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Self-interstitials structure in the hcp metals: A further perspective from first-principles calculations

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ABSTRACT

We study the structure of several standard and non-standard self-interstitial configurations in a series of hcp metals, by using Density Functional Theory as embodied in the computer codes SIESTA and WIEN2k. The considered metals include Be, Mg, Ti, Zr, Co, Zn, and Cd, thus spanning the whole range of experimental c/a ratios, different kinds of bonding, and even magnetism (Co). The results show the importance of low symmetry configurations, closely related to the non-basal crowdion, in order to rationalize the experimental data on self-interstitial structure and migration.

1. Introduction

Proper knowledge of the self-interstitial structure in metals is essential for the understanding of how those metals change their microstructure, e. g. when exposed to irradiation environments or while undergoing heavy mechanical work. Microstructure evolution impacts chiefly the mechanical properties and may thus become a critical issue for in-vessel components of nuclear reactors. From a fundamental perspective, knowledge of this kind informs the modeling of irradiation effects in solids, subject initiated in the 1950s, that has received renewed interest in more recent times, as witnessed for instance in the COSIRES series of conferences. Among these modelings, worth of noticing are the ones aimed at producing tools for the assessment of power plant life extension, motivated by the many plants worldwide that nowadays are approaching their planned end of life. A few examples along these lines are efforts undertaken in the framework of several recent projects, such as REVE [1], PERFORM 60 [2], and PERFECT [3].

Within this context, the application of the Density Functional Theory (DFT), that has taken place in the past 15 years or so, to study the structure of defects and their interactions with impurities, represents a major step. Both, the wider availability of codes and the increase (and availability) of computing power, contributed to make it possible. Focusing on the interstitial defect, DFT was able, for instance, to provide a consistent picture of the structure across the bcc transition metals of the periodic chart [4,5], where the <110> and <111> dumbbells compete for the lowest energy configuration. In particular, the experimentally observed [6] <110> structure in Fe, somewhat off-trend from theoretical expectations, was explained as due to magnetic effects, and even reasonable quantitative agreement with experiment was obtained for the kinetics of irradiation recovery [7].

The situation regarding the hcp metals, however, is less satisfactory. In a former work by the present authors [8], an interatomic potential for Zr of the Embedded Atom Method (EAM [9]) kind, was carefully fitted to available experimental data, and applied to simulating some defect structures. It was predicted that six of the assumed standard interstitial configurations for the hcp lattice, had formation energy within 0.3 eV. Moreover, the reported lowest energy configuration, basal split (Bs), showing one-dimensional (1D) migration at low temperatures [10] (though switching gradually to 3D at higher ones), might not be entirely consistent with experiments. However, we also pointed out that experiments carry some degree of conflict. Internal friction (IF) measurements after neutron irradiation at liquid Nitrogen temperatures favor a defect

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with a monoclinic elastic dipole [11], whereas Huang diffuse X-rays scattering (DXS) after electron irradiation at liquid Helium temperatures is consistent with a dipole isotropic on the basal plane [12], though other possible symmetries cannot be ruled out. A later theoretical study on Zr [13], this time applying the DFT methodology implemented in the VASP code [14], reported five configurations with formation energy within 0.24 eV, though not the same set as before and not in the same order of energies. Besides, the predicted most stable structure, octahedral (O), is not responsive to internal friction. A more recent study on Zr [15], also using VASP but employing larger simulation cells (up to 288 hcp sites against former 96), reported the basal octahedral (Bo) as the most stable configuration, closely followed by Bs and then O. This preference for basal structures suggests a defect that will mainly diffuse in 2D; besides, even though Bs responds to internal friction, it does not posses monoclinic symmetry. To essentially the same results arrived a further study [16] where both codes, VASP and SIESTA [17], were used; this is after discarding their reported, low-symmetry, BC$'$ configuration which was later shown to have a negligible barrier for decaying to Bo [18]. Interestingly, ref. [16] also reports another low-symmetry configuration that possesses a screw-like structure along the c axis (PS-C$'$) and a very flat energy profile; this ought to migrate along the c axis almost athermally but, lying about 0.25 eV above Bo, it would take some thermal activation to be significantly populated.

Here we undertake to study the structure of standard (assumed) and non-standard self-interstitial atoms (SIA) for a range of hcp metals, comprising Be, Mg, Ti, Zr, Co, Zn, and Cd. Thus, a relatively large variation in the c/a ratio is explored, as well as different types of bonding. The main aim is to gain insight on the possible migration mechanisms, on a wider perspective than group *IV* B metals, to be tested against the (limited) experimental data. The methodology, based on the application of DFT, is explained in sec. 2 below; results together with the discussion and comparison with experiments, are reported in sec. 3; finally, sec. 4 is devoted to the conclusions, also including a brief summary of the main findings.

2. Methodology

The calculation procedure consists on the sequential application of two DFT codes: i) SIESTA [17] (ver.3.0), which is based on pseudopotentials and numerical, strictly localized, atomic-like basis functions for wave-functions expansion, and ii) the all-electron, full-potential, WIEN2k code [19] (ver.12.1), which implements the Augmented Plane Wave plus Local Orbitals technique, in order to expand the wave-functions, thus more accurate but also requiring much more computational resources than the former. Final energies of the tested configurations are taken from the output of the latter code, in order to assure maximum reliability for the simulation supercell size employed; this is limited to 96 hcp sites ($4 \times 4 \times 3$ repeated hexagonal cells). Though this supercell size has been used in previous works, e.g. Ref. [13], it has later been shown [15] that for SIA configurations falling very close in formation energy, cells about twice as large may be needed to get the correct energy ordering. Our arguments, however, are qualitative in nature, based on identifying groups of configurations of lowest energy and analyzing their structures. Even though larger simulation cells may be necessary to reveal the fine details of energy ordering within such groups, the groups themselves are correctly captured by our present methodology.

In short, firstly each SIA configuration is handled to SIESTA for coordinates relaxation in order to minimize their energy (conjugate gradients technique) under the action of a given pseudopotential, aiming at individual forces typically below about 0.01 eV/Å. During the process, the simulation cell size and shape are kept fixed, consistent with the equilibrium lattice parameters previously determined for that same pseudopotential. Secondly, the cell energy is re-computed by using the all-electron code WIEN2k, after re-scaling to the lattice parameters determined beforehand, now with the latter code. Thirdly and eventually, a further coordinates relaxation is undertaken by using WIEN2k, as a check and for selected instances. This last step is very much expensive in computational resources than the first one (and this is the whole point of our sequential approach), but is also generally not needed within the bounds of our current purposes, because the further energy decrease typically amounts to some 0.02–0.03 eV for the whole cell, though it may vary somewhat across configurations. Thus the formation energies we consider to be representative are the ones derived from the second step. An example of the consistency of this approach is given in Table 1 for the case of Zr, where the formation energy of several SIA configurations (to be detailed later on) is reported after application of each of the three steps just mentioned. For comparison, also reported are the values from Ref. [13] for the same supercell and boundary conditions, but using the VASP code furnished with an ultrasoft pseudopotential. Moreover, on the last row we have applied the defect-defect elastic interaction correction according to Ref. [18] to step 3 results (using dipoles from SIESTA simulations and experimental elastic constants), obtaining agreement with their Fig. 3 for the same size, and almost the converged energy ordering of larger cells. Clearly, the only significant differences for our purposes are reflected in the first two rows.

More technical details regarding pseudopotentials, basis functions, and calculation parameters are as follows. Pseudopotentials are of the so called norm-conserving Troullier-Martins kind [20], build upon the PBE [21] GGA exchange and correlation functional, including relativistic effects and core charge corrections. The Zr and Ti pseudopotentials, already used in some of our previous works [22–24], were taken from SIESTA's home page. The remaining ones were build by us, using the ATOM utility bundled with the SIESTA package, mainly because of consistency reasons with the former two (GGA and core corrections). Table 2 gathers the reference electronic configurations for pseudopotential generation; also reported is the quality of the atomic-like basis functions for wave-functions expansion needed in SIESTA's method. Overall, Zr and Ti include the s and p states from the core and correspond to ionic (+2) configurations; Zn includes the complete $3d^{10}$ shell, all the rest are standard atomic ground state (valence) configurations. The (parameters of the) basis functions, that broadly can be termed as double-zeta polarized (DZP, two radial functions per l-angular momentum channel, plus a third, $l+1$, orbital, polarizing the former two), were optimized for a small hcp cell with the simplex technique, checking a posteriori for reasonable match to the experimental hcp lattice parameters, while assuring stability with respect to the fcc and bcc lattices. Such a procedure failed for Cd, however, having developed the Zn case, which possesses about the same, relatively large, c/a ratio, this posed no real problem for the subsequent stage involving the WIEN2k code.

Table 1
Calculated SIA (heading row) formation energies (eV) for Zr after each of the three steps in our sequential approach.

	O	Bo	C	S	S^*	Bs
Step 1 (SIESTA)	3.37	3.44	3.68	3.48	3.48	3.70
Step 2 (WIEN2k)	3.05	3.07	3.46	3.23	3.19	3.18
Step 3 (WIEN2k)	3.04	3.04	3.42	3.20	3.17	3.13
Ref. [13]	2.94	2.98	3.25	3.12	–	3.09
Step 3 corrected[a]	2.95	2.90	3.32	3.09	3.08	2.95

[a] Elastic correction according to Ref. [18].