CoPt [61]	AuCu	P4/mmm	-0.19	-0.15	-0.15	-0.04
	Au	fcc	—	—	—	0.00	0.77	0.77	-0.77

[†] for elements that form a solid solution with cobalt at all compositions or those that have no solubility in cobalt (indicated by — in the corresponding columns), the ΔH_{sol} is reported simply as the negative of the impurity formation energy ($E_{\text{imp}}^{\text{eq}}$).

Figure 5: (Color online) The calculated (a) impurity formation energy, and (b) solubility enthalpy, as a function of d -occupancy, of all transition metal solutes considered in this work.

ergy $E_{\text{imp}}^{\text{eq}}$ (see Eq. 6). The results for ΔH_{sol} are shown in Table 2 and plotted
 265 in Fig. 5. The solubility enthalpy is directly related to the temperature dependence of solubility the respective solute, as described in Eq. 7—large negative values lead to low solubility or solubility only at high temperatures. Solubilities calculated using DFT have previously shown reasonable agreement with experimental data where available, e.g., in the case of Al [33, 35, 36].

270 As seen in Fig. 5, 4*d* and 5*d* transition metals, except those belonging to groups 9 and 10, have large negative ΔH_{sol} compared to 3*d* transition metals. The large negative values for the majority of 4*d* and 5*d* solutes result in their low solubility in fcc cobalt, consistent with previous observations of their low solubility in almost all 3*d* transition metal hosts [62]. For example, Ag with a
 275 very large negative value of $\Delta H_{\text{sol}} = -1.42$ eV has negligible solubility in fcc cobalt, in agreement with experimental phase diagrams [63], where little to no solubility is observed for temperatures below the melting point of cobalt. The calculated solubility data is roughly consistent with the size factor statement of Hume-Rothery rules [64]: the solubility is unlikely to be high when the atomic
 280 radius of the solute differs more than $\sim 15\%$ from that of the host, here fcc cobalt. In terms of volume, this means that solutes with an impurity volume of roughly $\geq 6 \text{ \AA}^3$ (see Fig. 1) are expected to have low solubility in fcc cobalt. Among the solutes considered in this work, only Au, Ag, Hf, and Zr fulfill this criterion and all of them are calculated to have very low solubility (seen in
 285 Fig. 5), consistent with experimental phase diagrams [65].

We found that 3*d* transition metals generally have higher solubility than 4*d* and 5*d* ones. Among 3*d* transition metals nickel has nearly zero ΔH_{sol} indicating nearly complete solubility (see Eq. 7), in agreement with experimental observations of a Co–Ni solid solution for all compositions [66]. Among 4*d* and
 290 5*d* transition metals those belonging to groups 9 and 10, i.e., Pd, Pt, Rh and Ir, have exceptionally large solubility in fcc cobalt, even larger than many 3*d* transition metals, according to our calculations. This is consistent with experimental phase diagrams of binary systems Co-*X* (*X* = Pd, Pt, Rh, Ir) [52, 61, 67], which show solid solutions at 1000 K for all compositions. While there is a

295 good qualitative agreement between our calculations and experimental phase diagrams data, for an accurate calculation of solubility, estimating the vibrational entropic contributions is likely important, even necessary [33, 35]. This will be the subject of future work.

4. Conclusion

300 We have presented here accurate density functional calculations of a host of thermodynamic properties for 25 different solutes in fcc cobalt, including solute–vacancy binding energies, enthalpy of formation of ordered phases, impurity formation energies with respect to equilibrium and hypothetical fcc reference states, and solubility enthalpies.

305 We have studied the physical and chemical effects controlling solute–□ interactions. We find that there is a strong correlation between solute–□ binding energy and solute size, with larger solute atoms possessing a stronger binding with vacancies. This effect of solute size was understood in the terms of: (a) a strain-relief argument, in which a vacancy relieves the strain associated with large solute atoms, (b) secondary bonding interactions between the solute and
310 the next-nearest neighbor atoms mediated by a vacancy.

Besides the effect of solute size, the solute–□ binding energy follows a parabolic trend as a function of d -occupancy across the transition metal series, falling to a minimum at the middle of the series. This parabolic effect is
315 explained in terms of a d -band filling effect, also known as Friedel’s model. In the case of $3d$ solutes in fcc cobalt, magnetic exchange effect increases the solute–□ binding energies resulting in flattening of the parabolic trend compared to $4d$ and $5d$ transition metals. In general, $4d$ and their counterpart $5d$ transition metals have nearly similar solute–vacancy binding energies, much larger than
320 those of $3d$ transition metals.

The large number of thermodynamic properties calculated in this work not only helps in understanding phase stability of various phases in fcc cobalt but can also be used as input for calculating multicomponent phase diagrams using

methods such as CALPHAD. Overall, our extensive first-principles investigation
325 of thermodynamics in fcc cobalt will significantly accelerate the design and
development of new cobalt-based superalloys.

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- [1] J. Sato, T. Omori, K. Oikawa, I. Ohnuma, R. Kainuma, K. Ishida, Cobalt-
Base High-Temperature Alloys, *Science* 312 (5770) (2006) 90–91. doi:
10.1126/science.1121738.
- [2] M. Tsunekane, A. Suzuki, T. M. Pollock, Single-crystal solidification of
340 new Co–Al–W–base alloys, *Intermetallics* 19 (5) (2011) 636–643. doi:
10.1016/j.intermet.2010.12.018.
- [3] T. M. Pollock, J. Dibbern, M. Tsunekane, J. Zhu, a. Suzuki, New Co-based
 $\gamma-\gamma'$ High-temperature alloys, *Jom–J Min Met Mat S* 62 (1) (2010) 58–63.
doi:10.1007/s11837-010-0013-y.
- [4] S. Miura, K. Ohkubo, T. Mohri, Mechanical Properties of Co-Based $L1_2$
345 Intermetallic Compound $Co_3(Al,W)$, *Mater. Trans.* 48 (9) (2007) 2403–
2408. doi:10.2320/matertrans.MAW200734.
- [5] M. Ooshima, K. Tanaka, N. L. Okamoto, K. Kishida, H. Inui, Effects of
quaternary alloying elements on the γ' solvus temperature of Co–Al–W
350 based alloys with fcc/ $L1_2$ two-phase microstructures, *J. Alloys Compd.*
508 (1) (2010) 71–78. doi:10.1016/j.jallcom.2010.08.050.

- [6] A. Suzuki, H. Inui, T. M. Pollock, L1₂–Strengthened Cobalt-Base Superalloys, *Annu. Rev. Mater. Res.* 45 (1) (2015) 345–368. doi:[10.1146/annurev-matsci-070214-021043](https://doi.org/10.1146/annurev-matsci-070214-021043).
- 355 [7] D. L. Klarstrom, Wrought cobalt- base superalloys, *J. Mater. Eng. Perform.* 2 (4) (1993) 523–530. doi:[10.1007/BF02661736](https://doi.org/10.1007/BF02661736).
- [8] H.-Y. Yan, V. Vorontsov, D. Dye, Alloying effects in polycrystalline γ' strengthened Co–Al–W base alloys, *Intermetallics* 48 (2014) 44–53. doi:[10.1016/j.intermet.2013.10.022](https://doi.org/10.1016/j.intermet.2013.10.022).
- 360 [9] J. Koßmann, T. Hammerschmidt, S. Maisel, S. Müller, R. Drautz, Solubility and ordering of Ti, Ta, Mo and W on the Al sublattice in L1₂-Co₃Al, *Intermetallics* 64 (2015) 44–50. doi:[10.1016/j.intermet.2015.04.009](https://doi.org/10.1016/j.intermet.2015.04.009).
- [10] A. Bauer, S. Neumeier, F. Pyczak, R. Singer, M. Göken, Creep properties of different γ' -strengthened Co-base superalloys, *Mater. Sci. Eng. A* 550 (2012) 333–341. doi:[10.1016/j.msea.2012.04.083](https://doi.org/10.1016/j.msea.2012.04.083).
- 365 [11] S. Kobayashi, Y. Tsukamoto, T. Takasugi, The effects of alloying elements (Ta, Hf) on the thermodynamic stability of γ' –Co₃(Al,W) phase, *Intermetallics* 31 (2012) 94–98. doi:[10.1016/j.intermet.2012.06.006](https://doi.org/10.1016/j.intermet.2012.06.006).
- [12] A. Suzuki, High-temperature strength and deformation of γ/γ' two-phase Co–Al–W–base alloys, *Acta Mater.* 56 (6) (2008) 1288–1297. doi:[10.1016/j.actamat.2007.11.014](https://doi.org/10.1016/j.actamat.2007.11.014).
- 370 [13] D. Simonovic, M. H. F. Sluiter, Impurity diffusion activation energies in Al from first principles, *Phys. Rev. B* 79 (5) (2009) 054304. doi:[10.1103/PhysRevB.79.054304](https://doi.org/10.1103/PhysRevB.79.054304).
- [14] C. Wolverton, Solute-vacancy binding in aluminum, *Acta Mater.* 55 (17) (2007) 5867–5872. doi:[10.1016/j.actamat.2007.06.039](https://doi.org/10.1016/j.actamat.2007.06.039).
- 375 [15] J. E. Saal, C. Wolverton, Solute-vacancy binding of the rare earths in magnesium from first principles, *Acta Mater.* 60 (13-14) (2012) 5151–5159. doi:[10.1016/j.actamat.2012.06.016](https://doi.org/10.1016/j.actamat.2012.06.016).

- 380 [16] B. RW, H. PS., In: Diffusion metals park., OH: Am Soc Metals, 1973, p 83.
- [17] D. Shin, C. Wolverton, First-principles study of solute–vacancy binding in magnesium, *Acta Mater.* 58 (2010) 531–540. [doi:10.1016/j.actamat.2009.09.031](https://doi.org/10.1016/j.actamat.2009.09.031).
- 385 [18] Y. Wang, H. Gao, Y. Han, Y. Dai, F. Bian, J. Wang, B. Sun, First-principles study of solute–vacancy binding in Cu, *J. Alloys Compd.* 608 (2014) 334–337. [doi:10.1016/j.jallcom.2014.04.053](https://doi.org/10.1016/j.jallcom.2014.04.053).
- [19] N. Saunders, A. P. Miodownik, CALPHAD (calculation of phase diagrams): a comprehensive guide, Vol. 1, Elsevier, 1998.
- 390 [20] P. Spencer, Computer simulations from thermodynamic data: Materials protection and development, *MRS Bulletin* 24 (1999) 18–21. [doi:10.1557/S088376940005212X](https://doi.org/10.1557/S088376940005212X).
- [21] H. B. L. Kaufman, Computer Calculations of Phase Diagrams, Academic Press, New York, 1970.
- 395 [22] A. Costa e Silva, F. Rizzo, Summary report of XL CALPHADRio de Janeiro, Brasil, 2011, *Calphad* 39 (2012) 111–169. [doi:10.1016/j.calphad.2012.07.003](https://doi.org/10.1016/j.calphad.2012.07.003).
- [23] C. Wolverton, X.-Y. Yan, R. Vijayaraghavan, V. Ozoliņš, Incorporating first-principles energetics in computational thermodynamics approaches, *Acta Mater.* 50 (9) (2002) 2187–2197. [doi:10.1016/S1359-6454\(01\)00430-X](https://doi.org/10.1016/S1359-6454(01)00430-X).
- 400 [24] Y. Zhong, C. Wolverton, Y. A. Chang, Z. K. Liu, A combined CALPHAD/first-principles remodeling of the thermodynamics of Al-Sr: Unsuspected ground state energies by ”rounding up the (un)usual suspects”, *Acta Mater.* 52 (9) (2004) 2739–2754. [doi:10.1016/j.actamat.2004.02.022](https://doi.org/10.1016/j.actamat.2004.02.022).
- 405

- [25] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953–17979. doi:10.1103/PhysRevB.50.17953.
- [26] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B 59 (1999) 1758–1775. doi:10.1103/PhysRevB.59.1758.
- [27] G. Kresse, J. Furthmüller, Efficient iterative schemes for *ab-initio* total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169–11186. doi:10.1103/PhysRevB.54.11169.
- [28] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1) (1996) 15–50. doi:10.1016/0927-0256(96)00008-0.
- [29] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 78 (1997) 1396–1399. doi:10.1103/PhysRevLett.78.1396.
- [30] M. Methfessel, A. T. Paxton, High-precision sampling for Brillouin-zone integration in metals, Phys. Rev. B 40 (1989) 3616–3621. doi:10.1103/PhysRevB.40.3616.
- [31] J. D. Pack, H. J. Monkhorst, “Special points for Brillouin-zone integrations”-a reply, Phys. Rev. B 16 (1977) 1748–1749. doi:10.1103/PhysRevB.16.1748.
- [32] P. E. Blöchl, O. Jepsen, O. K. Andersen, Improved tetrahedron method for Brillouin-zone integrations, Phys. Rev. B 49 (1994) 16223–16233. doi:10.1103/PhysRevB.49.16223.
- [33] C. Ravi, C. Wolverton, V. Ozoliņš, Predicting metastable phase boundaries in AlCu alloys from first-principles calculations of free energies: The role of atomic vibrations, Europhys. Lett. 73 (5) (2006) 719–725. doi:10.1209/epl/i2005-10462-x.

- [34] Z. Mao, D. N. Seidman, C. Wolverton, First-principles phase stability, magnetic properties and solubility in aluminum-rare-earth (AlRE) alloys and compounds, *Acta Materialia* 59 (9) (2011) 3659–3666. [doi:10.1016/j.actamat.2011.02.040](https://doi.org/10.1016/j.actamat.2011.02.040).
- [35] V. Ozoliņš, M. Asta, Large Vibrational Effects upon Calculated Phase Boundaries in Al-Sc, *Phys. Rev. Lett.* 86 (2001) 448–451. [doi:10.1103/PhysRevLett.86.448](https://doi.org/10.1103/PhysRevLett.86.448).
- [36] C. Wolverton, V. Ozoliņš, First-principles aluminum database: Energetics of binary Al alloys and compounds, *Phys. Rev. B* 73 (14) (2006) 144104. [doi:10.1103/PhysRevB.73.144104](https://doi.org/10.1103/PhysRevB.73.144104).
- [37] U. Klemradt, B. Drittler, T. Hoshino, R. Zeller, P. H. Dederichs, N. Stefanou, Vacancy-solute interactions in Cu, Ni, Ag, and Pd, *Physical Review B* 43 (12) (1991) 9487–9497. [doi:10.1103/PhysRevB.43.9487](https://doi.org/10.1103/PhysRevB.43.9487).
- [38] S. Neumeier, H. Rehman, J. Neuner, C. Zenk, S. Michel, S. Schuwalow, J. Rogal, R. Drautz, M. Göken, Diffusion of solutes in fcc Cobalt investigated by diffusion couples and first principles kinetic Monte Carlo, *Acta Mater.* 106 (2016) 304–312. [doi:10.1016/j.actamat.2016.01.028](https://doi.org/10.1016/j.actamat.2016.01.028).
- [39] a. K. Shukla, C. Biswas, R. S. Dhaka, S. C. Das, P. Krüger, S. R. Barman, Influence of $sp-d$ hybridization on the electronic structure of Al-Mn alloys, *Phys. Rev. B* 77 (19) (2008) 195103. [doi:10.1103/PhysRevB.77.195103](https://doi.org/10.1103/PhysRevB.77.195103).
- [40] G. Frenking, N. Fröhlich, The Nature of the Bonding in Transition-Metal Compounds, *Chem. Rev.* 100 (2) (2000) 717–774. [doi:10.1021/cr9804011](https://doi.org/10.1021/cr9804011).
- [41] J. S. Márquez, M. F. Núñez, On the determination of bond lengths by ab initio methods: estimation of errors and some improvements, *Journal of Molecular Structure: THEOCHEM* 624 (1) (2003) 239–249. [doi:10.1016/S0166-1280\(02\)00793-5](https://doi.org/10.1016/S0166-1280(02)00793-5).

- [42] J. M. Ziman (Ed.), The Physics of Metals, Cambridge: Cambridge University Press, 1969.
- [43] A. P. Sutton, Electronic Structure of Materials, Oxford University Press, 2004.
- 465 [44] D. Pettifor, Bonding and Structure of Molecules and Solids, Oxford science publications, Clarendon Press, 1995.
- [45] P. A. Korzhavyi, I. A. Abrikosov, B. Johansson, A. V. Ruban, H. L. Skriver, First-principles calculations of the vacancy formation energy in transition and noble metals, Physical Review B 59 (18) (1999) 11693–11703. doi:
 470 [10.1103/PhysRevB.59.11693](https://doi.org/10.1103/PhysRevB.59.11693).
- [46] D. J. Hepburn, E. MacLeod, G. J. Ackland, Transition metal solute interactions with point defects in fcc iron from first principles, Physical Review B 92 (1) (2015) 014110. doi:[10.1103/PhysRevB.92.014110](https://doi.org/10.1103/PhysRevB.92.014110).
- 475 [47] O. Gorbатов, P. Korzhavyi, A. Ruban, B. Johansson, Y. Gornostyrev, Vacancysolute interactions in ferromagnetic and paramagnetic bcc iron: Ab initio calculations, Journal of Nuclear Materials 419 (1-3) (2011) 248–255. doi:[10.1016/j.jnucmat.2011.09.002](https://doi.org/10.1016/j.jnucmat.2011.09.002).
- 480 [48] N. Stefanou, N. Papanikolaou, P. H. Dederichs, Solute-vacancy interactions in Cu and Ag, Journal of Physics: Condensed Matter 3 (45) (1991) 8793–8801. doi:[10.1088/0953-8984/3/45/004](https://doi.org/10.1088/0953-8984/3/45/004).
- [49] M. S. S. Brooks, B. Johansson, Exchange integral matrices and cohesive energies of transition metal atoms, Journal of Physics F: Metal Physics 13 (10) (1983) L197–L202. doi:[10.1088/0305-4608/13/10/003](https://doi.org/10.1088/0305-4608/13/10/003).
- 485 [50] H. Ohtani, M. Yamano, M. Hasebe, Thermodynamic analysis of the CoAlC and NiAlC systems by incorporating ab initio energetic calculations into the CALPHAD approach, Calphad 28 (2) (2004) 177–190. doi:[10.1016/j.calphad.2004.08.003](https://doi.org/10.1016/j.calphad.2004.08.003).

- [51] L. Zhang, Y. Du, H. Xu, Z. Pan, Experimental investigation and thermodynamic description of the CoSi system, *Calphad* 30 (4) (2006) 470–481. doi:10.1016/j.calphad.2006.06.001.
- [52] T. B. Massalski, H. Okamoto, P. Subramanian, L. Kacprzak, W. W. Scott, *Binary alloy phase diagrams*, Vol. 1, American Society for Metals Metals Park, OH, 1986.
- [53] J. Bratberg, B. Sundman, A thermodynamic assessment of the Co-V system, *J. Phase Equilibria* 24 (6) (2003) 495–503. doi:10.1361/105497103772084534.
- [54] K. Ishida, T. Nishizawa, The Co-Mn (Cobalt-Manganese) system, *Bull. Alloy Phase Diagrams* 11 (2) (1990) 125–137. doi:10.1007/BF02841695.
- [55] Y. I. Ustinovshikov, B. E. Pushkarev, I. V. Sapegina, Phase separation and ordering in the Fe-Co system, *Inorg. Mater.* 42 (4) (2006) 354–359. doi:10.1134/S0020168506040042.
- [56] A. Durga, K. Hari Kumar, Thermodynamic optimization of the CoZr system, *Calphad* 34 (2) (2010) 200–205. doi:10.1016/j.calphad.2010.02.006.
- [57] H. Okamoto, Co-Nb (Cobalt-Niobium), *J. Phase Equilibria Diffus.* 31 (1) (2010) 94–95. doi:10.1007/s11669-009-9632-9.
- [58] C. Wang, J. Wang, S. Guo, X. Liu, I. Ohnuma, R. Kainuma, K. Ishida, Experimental investigation and thermodynamic calculation of the phase equilibria in the CoMoW system, *Intermetallics* 17 (8) (2009) 642–650. doi:10.1016/j.intermet.2009.02.004.
- [59] J. Bratberg, B. Jansson, Thermodynamic evaluation of the CCoWHfZr system for cemented carbides applications, *J. Phase Equilibria Diffus.* 27 (3) (2006) 213–219. doi:10.1361/154770306X109746.

- [60] K. C. H. Kumar, T. Van Rompaey, P. Wollants, Thermodynamic calculation of the phase diagram of the CoNbTa system, *Zeitschrift für Met.* 93 (11) (2002) 1146–1153. [doi:10.3139/146.021146](https://doi.org/10.3139/146.021146).
- [61] H. Okamoto, Co-pt (cobalt-platinum), *Journal of Phase Equilibria* 22 (5) (2001) 591–591. [doi:10.1361/105497101770332848](https://doi.org/10.1361/105497101770332848).
- [62] H. P. J. Wijn, Alloys and compounds of 3d elements and 4d or 5d elements, Springer Berlin Heidelberg, 1991, pp. 68–94. [doi:10.1007/978-3-642-58218-9_4](https://doi.org/10.1007/978-3-642-58218-9_4).
- [63] W. Zhu, H. Liu, J. Wang, H. Dong, Z. Jin, Thermodynamic assessment of the SnAgCo system and solidification simulation of the ternary alloy , *Journal of Alloys and Compounds* 481 (12) (2009) 503 – 508. [doi:10.1016/j.jallcom.2009.03.025](https://doi.org/10.1016/j.jallcom.2009.03.025).
- [64] W. Hume-Rothery, H. M. Powell, On the theory of super-lattice structures in alloys, *Z. Kristallogr.* 91 (1) (1935) 23–47.
- [65] H. Okamoto, K. Cenzual (Eds.), ASM Alloy Phase Diagrams Database, ASM International, Materials Park, OH, 2006.
- [66] F. Guillermet, Assessment of the thermodynamic properties of the Ni-Co system, *Zeitschrift für Metallkunde* 78 (1987) 639–647.
- [67] G. Ghosh, C. Kantner, G. B. Olson, Thermodynamic modeling of the Pd-X (X=Ag, Co, Fe, Ni) systems, *Journal of Phase Equilibria* 20 (3) (1999) 295–308. [doi:10.1361/105497199770335811](https://doi.org/10.1361/105497199770335811).