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First-principles calculation of the vacancy formation energy in nickel

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Abstract: Within the framework of density functional theory, we investigate with the VASP code three key properties of a vacancy in crystalline nickel: the formation, migration and activation energy. We use Blochl's all-electron-like projector augmented wave method (PAW) to perform self-consistent total-energy structure calculations in the supercell approximation and pseudopotentials to describe the computationally expensive core-valence interaction. All calculations have been carried out using either the local spin density approximation (LSDA) or the generalized gradient approximations (GGA). In a first step we show that the inclusion of non local effects improves significantly the determination of various well known experimental properties of the bulk (lattice parameter, magnetic moment, bulk modulus, cohesion energy ...). Thus, we conclude that the non local approach leads to a better estimation of vacancy formation (1.4 eV), migration (1.28 eV) and activation (2.65 eV) energies at 0 K.

1. Introduction

The existence of vacancies in metals and intermetallic compounds plays an important role for the kinetic and thermodynamique properties of materials. In this connection the vacancy formation energy is a key concept in the understanding of the processes which occur in alloys during mechanical deformation or heat treatment. Certainly large defects like grain boundaries and long-ranged dislocations are important, but even one of the simplest defect, the lattice vacancy, can be responsible for a variety of phenomena such as trapping of impurities and vacancy-mediated dopant diffusion. Both the structure and the energetics of the vacancy are expected to play a significant role in these phenomena, therefore, it is important to have

thorough understanding of the vacancy in order to make a detailed study of other phenomena involving the vacancy.

The formation energies of point defects in metals [1-2] and compounds [3-5] can nowadays be obtained from ab initio electronic structure calculations based on density functional theory [6]. These energies may be used to evaluate the equilibrium concentrations of point defects as a function of temperature and composition within the framework of statistical mechanical approaches. Many theoretical [7-8] and experimental works [9-12] are available concerning the vacancy formation energy in nickel. The range of the data is very large even for experimental and theoretical approaches between nearly 1.4 and 1.8 eV. The goal of this paper is to

provide a converged ab initio density functional theory within the pseudopotential approximation results for the energetic of monovacancy in crystalline nickel.

2. Methodology

The first-principles calculation are based on the density functional theory [13] calculations were performed with the VASP [14] Code which uses Blochl's all-electron-like projector augmented wave method (PAW) [15] to describe the electron-ion interaction. The PAW method is a frozen core all-electron method and, in many aspects, resembles the ultrasoft pseudopotential method of Vanderbilt [16]. It has the advantage that the exact shape of the valence wave function is taken into account, and this in turn improves the description of the magnetic materials considerably [17]. Brillouin zone sampling in the reciprocal space was performed using a Monkhorst-Pack grid [18] of special k points, and electronics occupancies were determined according to Methfessel-Paxton scheme [19] with an energy smearing of 0.2 eV. Independent k-point convergence tests were conducted for each distinct supercell geometry, ranging from the primitive cell of bulk Ni up to the largest 108-atom cells. For exchange-correlation functional, we use both the generalized gradient approximation (GGA) with the exchange-correlation functional of Perdew and Wang (PW91) [20], and local spin density (LSDA) with the exchange-correlation functional of Ceperly and Adler [21] as parameterized by Perdew and Zunger [22]. Concerning the computational parameters, the plane wave energy cut-off is fixed to 400 eV for all calculations. Supercells containing 7 (face-centred cubic), 31 (simple cubic), 71 (simple tetragonal cell) and 107 (simple cubic) atoms were used to model an isolated vacancy and bulk calculations were performed in corresponding cells containing 8, 32, 72, and 108 atoms. For these supercells, the minimum separations between periodically repeated vacancies are 4.98, 7.04, and 10.56 Å for 8, 32, 108 supercells respectively. For the 72 supercell, the separation between vacancies is 7.04 in the z direction and 10.56 Å in the x, y directions. The convergence was checked with respect to the number of sampling points. As expected, we

found that the number of sampling points required for convergence decreased with increasing cell size: for 7/8-atom cell Monkhorst-Pack parameters (8,8,8) were sufficient while (6,6,6) and (4,4,4) were adequate for the 31/32-atom and 71/72-atom cells, the biggest unit cell 127/128-atom converged at (2,2,2) within 10 meV. For the pseudopotentials, we have taken the Paw-GGA and Paw-LSDA in VASP library similar to those proposed and tested in Ref. [17].

The determination of the cohesive energy is obtained as being the difference between the energy of the isolated nickel and that of the bulk per unit atom. Thus, we had to determine the energy of the nickel atom and more particularly the polarisation and broken symmetry contribution, since the reference energy used in VASP concerns the nonpolarized case. Unfortunately, DFT approach is unavailable to describe the ground triplet state of $4s^2 3d^8$ because this latter has a multireferential character, while DFT works only with a single determinant. In fact the mono-referential $4s^2 3d^8$ triplet corresponding to total kinetic moment $J=2, 3, 4$ whose energies are 0, 0.165 and 0.275 eV. Thus, we can expect that the DFT calculated cohesive energy will be overestimated by 0.1 to 0.3 eV.

3. Results

3.1 Structural and elastic properties of the bulk

As a first test of our method we calculated the properties of bulk Ni. Using primitive cell geometry, 128 irreducible k points and plane wave cut-off energy of 400 eV were needed to converge the total energy per atom to within 1 meV.

In table I, computational results concerning the bulk parameter a_0 the cohesive energy E_{coh} , the magnetic

moment M_0 and the bulk modulus B_0 . The GGA calculated bulk parameter is closed to the experimental data (less than 0.1%) while the local approach is underestimate a_0 by 3%. The cohesive energies in each case are overestimated more particularly at the local level. The contribution of both spin polarization and broken symmetry enhance of 0.58 eV and 0.63 eV the local and GGA approximation. Finally, the discrepancy with experiment is significant in GGA (8%) and dramatic in local (33%). As explained above, the

monodeterminantal description of the wave function overestimates the energy of isolated atom nickel of nearly 0.1 eV to 0.3 eV. Taking into account this correction we can say that the GGA approach leads to a cohesive energy of nearly 4.50-4.60 eV which is so not bad while the local approach remains unsatisfactory.

Table I. Comparison of calculated Ni properties to experimental and others ab initio calculations. LSDA refers to spin-polarized LDA

Method	a_0 (Å)	B_0 (GPa)	M_0 (μ_b)	E_{coh} (eV)
This works				
PAW-LSDA	3.425	280.6	0.60	5.92
PAW-GGA	3.522	195.1	0.61	4.82
Other works				
LSDA, PP-LAPW ^a	3.44	239	0.60	
GGA, PP-LAPW ^a	3.53	192	0.64	
FLAPW-GGA ^b	3.52	200	0.60	
Experiment ^c	3.524	186	0.61	4.44

^a Reference 23, ^bReference 24, ^c Reference 25

3.2 Formation and migration energy of vacancy

We study the vacancy in nickel by supercell method; that is, we begin with the periodic FCC nickel lattice and remove atoms in periodic array so that each supercell of the lattice contains one vacancy.

The formation enthalpy of a vacancy is given by:

$$H_v^f = E_v^f - pV$$

Where E_v^f is the formation energy of monovacancy and p is the external pressure applied to the solid. This latter term is significative only for pressure of several KBar; thus, in the following H_v^f will be

equivalent to E_v^f because all calculations are done for zero pressure.

If N is the number of lattice sites of the supercell containing $N-1$ atoms and one monovacancy,

H_v^f can be calculated as:

$$H_v^f = E(1, \Omega_1) - \frac{N-1}{N} E(0, \Omega_0)$$

where the $E(1, \Omega_1)$ is the total energy of the supercell with $N-1$ atoms and one vacancy at a relaxed unit cell volume Ω_1 and $E(0, \Omega_0)$ the total energy of the supercell with N atom at a relaxed unit cell volume Ω_0

The migration enthalpy of the vacancy can be expressed as:

$$H_v^m = E_m(1, \Omega_2) - E(1, \Omega_1)$$

where E_m is the total energy of the supercell with $N-1$ atoms and one monovacancy located at the saddle site at relaxed volume Ω_2 . Finally, the diffusion enthalpy Q_1 is calculated as:

$$Q_1 = H_v^f + H_v^m$$

In table II the results for the vacancy parameters (formation, migration and formation volume) are presented at both the LSDA and GGA levels.

Table II. Formation, migration and activation energies of the monovacancy at the local and non-local levels. LSDA for PAW-LSDA calculation, GGA for PAW-GGA calculation. NR and FR refers to the non-relaxed and full relaxed calculations.

	LSDA		GGA		Experiment
	NR	FR	NR	FR	
H^f	1.71	1.62	1.43	1.38	1.39 ^a , 1.79 ^b 1.72 ^c
H_v^m	1.80	1.51	1.58	1.28	1.04 ^b
Q_1	3.51	3.13	3.02	2.65	2.77 ^b

^a Reference 26, ^bReference 12, ^cReference 10

4. Conclusions

Firstly, we discuss the accuracy of the present calculation, for the bulk properties, which serve as guide to access to accuracy for other properties. The lattice parameter a_0 , and bulk modulus B_0 . The LSDA calculation underestimate a_0 and overestimate B_0 strongly as already know. it seen

that the GGA calculation considerably improve the LSDA values and reproduce the measured values almost completely. We also found that the presents results agree very well the results of full-potential-linearised-augmented-plane-wave calculation [23].

Secondly, we discuss the calculated values for vacancy formation energy in nickel which as the central result of the present work. Table III lists the results both for local and non-local calculations. The non-local result agrees very well with the experimental values. It's also seen that the LSDA reproduce well the measured values. However, we must be careful for the comparison in the case of LSDA results, because all calculations was done at the relaxed lattice parameter listed in table I which are shorter 3% than the experimental values. If we take the experimental lattice parameter, the vacancy formation energy will be nearly 2.1 eV, strongly overestimated (~20%) compared with the measured values. Detail results will be published elsewhere. We conclude that the GGA corrects not only the deficiencies of LSDA for lattice parameter and bulk modulus, but also the deficiency (overestimation) of LSDA for vacancy formation energy.

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