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First-principle calculation of monovacancy and divacancy interactions with atomic oxygen in nickel: thermal expansion effects

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Abstract. The insertion and diffusion energies of oxygen in presence of vacancies in nickel are studied by using the first-principle projector augmented waves (PAW). When the oxygen atom is located in a substitution site, the formation of a vacancy-oxygen pair is observed. Furthermore, we show that the formation of divacancies allows the oxygen atom to migrate more easily in the metal. A model for the migration process of the three-defect system is proposed. Finally, thermal expansion effects are included in our study; it is shown that temperature effects emphasize the diffusion.

Introduction.

The solubility and diffusivity of oxygen is important to understand the process of internal oxidation in nickel. Generally, dissolved oxygen affects the mechanical properties of the metal [1]. Many years ago, several reports concerning the solubility and diffusion of atomic oxygen in nickel became available in the literature [2-4]. Several years later, Park and Altstetter [5] determined the diffusivity and thermodynamic functions of oxygen dissolved in solid nickel. They obtained a solubility energy of 0.57 ± 0.01 eV which differs significantly from those given in previous reports. Their study seems to be the most reliable because it was done with a pure nickel substrate, without any intermediate value of the solubility energy.

Concerning the oxygen migration, only one theoretical investigation of the diffusion of oxygen in solid nickel is available [6]. In this work, the authors study the insertion of atomic oxygen in the octahedral and tetrahedral sites. Furthermore, the insertion and migration energies are determined showing that the most favourable pathway for the migration between two octahedral sites corresponds to an intermediate metastable state located in a tetrahedral state. Finally, they show that the dilatation of the crystal induced by the temperature effects, leads to the same energetic stability of both sites and to a decrease of the migration enthalpy.

In order to study the monovacancy- oxygen and divacancy-oxygen interactions, it is necessary to have a good description of the formation and migration enthalpies of monovacancies as well as the diffusion process of atomic oxygen. In the first part of this work, we recall recent results concerning the thermal expansion effects on the diffusion of monovacancies [7] and the insertion and diffusion energies of oxygen [6]. In a second part, we describe preliminary results concerning the vacancy-vacancy [8] and vacancy-oxygen interactions together with the thermal expansion effects on their migration energies. Finally, a migration process involving the coupling between a divacancy and atomic oxygen is proposed.

Method of calculation

The calculations are performed within the DFT formalism and the pseudo-potential approximation. They are done by means of the Vienna Ab initio Simulation Program (VASP) developed at the Institut für Materialphysik of the Universität Wien [9,10]. The spin-polarized self-consistent Kohn-Sham equations are solved within the projected-augmented wave (PAW) method [11,12]. This leads to a powerful efficiency concerning the computation time. One kind of pseudo-potential has been tested at the GGA level. It uses the Perdew-Wang 91 functional (PW91) [13] to describe the exchange correlation effects. Concerning the computational parameters, the plane-wave energy cut-off is fixed to 14.7 Ryd (400 eV) for all calculations independently of the size of the unit cell. On the other side, 4x4x4 and 6x6x6 Monkhorst-Pack [14] meshes are used to sample the Brillouin zone in the reciprocal space, depending on the size of the studied unit cell. These contributions allow describing the triplet nature of the ground state. To determine the insertion energies of oxygen, two sizes of fcc primitive cells were tested i.e. 32 and 108 lattice sites per unit cell (see Fig.1), in order to minimize the nearest-neighbour oxygen interactions. We consider that the convergence with respect to the size dependency occurs when insertion energies vary by no more than 0.01 eV. In each case we take into account the lattice relaxation. The relaxation is introduced by using a conjugate-gradient algorithm for formation enthalpies and all ions were allowed to relax, i.e. at the saddle point corresponding to the migration energy of the atomic oxygen, first and second nearest neighbours of the migrating atoms were allowed to move. The thermal expansion contribution is estimated by studying there dependency with respect to the lattice parameter a . Insertion energies were calculated for five values of the lattice parameter a , and fitted to a polynomial function of degree two.

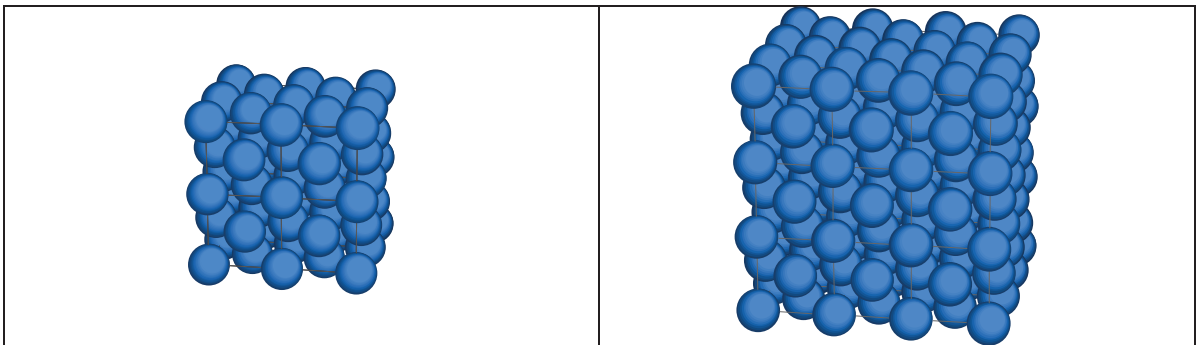


Figure 1. Unit supercells including 32 and 108 atoms.

Results

a) monovacancy: formation and migration enthalpies

Formation and migration enthalpies H_v^f and H_v^m , respectively of a monovacancy are calculated in a first step with a lattice parameter a_0 of 6.65 a.u. corresponding to a temperature of 0K. In a second step, the anharmonic contribution of the temperature to the thermal expansion of the crystal has been included. The enthalpies have been calculated as functions of the relative linear expansion $\Delta a/a_0$. Fig. 2 shows the variations of H_v^f and H_v^m with the linear expansion of the bulk lattice parameter a_0 .

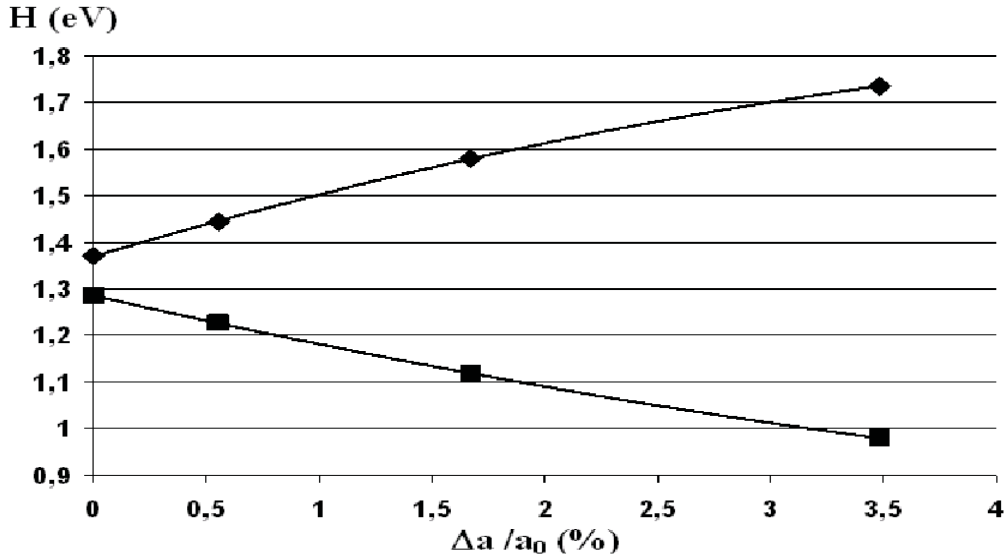


Figure 2. Relative linear expansion dependence of the formation H_v^F (◆) and migration H_v^m (■) enthalpies.

In order to estimate the temperature corresponding to $\Delta a/a_0$, we used the analytical form given by Suh *et al.* [15] for nickel. We give in Table 1 the values of H_v^f and H_v^m for various significant temperatures (0K, room temperature, mean temperature used in the positron annihilation experimental methods and melting point).

Table 1. Temperature dependency of the theoretical formation and migration enthalpies (in eV) of a monovacancy. α is the linear coefficient of thermal expansion.

$\Delta a/a_0$ (%)	α (10^{-6} K^{-1})	T (K)	H_v^f	H_v^m
0	0	0	1.42	1.29
0.114	13.1	293	1.44	1.27
2.370	23.22	1600	1.71	1.05
2.674	24.22	1728	1.74	1.03
Exp.			1.73 [16], 1.79 [17]	1.04 [16]

As seen in Fig. 1 and Table 1, the formation enthalpy increases with the thermal expansion and thus with the temperature due to an increase of the formation entropy. However, the migration enthalpy decreases because the dilatation of the crystal allows the nickel atoms to move more easily from one site to another. The results clearly show that the inclusion of the temperature effects in the calculations allows to reproduce very well the experimental data obtained at temperature near the melting point. More details concerning the diffusion of vacancies in nickel are given in [7].

b) Insertion and diffusion of atomic oxygen

A theoretical study has been made recently [6] concerning the diffusion process of atomic oxygen in nickel. Two interstitial sites of oxygen in the fcc crystal system have been studied: the insertion and the diffusion energy have been calculated. At 0K, the octahedral site is the most stable while the insertion in the tetrahedral site leads to a larger relaxation of the lattice (Table 2). In order to determine the diffusion energy, two pathways have been studied; they are shown in Fig. 3. The corresponding diffusion energies are given in Table 2, showing that the O-T-O pathway leads to an easier diffusion of O.

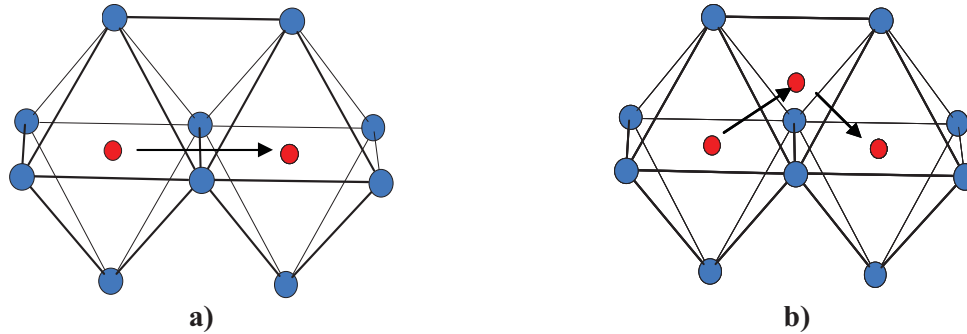


Figure 3. Pathways for the diffusion of oxygen: a) O-T-O diffusion pathway; b) direct O-O diffusion pathway.

In order to take into account the temperature effects, the linear thermal expansion was introduced in our calculations. In Table 2, we give the insertion and diffusion energies obtained with a value of 3.57 Å for the lattice parameter a_0 . This corresponds to the mean temperature (900 °C) at which Park and Altsetter measured the solubility and diffusion energies [18] of oxygen. Results are thus in good agreement with their results. As expected, temperature effects facilitate the insertion of oxygen in nickel; furthermore, the insertion energies of both O and T sites become of the same order. Temperature effects also allow oxygen to migrate more easily.

Table 2. Insertion and activation energies of oxygen in nickel calculated at 0K and 1170K. All values are in eV.

	Insertion		Diffusion	
	O site	T site	O-T-O pathway	O-O pathway
0K	2.65	2.48	1.25	1.54
1170K	3.16	3.10	1.10	1.39
Exp	3.12 [18]		0.94 [18]	

c) vacancy-vacancy interaction (preliminary results)

In experimental data made over a wide temperature slope, the Arrhenius plots of self-diffusion show significant curvature. It has been shown that one mechanism can be

involved in that case [7]: a two-defect model is proposed to define the self-diffusion coefficient:

$$D = D_0 \exp(-Q_1/k_B T) + D_{02} \exp(-Q_2/k_B T). \quad (1)$$

where the effects due to the presence of divacancies are included. Q_1 and Q_2 are the activations of mono- and divacancies, respectively; k_B is the Boltzmann constant and T the temperature. The insertion and migration enthalpies have been determined, as well as the binding energy between both vacancies. The results are given in Table 3. The thermal expansion effect on H_{2v}^f and H_{2v}^m is shown in Fig. 4.

Table 3. Temperature dependency of the theoretical formation, migration and binding enthalpies (in eV) of a divacancy. α is the linear coefficient of thermal expansion.

$\Delta a/a_0$ (%)	α (10^{-6} K^{-1})	T (K)	H_{2v}^f	H_{2v}^b	H_{2v}^m
0	0	0	2.71	0.03	0.78
0.114	13.1	293	2.74	0.03	0.77
2.370	23.22	1600	3.25	0.07	0.72
2.674	24.22	1728	3.30	0.07	0.72
		Exp	3.10 [19]	0.28 [20]	0.82±0.03 [20]

The results obtained at OK show that the formation enthalpy of a divacancy is nearly twice as large as that of a monovacancy, leading to a very small vacancy-vacancy binding energy of 0.03 eV. However, the formation of a divacancy allows the latter to migrate much more easily than an isolated monovacancy. The migration process of the divacancy is shown in Fig. 5. It migrates in the (111) plan by successive rotations of 60° . The contribution of the thermal expansion allows to improve the formation and binding energies. Finally, at 1600K the migration enthalpy of divacancy is 30% lower than that of the monovacancy.

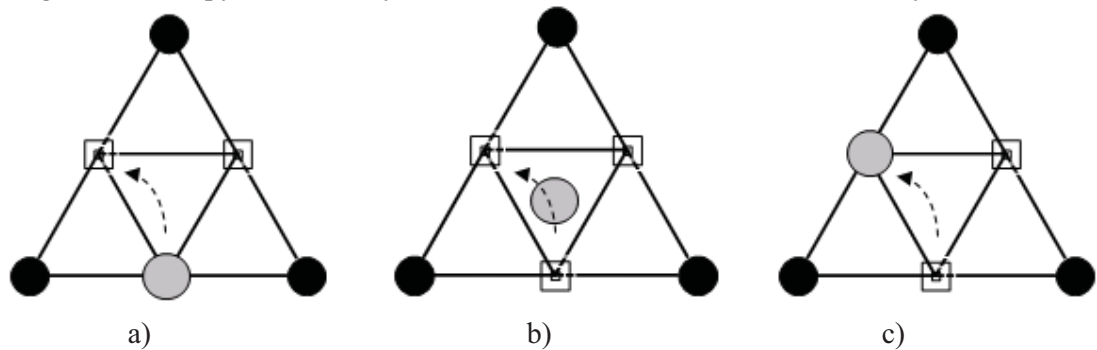


Figure 5. Migration process of a divacancy in the (111) plan. a) Initial state; b) transition state; c) final state

d) monovacancy-oxygen interaction (preliminary results)

Presently, we are doing some investigations, concerning the possible interaction of a monovacancy with an O atom and what the process of the migration of the pair monovacancy-oxygen could be. To this end, in a first step, we consider the case where the oxygen atom occupies a vacant position. We calculate the energy needed to substitute O to a Ni atom, taking into account the formation of a vacancy. In order to compare the stability of this process with respect to the insertion of oxygen in interstitial sites, the formation enthalpy of a monovacancy without interaction with these sites has to be added. The results are presented in Table 4. $E_{\text{Oct+lac}}$ and $E_{\text{Tet+lac}}$ are the energies of the interstitial Oxygen + monovacancy pair, $E_{\text{sub-lac}}$ is the energy of the substitution oxygen: E_b are the corresponding binding energies between the oxygen atom and the monovacancy.

Table 4. Energies of oxygen-monovacancy interactions when O is absorbed in an interstitial or substitution site. All values are in eV.

Tetrahedral site		Octahedral site		Substitution site	
$E_{\text{T+lac}}$	E_b	$E_{\text{O+lac}}$	E_b	$E_{\text{sub-lac}}$	E_b
1.06	0	1.23	0	1.97	0.91 ^a /0.74 ^b

^a Binding energy with respect to the Tet+Oxy pair.

^b Binding energy with respect to the Oct+Oxy pair.

Results in Table 4 show that the substitution site is the most stable showing that the O atom interacts strongly with the monovacancy.

Looking at the substitution site, it is shown that, in fact, the central position of the oxygen (in place of the removed Ni atom) does not correspond to a stable state, but that the O atom moves to the pseudo octahedral and tetrahedral sites located in the vacancy. The stable octahedral and tetrahedral positions are represented in Fig. 6. The displacement of O is of 0.941 Å for the octahedral site and 0.880 Å for the tetrahedral. The energy is stabilized of 0.77 eV for both sites, leading to a very strong binding energy of O with the monovacancy: 1.51 eV for the octahedral site and 1.68 eV for the tetrahedral one.

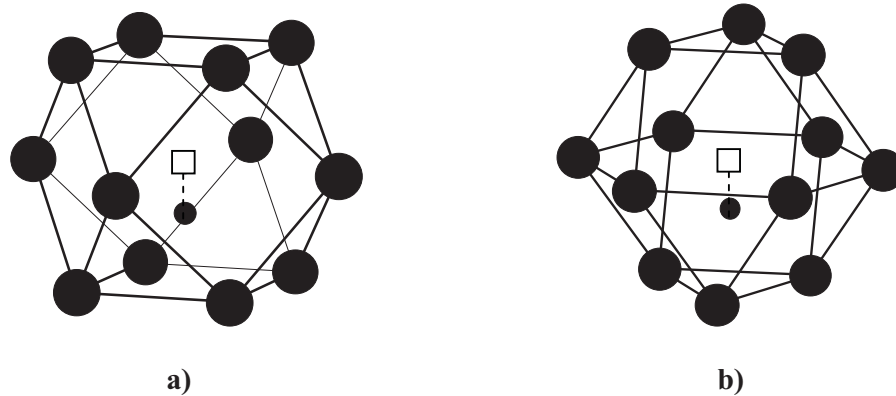


Figure 6. Position of the O atom (small full circle) with respect to the vacancy position (Open Square)

Effects of temperature as well as the migration enthalpy of the pair oxygen-monovacancy are in progress [21].

e) divacancy-oxygen interaction (preliminary results)

We present here the first results that we obtain concerning the interaction of oxygen with a divacancy. When the oxygen is located on one of the two substitution sites, we find a binding energy of 1.03 eV with the divacancy, which is lower than with the monovacancy-oxygen interaction; nevertheless, calculations allowing geometrical relaxation show that O migrates to a more stable position which is located exactly between the two vacancies. In that case the divacancy-oxygen binding energy is 1.61 eV, larger than in the case of a monovacancy. We may conclude with a first result: the presence of oxygen may facilitate the formation of divacancy. Effects of temperature as well as the migration enthalpy of the pair oxygen-monovacancy are in progress.

Conclusion

We may conclude briefly on the meaning of the results presented in this paper. Firstly, first-principle calculations allow obtaining a good estimation of some energetic properties of defects (vacancies or oxygen) in metals (nickel) providing that thermal expansion effects are taken into account. Secondly, vacancy-vacancy interaction is small but allows the divacancy to migrate more easily than the isolated monovacancy. Finally, the coupling between oxygen and vacancies is significant and we may expect that it allows oxygen to migrate faster through the metal as well as the formation of di- or multiple vacancies.

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