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Ab-initio approach to the effect of Fe on the diffusion in hcp Zr

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Abstract

The role of Fe in the hcp Zr diffusion process is analyzed, given its ultra-fast diffusion (up to nine orders of magnitude higher than the self-diffusion in the temperature range 779–1128 K) and the enhancement observed in the self and substitutional diffusion induced by its unavoidable presence as impurity. Ab-initio calculations using SIESTA and WIEN2K codes were performed in order to find the actual Fe minimum energy configuration within the hcp Zr matrix and its interaction with vacancies. Several off-centre quasi-interstitial positions with energies similar to substitutional Fe were encountered. The comparison with diffusion coefficient measurements and Mössbauer experiments allows us to discard the substitutional position of the Fe atom as well as to affirm that its presence creates a considerable lattice distortion together with an increment in the number of vacancies. The above effects could be responsible for the enhancement in the self and substitutional diffusion, whereas the large amount of quasi-interstitial positions for Fe could be, at least partially, responsible for the ultra-fast Fe diffusion.
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1. Introduction

As it is well known, Zr belongs to the group IV B of the periodic table and presents a bcc (β) phase at high temperature and an hcp (α) one at low temperature. The transformation temperature $T_{\alpha\beta}$ is 1136 K ($0.6T_{m\alpha}$ where $T_{m\alpha}$ is the hypothetical melting temperature of the α phase).

It is also known that traces of Fe have a critical influence on the mass transport in α-Zr. Fe is also implicated in various processes of high relevance for the nuclear industry such as in the irradiation–deformation behaviour of Zr–2.5Nb [1] and in the phenomenon of breakaway growth in Zircaloy-2 [2]. The knowledge of the Fe–Zr interaction at atomic level could be the key to the comprehension of such phenomena.

Experimentally, an extremely fast diffusivity of Fe in α-Zr [3], coupled with a very low solubility [4] has been

determined. From these tracer diffusion studies it has been established that Fe diffusion [5] is up to nine orders of magnitude faster than α-Zr self-diffusion, as we can see in Fig. 1. This is supposed to be due – at least partially – to impurities on interstitial sites, although there is no clear experimental proof for such assumption. The octahedral interstitial sites are the largest available spaces in the hcp structure, so that it is usually assumed that Fe is located there. However, when Mössbauer spectroscopy [6] was used in α-Zr samples implanted with very low doses of ^{57}Fe, only 30% of the Fe atoms were found in non-substitutional positions and, even this fraction, did not reside on a symmetrical site in the hcp lattice (octahedral or tetrahedral) but on 'off-centre' (asymmetrical) positions. Moreover, previous work [7] has shown that when larger amounts of ^{57}Fe were implanted, the linewidth and/or hyperfine parameters measured appear to represent some phases of the Fe–Zr system (such as Zr_3Fe) and not isolated Fe atoms, showing once more the extremely low Fe solubility in α-Zr, even lower than that reported in the literature [4].

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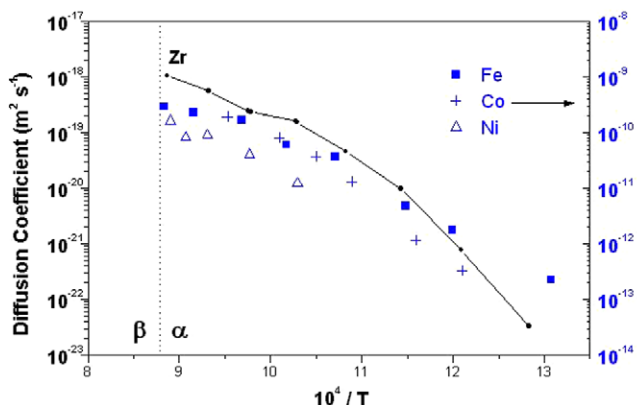[1] Members of Carrera del Investigador del CONICET.

Fig. 1. Diffusion coefficients for α-Zr self-diffusion and for the ultra-fast diffusers Fe, Co and Ni. The scale on the left corresponds to self-diffusion, the one on right to the ultra-fast impurities.

On the other hand, the parameters of the α-Zr self-diffusion are not consistent with the so-called 'normal behaviour' for metals; a downward curvature in the Arrhenius plot was observed for self-diffusion [8] and also for the substitutional diffusers Hf [9], Pb [10] and Au [11] when experiments in a temperature range large enough to observe such curvature, could be performed. The ultra-fast diffusion of Fe [3], which is not considered substitutional, as was mentioned above, also presents such a curvature.

There is some experimental evidence [12] that small amounts (few ppm) of Fe and other transition elements like Co and Ni in the Zr matrix can modify the diffusion behaviour of substitutional diffusers. In all cases, samples with higher amounts of Fe increase the diffusion coefficient, as shown for example in Fig. 3 of Ref. [12] for self-diffusion. A strong Fe-vacancy interaction, followed by a fast movement of this pair is postulated as responsible for that enhancement.

Different authors [13,14] have suggested that the curvature of the Arrhenius plot is an extrinsic effect due to the influence of these fast diffusing transition elements, unavoidably present as impurities in the α-Zr experimental samples. The central idea of these models is based on two hypotheses. First a strong Fe-vacancy interaction, followed by a fast movement of this pair and second, only Fe in solution is responsible for the formation of such pairs. The curvature of the Arrhenius plots would therefore be caused by Fe precipitation at low temperatures, where its solubility is almost zero and where rapid pairs would become trapped. A more detailed analysis of these models is given in Ref. [15]. However, they have been seriously questioned by recent measurements of Au diffusion in α-Zr matrices with different amounts of Fe [11] as impurity. They show that the enhancement persists even at temperatures where the Fe solubility is reported as zero (773 K) so that all the Fe present, not only Fe in solution, seems to be responsible for the diffusion enhancement.

There are several unanswered questions in this field that we believe theoretical ab-initio work could help to answer.

- Which are the equilibrium positions of the Fe atoms in the α-Zr matrix?
- Are they isolated, or do they form pairs with vacancies, or embryos of any of the Zr–Fe phases present in the binary phase diagram?
- Which is the mechanism for the ultra-fast Fe diffusion?
- Which is the mechanism for the enhancement of self and substitutional diffusion due to the presence of Fe in α-Zr as impurity?
- Is the unavoidable presence of small amounts of Fe responsible for the curvature observed in the Arrhenius plot or is it an intrinsic property of α-Zr?

Previous theoretical work has studied point defects in pure α-Zr, for example the vacancy formation and migration energies [16,17] and also the electronic structure surrounding the interstitial Fe [18]. In the present paper we will address some of the previous questions, in particular the Fe-vacancy interaction, and relate the obtained results to the diffusion process.

2. Calculation method

For the calculations we used two different ab-initio codes. SIESTA [19,20] and WIEN2K [21], both based on the local density approximation, to find the energies and magnetic moments of Fe in different positions of the hcp Zr lattice. The SIESTA code was used to obtain the relaxed atomic distribution in a 36 Zr atom supercell containing one Fe atom and the WIEN2K code assured us that those structures were effectively of lower energy than the unrelaxed ones, and provided magnetic moments, electric field gradients and isomer shifts.

The WIEN2K code is an implementation of the FPLAPW (full potential linear augmented plane waves) method. We used a spin polarized approach and the exchange and correlation given by Perdew, Burke and Ernzerhoff [22,23]. We also used the GGA (generalized gradient approximation) because it gives better results for the bulk lattice parameters and cohesive energies of Fe and Zr. The number of plane waves used, given by the parameter RKM = 7, corresponds to an energy cutoff of 15 Ry. The calculation is scalar relativistic and includes local orbitals for the 3p states of Fe and for 4s and 4p of Zr. The atomic sphere radii (muffin tins) were taken as 2 a.u.

For the relaxation of the structures we found it more convenient to use the SIESTA code [24] which replaces the core electrons by non-local norm-conserving pseudopotentials and describes the valence electrons by a linear combination of numerical pseudo-atomic orbitals. The pseudopotential and the basis set for Zr were obtained from the internet site of the SIESTA code, and for this reason the relaxations were performed in the LDA approximation. For Fe we used parameters from previous works by our group [25]. Relaxation of the structure by the conjugate gradient method was performed until the forces on each atom were less than 0.4 eV/nm.

Our strategy was to relax an hcp supercell with 36 Zr atoms, and the same supercell with one Fe atom in substitutional or interstitial positions, with and without a vacancy, using the SIESTA code. The coordinates obtained from the relaxations were used as input for the WIEN2K calculations, which we believe to be more accurate, and these values were used for the quantitative analysis. This procedure is similar to that used in Ref. [26].

3. Results and discussion

We studied the following seven configurations, with the same fixed supercell size:

(a) 36 Zr atom supercell.
(b) 35 Zr atoms and one Fe atom in a substitutional position.
(c) 36 Zr atoms and one Fe in an octahedral position.
(d) 36 Zr atoms and one Fe in a tetrahedral position.
(e) 35 Zr atoms with a vacant site.
(f) 35 Zr atoms and one Fe in an octahedral position with the vacant site nearest-neighbour to the Fe.
(g) 35 Zr atoms and one Fe in a tetrahedral position with the vacant site nearest-neighbour to the Fe.

The relaxation is small if Fe is forced to remain in a substitutional position and it is also small for a single Zr vacancy. This is due to the small and fixed size of the supercell used, so the reported results must be considered as corresponding to the unrelaxed situations (cases b and e). On the contrary, the relaxation is considerable in cases with an interstitial Fe and a nearby vacancy (cases f and g), where Fe moves towards the substitutional position but does not reach it and ends in an asymmetrical situation. The final positions are quite similar for cases f and g, as can be seen in Figs. 2 and 3 and have a small ($<0.3\ \mu_B$) or zero magnetic moment, while the substitutional position has a large magnetic moment ($3\ \mu_B$), mostly concentrated in the Fe site.

Values of cohesive energy per unit cell, electric field gradients and isomer shifts at the Fe site are shown in Table 1. From this table several relevant energies can be calculated. The energy required to form a single Zr vacancy can be obtained as

$$E(\text{vac}) = E(e) - 35 \times E(a)/36 = 1.98\text{eV}, \qquad (1)$$

which is in good agreement with previous calculations [16,17].

In order to establish the more stable position for Fe (substitutional, interstitial in octahedral or interstitial in tetrahedral site) we evaluate

$$\Delta E(\text{oct-subst}) = E(b) + E(a)/36 - E(c) = 0.1\text{eV}, \qquad (2)$$

$$\Delta E(\text{tetra-subst}) = E(b) + E(a)/36 - E(d) = 0.98\text{eV}. \qquad (3)$$

Therefore, Fe in a substitutional position is the more stable situation; however, the energy difference with the octahe-
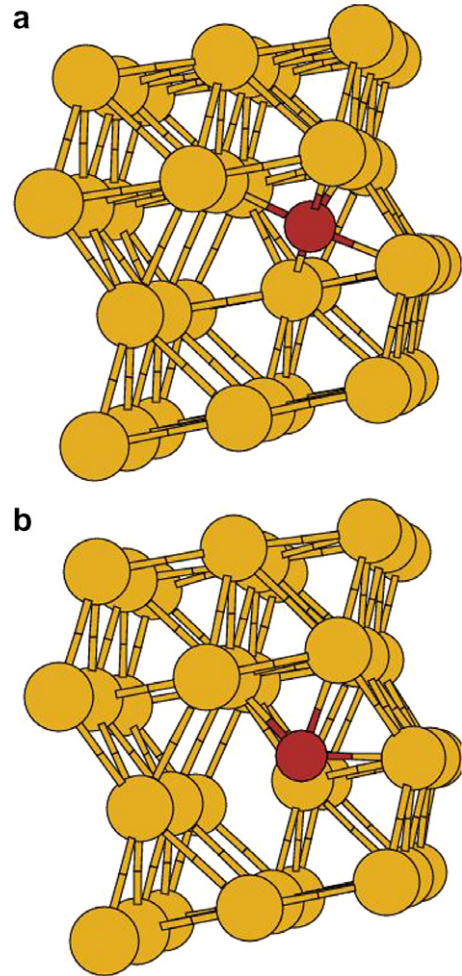

Fig. 2. Supercell with an Fe atom at octahedral site with a first-neighbour site vacant. (a) Initial position and (b) after relaxation.

dral position is small and almost within the calculation error. On the other hand, the energy at the tetrahedral site is much higher.

The energy required to form a vacancy in a nearest-neighbour position to an interstitial Fe, that was initially in an octahedral position and then relaxed, is

$$E(\text{vac-nnFe}) = E(c) - E(a)/36 - E(f) = -0.14\text{eV}. \qquad (4)$$

A similar analysis for a relaxed interstitial tetrahedral Fe with a nearest-neighbour vacancy gives

$$E(\text{vac-nnFe}) = E(d) - E(a)/36 - E(g) = -0.85\text{eV}. \qquad (5)$$

Eqs. (4) and (5) prove that in both cases the system lowers its energy if a vacancy is placed in the vicinity of an Fe atom in an interstitial position. The large energy gain when forming a vacancy close to a tetrahedral Fe is due to the fact that the tetrahedral position is much less stable than the octahedral one; what is important to remark is that after relaxation the total energy of cases b, c, f and g ends up very similar, being f the more stable one.

Another important quantity to consider is the vacancy-Fe binding energy calculated as
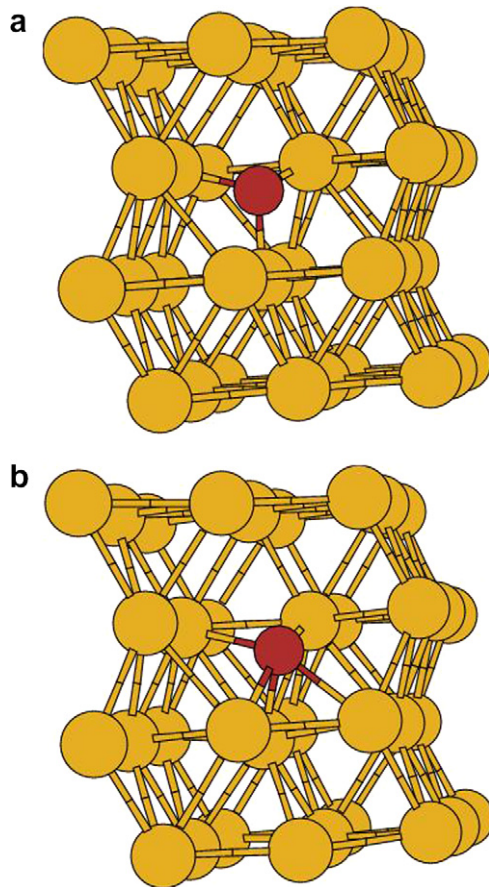
Fig. 3. Supercell with an Fe atom at tetrahedral site with a first-neighbour site vacant. (a) Initial position and (b) after relaxation.

$$E_{\text{bond}}(\text{vac-Fe}) = E(f) + E(a) – [E(c) + E(e)] = 2.074\text{eV},$$

(6)

which shows a strong bonding of this pair.

With these results we can put forward a possible explanation for the enhancement of self and substitutional diffusion due to the presence of Fe. It is based on the negative value for the vacancy formation energy in a nearest-neighbour position of Fe. If diffusion arises from a vacancy mechanism, the dependence of the diffusion coefficient D with temperature is mainly determined by the number of vacancies (N_v) formed at such temperature. N_v has an exponential dependence with the vacancy formation energy, which in our case is 1.98 eV for pure α-Zr but is negligible if a Fe atom is near the vacancy. This means that Fe introduces an additional amount of vacancies over those coming from the thermal equilibrium in the pure material. The additional vacancies would be responsible for the increase of the diffusion coefficients with respect to those of pure α-Zr: the higher the amount of Fe, the higher the number of vacancies present in the matrix for a given temperature, and consequently the larger the diffusion coefficients.

This simple approach could be refined if we consider that most of the additional vacancies would be tightly bound to the Fe atoms and probably migrate together, this second kind of defect is also responsible for the diffusion

enhancement. The mechanism of migration of such kind of defect is beyond the scope of this work.

On the other hand, comparing the cases b, c, f and g we find that Fe in a strictly substitutional or strictly octahedral or in a somewhat delocalized position towards the octahedral or tetrahedral holes has a very similar cohesive energy. Not all possible off-centre positions were explored in the present work, so presumably other similar arrangements of atoms could be also stable. Recalling the ultra-fast diffusion coefficient measured for Fe, it is easy to relate it with the number of possible stable sites for Fe, much larger than those available in a simple interstitial mechanism. This fact could be a partial explanation for the nine orders of magnitude difference between Fe diffusion and self-diffusion in α-Zr. Of course the high availability of very close jump sites should be completed by the study of the corresponding migration barriers, but it is not clear how to perform this calculation due to the strong asymmetry of the atomic positions in the off-centre quasi-interstitial cases.

Fig. 4 is a schematic reproduction of the Mössbauer measurements performed in Ref. [6] at 24 K after the implantation of a small amount of Fe (less than 10^{10} ions/cm²). The dotted line represents the actual measurement, whereas the dashed areas are the fittings performed by the authors. They fit the spectra with three different positions for Fe; a broad peak with an unresolved quadrupole splitting ΔE_q (≈ 0.1 mm/s) 65% of relative intensity and a negative centre shift δ (-0.34 mm/s) and two doublets: one with $\Delta E_q = 0.95$ mm/s, 30% population and $\delta = +0.40$ mm/s at the right side and another with $\Delta E_q = 0.80$ mm/s, 5% and $\delta = -0.45$. No magnetic dipolar splitting was observed, so that we infer that no magnetic Fe is present in the samples and, consequently, that the substitutional Fe (type b) is not observed experimentally.

With the calculated values of the electric field gradient and the isomer shift, shown in the last two columns of Table 1, we attempt a comparison with the Mössbauer spectra. It is straightforward to relate the highest peak with the off-centred positions all of them having a low ΔE_q (between 0.1 and 0.3 mm/s) and a negative δ (around -0.2 mm/s) supporting the suggestion of Ref. [6] that there is not one or two but several positions of similar cohesive energy,

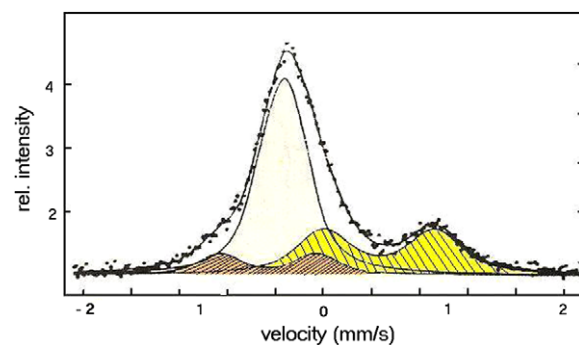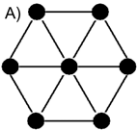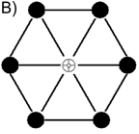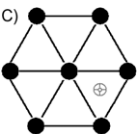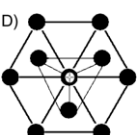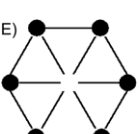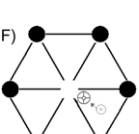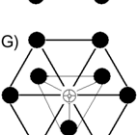Fig. 4. Mössbauer measurement at 24 K of ^{57}Fe implanted in α-Zr with a dose less than 10^{10} ions/cm² from Ref. [6].

Table 1
Cohesive energies (in eV), quadrupole splitting ΔE_q at the Fe site and centre shift δ, for the cases studied

Configuration	E per cell	N	ΔE_q (mm/s)	δ (mm/s)
A)	221.292	36	–	–
B)	220.142	36	0.088	0.11
C)	226.190 (220.043)[a]	37(36)	0.52	−0.77
D)	225.3050 (219.158)[a]	37(36)	0.076	−0.31
E)	213.207	35	–	–
F)	220.179	36	0.33	−0.19
G)	220.011	36	0.20	−0.18

[a] The quantities in parentheses indicate that the energy of one Zr atom was subtracted, so the cohesive energies of all cases containing one Fe atom are comparable.

giving origin to a broad spectra. The small doublet with 5% population, negative δ and large ΔE_q could be related with one of the pure interstitial situations (with no nearest-neighbour vacancies) and finally the 30% doublet with a high positive δ could be a non equilibrium situation, characteristic of an as-implanted sample kept at 24 K. In fact Mössbauer measurements at higher temperatures show that the doublet disappears at room temperature.

4. Conclusions

The interaction between Fe atoms and the hcp α-Zr matrix was studied with ab-initio calculations, in order to comprehend the mechanism involved in the ultra-fast diffusion of Fe in α-Zr and the enhancement observed in self and substitutional diffusion.

It was found that the presence of Fe induces the formation of neighbour vacancies, increasing the number of vacancies with respect to those in pure α-Zr at a given temperature. The Fe atom is located in one of various off-centre quasi-interstitial positions, all of them having almost degenerate energies.

The comparison between these calculations and previous Mössbauer measurements, allows us to discard a simple substitutional position for the Fe atoms, being most of them in asymmetrical positions which cause a considerable distortion of the hcp Zr lattice.

This distortion, together with the increment in the number of vacancies could be responsible for the enhancement in the self and substitutional diffusion, whereas the large amount of quasi-interstitial positions for Fe could be, at least partially, responsible for the ultra-fast Fe diffusion.

Acknowledgements

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