



# First-principles nickel database: Energetics of impurities and defects



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## ABSTRACT

A database of thermodynamic solubility energies of impurities and defects in solid solution in fcc-nickel is reported using an extensive series of first-principles calculations, based on density functional theory (DFT). The solubility and insertion energies of solute elements, intrinsic (vacancies) and self-interstitial defects (dumbbells) are computed. The DFT energies of the main elements of the periodic table are compared to the experimental and theoretical literature, and the influence of the solute atoms on the network is discussed. We obtained that for most of the species the substitution sites are preferred to the interstitial sites (including He, Li, F, P, S and Cl atoms), except in the case of the five elements, B, C, N, O and H, which are observed preferentially in interstitial octahedral sites. The migration mechanisms are presented for these interstitial elements and for the particular case of He, including the vibrational contribution.

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## 1. Introduction

Due to their relevance for a wide variety of phenomena arising in materials processing, extensive efforts are devoted to the development of databases for solubility energies in multi-component alloys, as illustrated by the strong development of the thermodynamics databases. Ni-based alloys are commonly used as refractory structural materials due to their mechanical properties. This specific properties are partly attributed to the elements dissolved in the fcc Ni-matrix, which contribute to the mechanical properties by different strengthening mechanisms [1,2]. The solid-solution strengthening due to lattice distortion and the interference of the alloying in the lattice periodicity is the first mechanism [1]. In Ni-based alloys, W, V, Mo, Co, Re, Cr and Al are involved in the solid-solute strengthening. When used at high temperatures, the dissolution and diffusion of O, N, C, and S are also involved with high temperature corrosion, internal oxidation, nitration or carburization. These elements can also cause the embrittlement of the alloys. Together with boron and hydrogen, they can be found to segregate at grain boundaries and inter-phases and interact strongly with point-defects [3,4]. To protect Ni-based alloys from high temperature oxidation, it is necessary to alloy them with Al, Cr or Si to form an external protective oxide layer of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>. To do so, the alloy must accept a sufficient quantity of atoms (Al, Cr or Si) and must have a limited diffusivity of oxygen,

i.e., a limited solubility and diffusion coefficient for oxygen [5]. When adding elements such as Al, Ti, Ta, Nb, and C, their solubility and diffusion also control the nucleation and growth kinetics of precipitates (e.g.,  $\gamma'$ -Ni<sub>3</sub>Al, or  $\delta$  or  $\gamma''$ -Ni<sub>3</sub>Nb and Cr-carbides), that control the mechanical properties of Ni-based alloys.

However, few data are available in the experimental and theoretical literature for elements in solid solution. The strength of the numerical simulations (DFT) allows a systematic study to obtain experimental and theoretical data on the solubility properties in fcc-nickel. Janotti et al. [6] studied the solute diffusion for different transition metals (Ti, V, Cr, Mn, Fe, Co, Ni and Cu) without giving the solubility energies. They showed that, according to the interactions between solute and vacancy, larger atoms can move faster than lighter atoms. Yamaguchi [7] studied the segregation for a large number of elements in symmetric grain boundaries  $\Sigma_5$ -Ni and free surfaces. Some species have already been studied in detail: Nb [8], C [9], O [10,11], H [12,3], S [13,14] and He [15].

The aim of this work is to provide information on all impurities and solutes in nickel. We present a complete database of solubility and insertion energies for most species in solid solution in nickel using first-principles calculations. With the state-of-art techniques (highly converged calculations on large super-cells) we present an accurate reference database. For interstitial elements, we also report migration mechanisms.

Section 2 is devoted to numerical approximations. The results for each element are presented and discussed in Section 3. In Section 4, the migration mechanisms of interstitial elements are discussed.

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**Table 1**  
Insertion ( $E_{\text{ins}}$ ) and solubility ( $E_{\text{sol}}$ ) energies (eV) and magnetic moment (in Bohr's unit, of the system) of the impurities in the substitution position as a function of the unit cell size. For the He and Ba atoms (indicated with \*),  $4 \times 4 \times 4$  supercells simulations are also listed. The first  $E_{\text{sol}}$  value corresponds to the value computed using Kittel's cohesive energy.

|    | $2 \times 2 \times 2$ |         | $3 \times 3 \times 3$ |                  |         |    | $2 \times 2 \times 2$ |         | $3 \times 3 \times 3$ |                  |         |
|----|-----------------------|---------|-----------------------|------------------|---------|----|-----------------------|---------|-----------------------|------------------|---------|
|    | $E_{\text{ins}}$      | $\mu_B$ | $E_{\text{ins}}$      | $E_{\text{sol}}$ | $\mu_B$ |    | $E_{\text{ins}}$      | $\mu_B$ | $E_{\text{ins}}$      | $E_{\text{sol}}$ | $\mu_B$ |
| H  | -0.168                | 18.5    | -                     | -                | -       | Zr | -7.308                | 15.6    | -7.376                | -1.126/-0.946    | 61.5    |
| He | 3.234                 | 19.0    | 3.212/3.205*          | 0.000/3.212      | 64.9    | Nb | -7.739                | 14.9    | -7.735                | -0.165/-0.704    | 60.7    |
| Li | -1.690                | 18.3    | -1.732                | -0.102/-0.112    | 64.3    | Mo | -6.477                | 14.9    | -6.411                | 0.409/-0.027     | 60.3    |
| Be | -4.333                | 17.6    | -4.384                | -1.064/-0.695    | 63.7    | Tc | -6.850                | 16.6    | -6.727                | 0.123/0.354      | 63.0    |
| B  | -5.668                | 17.2    | -5.704                | 0.106/0.727      | 63.3    | Ru | -6.454                | 19.2    | -6.442                | 0.298/0.445      | 66.3    |
| C  | -4.290                | 17.8    | -                     | -                | -       | Rh | -5.733                | 19.9    | -5.729                | 0.021/0.097      | 66.0    |
| N  | -1.642                | 19.4    | -                     | -                | -       | Pd | -3.473                | 19.3    | -3.463                | 0.427/0.252      | 65.3    |
| O  | -1.773                | 19.5    | -                     | -                | -       | Ag | -1.462                | 18.5    | -1.432                | 1.518/1.115      | 64.6    |
| F  | -0.869                | 19.3    | -0.872                | -0.032/0.380     | 65.4    | Cd | 0.030                 | 17.9    | 0.047                 | 1.207/0.817      | 63.9    |
| Ne | 4.389                 | 19.0    | 4.367                 | 4.387/4.413      | 64.9    | In | -2.200                | 17.2    | -2.192                | 0.328/0.173      | 63.2    |
| Na | 0.942                 | 18.4    | 0.904                 | 2.017/2.002      | 64.3    | Sn | -3.491                | 16.6    | -3.471                | -0.331/-0.211    | 62.7    |
| Mg | -1.739                | 17.6    | -1.781                | -0.271/-0.297    | 63.6    | Sb | -3.023                | 16.2    | -2.990                | -0.240/-0.173    | 62.4    |
| Al | -5.025                | 16.9    | -5.069                | -1.679/-1.636    | 63.0    | Te | -2.137                | 16.1    | -2.100                | 0.090/0.421      | 62.5    |
| Si | -6.207                | 16.4    | -6.231                | -1.601/-1.577    | 62.6    | I  | 1.044                 | 16.6    | 1.089                 | 2.199/2.258      | 62.8    |
| P  | -4.576                | 16.6    | -4.602                | -1.172/-1.140    | 62.9    | Xe | 7.457                 | 17.2    | 7.585                 | 7.745/7.639      | 63.5    |
| S  | -2.783                | 17.8    | -2.827                | -0.627/-0.242    | 63.9    | Cs | 5.699                 | 16.9    | 5.836                 | 6.640/6.541      | 63.2    |
| Cl | 0.723                 | 18.4    | 0.716                 | 2.116/2.214      | 64.7    | Ba | 2.384                 | 16.5    | 2.513/2.604*          | 4.413/4.406      | 62.8    |
| Ar | 6.685                 | 18.3    | 6.656                 | 6.736/6.656      | 64.7    | Ce | -4.621                | 14.6    | -4.560                | -0.240/-0.195    | 60.7    |
| K  | 4.005                 | 18.2    | 3.979                 | 4.913/4.850      | 64.0    | Pr | -3.074                | 16.2    | -2.959                | 0.741/1.505      | 61.8    |
| Ca | -0.344                | 17.5    | -0.395                | 1.445/1.502      | 63.4    | Nd | -3.193                | 16.2    | -3.109                | 0.291/1.214      | 61.9    |
| Sc | -5.827                | 16.5    | -5.901                | -2.001/-1.150    | 62.5    | Pm | -3.793                | 16.3    | -3.723                | -/-3.723         | 61.9    |
| Ti | -7.071                | 15.6    | -7.119                | -2.269/-1.526    | 61.6    | Sm | -4.040                | 16.3    | -3.993                | -1.853/0.800     | 62.0    |
| V  | -6.277                | 15.1    | -6.273                | -0.963/-0.821    | 60.8    | Eu | -1.237                | 16.9    | -1.282                | 0.578/0.588      | 62.8    |
| Cr | -4.100                | 14.3    | -3.966                | 0.134/0.238      | 64.6    | Gd | -3.977                | 16.4    | -3.947                | 0.193/0.365      | 62.0    |
| Mn | -4.320                | 21.8    | -4.361                | -1.441/-0.245    | 68.0    | Tb | -4.141                | 16.4    | -4.130                | -0.080/0.199     | 62.1    |
| Fe | -5.360                | 21.3    | -5.367                | -1.087/-0.320    | 67.5    | Dy | -4.284                | 16.4    | -4.280                | -1.240/0.054     | 62.1    |
| Co | -5.480                | 20.5    | -5.490                | -1.100/-0.056    | 67.8    | Ho | -4.322                | 16.4    | -4.324                | -1.184/-0.070    | 62.0    |
| Ni | -4.913                | 19.4    | -4.913                | 0.000/0.004      | 67.3    | Er | -4.425                | 16.5    | -4.436                | -1.146/-0.203    | 62.2    |
| Cu | -3.346                | 18.4    | -3.372                | 0.118/0.122      | 64.5    | Yb | -1.306                | 17.2    | -1.372                | 0.228/0.098      | 63.0    |
| Zn | -1.554                | 17.7    | -1.611                | -0.261/-0.495    | 63.8    | Hf | -7.802                | 15.6    | -7.860                | -1.420/-1.360    | 61.6    |
| Ga | -3.692                | 17.1    | -3.721                | -0.911/-1.033    | 63.1    | Ta | -9.746                | 14.8    | -9.751                | -1.651/-1.071    | 60.7    |
| Ge | -4.693                | 16.6    | -4.722                | -0.872/-0.886    | 62.8    | W  | -8.700                | 14.4    | -8.661                | 0.239/-0.216     | 60.0    |
| As | -3.611                | 16.6    | -3.638                | -0.678/-0.659    | 62.9    | Os | -8.084                | 17.6    | -8.015                | 0.155/0.524      | 64.9    |
| Se | -2.353                | 17.2    | -2.388                | 0.072/0.351      | 63.4    | Ir | -7.407                | 19.4    | -7.401                | -0.461/0.021     | 65.9    |
| Br | 1.041                 | 18.0    | 1.056                 | 2.276/2.357      | 64.2    | Pt | -5.713                | 19.3    | -5.706                | 0.134/-0.175     | 65.3    |
| Kr | 7.197                 | 17.9    | 7.232                 | 7.348/7.281      | 64.3    | Au | -2.461                | 18.6    | -2.404                | 1.406/0.639      | 64.6    |
| Rb | 5.213                 | 17.7    | 5.273                 | 6.125/6.045      | 64.1    | Hg | 0.994                 | 18.0    | 1.037                 | 1.707/1.233      | 64.0    |
| Sr | 1.343                 | 17.3    | 1.348                 | 3.068/2.956      | 63.2    | Pb | -1.777                | 16.8    | -1.715                | 0.315/1.299      | 62.9    |
| Y  | -4.720                | 16.5    | -4.723                | -0.353/0.270     | 62.4    | Bi | -1.425                | 16.5    | -1.353                | 0.827/1.139      | 62.7    |

## 2. Computational details

The calculations were performed within the density functional theory (DFT) formalism, using the Vienna *ab initio* simulation program (VASP) [16–19] using the projector-augmented-wave (PAW) pseudopotentials [20]. The spin-polarized version of the Perdew–Wang (PW91 [21]) generalized gradient approximation (GGA) was used for the exchange and correlation functional. The cut-off energy was maintained at 600 eV for all elements, and the Brillouin zones were sampled using  $24 \times 24 \times 24$   $k$ -mesh grids for the fcc unit cell with four atoms, and a band-folding approach [22] for supercells. These parameters provide an excellent convergence for the energy values (<1 meV per atom). The lattice parameters and the ions were allowed to relax. Within these criteria, the ground state properties of fcc nickel (the lattice parameter, the cohesive energy and the magnetic moment were equal to 3.52 Å, 4.89 eV/atom and  $0.62 \mu_B$ , respectively) agreeing with previous DFT calculations [8] and the experimental values [23]. We employed supercells to model the defects and to study the impurities. To determine the preferred site, we used  $2 \times 2 \times 2$  cubic supercells (32 atoms). The converged energies were then calculated on larger supercells ( $3 \times 3 \times 3$ , i.e., 108 Ni atoms). However, to limit the number of simulations, when the substitutional site (or the interstitial site) was the more stable configuration, the energy of the interstitial (substitutional) sites was only evaluated

on the  $2 \times 2 \times 2$  supercells. The atomic energies of the solutes  $X$  (labeled  $\mu_{\text{at}}^0[X]$ ) were calculated on large non-cubic supercells ( $10 \times 11 \times 12 \text{ \AA}^3$ ). The energies of the reference states were also computed. In most of cases, the reference states were given by Kittel [23], i.e., either a hexagonal close-packed structure (hcp, with two atoms per unit-cell), a cubic structure (fcc, bcc, sc or diamond, with one or two atoms in the primitive cell) or a molecule (diatomic). However, for As, [24] B, [25] Be, [26] Ga, [27] Mn, [28] P, [29] Pr, [30] Sb, [31] Se, [32] Sm [33] and Te, [34] the reference states have more complex structures. Fine Monkhorst–Pack grids [35] were adopted to calculate the ground-state energies ( $\Gamma$ -centered grids, with more than 14,000  $k$ -points per atom to sample the reciprocal Brillouin zone). We show in Tables B.9 and B.10 the results for the reference states: the lattice parameters, the cohesive energies and the magnetic moment, to verify that our results for the reference states agree satisfactorily with the experimental results.

## 3. Interstitial or substitutional site

In the face-centered cubic structures, there are three main sites for the added atoms: (i) the two interstitial sites, i.e., the octahedral and the tetrahedral site (labeled in the following as (O) and (T), respectively) and (ii) the substitutional site (i.e., replacing a Ni

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