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Non-classical interstitial sites and anomalous diffusion mechanisms in hcp-titanium

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Abstract

It is well known that Fe, Co and Ni are characterised by abnormally fast diffusivity in the hcp phase of Ti (α -Ti). Their diffusivity values are 10^5 times higher than self-diffusion data, which is atypical for vacancy-mediated diffusion yet too slow for interstitial diffusion. Also, addition of Fe, Co and Ni appears to accelerate the solvent diffusivity, with dramatic ramifications on a number of diffusion-controlled mechanisms. The fast diffusivity of these elements in α -Ti seems to be the result of their ability to dissolve both interstitially and substitutionally. In fact, while the majority of Fe, Co and Ni atoms sit substitutionally within the hcp lattice, a small concentration of these solute atoms can move very fast through interstitial sites, determining the high diffusion coefficient values. In this work, a combination of density functional theory and Kinetic Monte Carlo simulations is used to investigate possible migration processes for both solute and solvent atoms and their effect on the macroscopic diffusivity. We find that traditional classical interstitial sites are unsuitable for these solute atoms, and that alternative

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interstitial sites are instead preferred. Calculations confirm that the fast diffusivity of these solute atoms is a result of their ability to diffuse both interstitially and by vacancy-mediated mechanisms, yielding excellent agreement with experimental values. It is possible for these solute atoms to swap position with solvent atoms without the presence of vacancies, leading to an accelerated solvent diffusion in the presence of relatively dilute levels of these solute elements.

Keywords: Titanium; anomalous diffusion; interstitial sites; Density Functional Theory; Kinetic Monte Carlo

1. Introduction

The migration and diffusion behaviour of solute and solvent atoms in alloys is extremely important as it affects processing, microstructure evolution and mechanical performance over a range of temperatures [1]. Traditionally, diffusion is expected to happen via vacancy-mediated mechanisms or via interstitial migration. In the earlier case, atoms located at lattice sites can move through the crystal structure by exchanging their position with a vacancy. In the latter case, atoms located at the classic interstitial sites can move between different interstitial sites, squeezing through gaps in the host lattice. Due to the fact vacancies are relatively rare occurrences in metals and alloys, vacancy-mediated diffusion is normally much slower when compared to interstitial diffusion: atoms can only move if a vacancy is present next to them. By contrast, most interstitial sites surrounding an interstitial solute atom are normally free, thereby resulting in a significantly lower activation energy for diffusion [1, 2]. The intrinsic diffusivity of a solute atom

is therefore usually attributed to its ability to diffuse via one of these two mechanisms. Solutes with size comparable to the host are expected to sit substitutionally within the lattice, and diffuse via vacancy-mediated mechanisms. On the other hand, solutes which are considerably smaller than the host are expected to occupy classical interstitial sites, and diffuse interstitially within the host lattice [1, 2]. Possible interstitial sites are normally dictated by classical considerations: treating the host lattice atoms as hard spheres, any gap between these hard spheres is considered an interstitial site, and the size of the interstitial site often determines which atoms can occupy that site. This simple approximation, often taken for granted in metallurgy, is rather effective and can explain, for example, why carbon is relatively soluble in the austenite phase of iron (where carbon atoms occupy octahedral interstitial sites), while it is pretty much insoluble in the ferrite phase [3].

Some solute atoms, however, do not appear to obey these simple rules. This is the case of Fe, Co and Ni in the hcp phase of titanium (α -Ti). The difference in behaviour becomes apparent when measuring the diffusivities of these solute atoms in α -Ti: their diffusivity values are 10^5 times larger than self-diffusivity data [4, 5, 6], and is comparable to the diffusivity of more conventional interstitial solute atoms, such as C [7]. Ti, Zr and Hf are usually referred as “open” metals because of their large ionic-to-atomic radius ratio [8]. This allows elements with relatively small metallic radius to dissolve both intrstitially and substitutionally. Fe, Co and Ni are indeed small relative to Ti, with metallic radii of $R_{\text{Fe}}=1.26 \text{ \AA}$, $R_{\text{Co}}=1.25 \text{ \AA}$, $R_{\text{Ni}}=1.24 \text{ \AA}$ [9], which suggests these solute atoms could dissolve interstitially in Ti. Yoshida and co-workers were able to experimentally show that this is the case [10, 11].

The ability of Fe, Co and Ni dissolve both interstitially and substitutionally in Ti suggests they are able to diffuse via a dissociative mechanism [12]. This mechanism was proposed by Frank and Turnbull to explain the fast diffusivity of Cu in Ge [12]. Cu in Ge is supposed to migrate from interstitial site to interstitial site until it combines with a vacancy becoming substitutional atom (combination reaction). On the other hand, the substitutional Cu solute can migrate into interstitial sites thereby creating a vacancy (dissociation reaction). In the general case, five microscopic processes are involved in the Frank-Turnbull diffusion mechanism:

- interstitial solute diffusion;
- substitutional solute diffusion;
- vacancy migration from the surface;
- vacancy production in the bulk;
- combination-dissociation reaction [13].

In the case of metals, the vacancy production from the surface (diffusion) and in the bulk (from and to dislocations) is such that the vacancy concentration is constant and equal to the equilibrium values, leaving the overall solute migration to be controlled by the interstitial and substitutional solute diffusion and the combination-dissociation reaction [13]. For the fast-diffusers in open metals, Frank and Turnbull concluded that the effective solute diffusion mostly depends on the few atoms that move interstitially [12].

The above can explain the abnormally fast diffusivity of Fe, Co and Ni in Ti, but does not paint a complete picture. The detrimental effect of fast

diffusers, even in small additions, on mechanical properties of the α -Ti is well reported [14, 15, 16, 17, 18, 19]. It is believed that this depends on the anomalous migration behaviour of these solutes. Fe, Co and Ni have also been reported to affect dislocation mobility [20, 17] and accelerate the self migration in α -Ti [8, 21]. It follows that understanding the diffusion behaviour of these solutes in α -Ti is very important to reduce the negative effective on the creep behaviour of these alloys. Diffusion coefficients can be measured through experiments. However, the empirical surveys cannot convey details on migration processes. On the other hand, *ab initio* calculations have been successfully used to predict the diffusivities of different solute in α -Ti [22, 23, 24, 7], as well as fundamentals aspects of the diffusion mechanism, such as the solute transitions and the influence of the Ti-solute bond on the diffusion behaviour. Bernstein *et al* [9] studied the migration barriers and defect formation energies for various solute atoms in Ti, observing that interstitial formation energies for the fast diffusers are comparatively low. This, alongside low interstitial migration energy barriers can help explain the anomalous diffusion behaviour. The conclusions were further strengthened by Zhang *et al* [25], using analytical formulations to calculate the interstitial and vacancy-mediated diffusivities of various solute atoms in α -Ti. These processes have also been studied in Zr. Pasianot and Pérez [26] have used density functional theory to rationalise the peculiar diffusion behaviour of Fe, Co and Ni in Zr, and how this deviates from the Arrhenius behaviour. Lu *et al* [27] have investigated the interstitial diffusivity behaviour of a number of dilute large solute elements in Zr, and Jain and co-workers developed a Green's function approach to study the competition between the interstitial

and vacancy-mediated behaviour of a number of solutes in Zr.

The purpose of this work is to study the anomalous migration of fast-diffusers, Fe, Co and Ni in α -Ti using kinetic Monte Carlo (KMC) simulations [28] informed with first-principles data. The theory of Frank and Turnbull [12] has been investigated determining the impact of combination-dissociation process [13], interstitial and solute diffusion on the migration of these elements and estimating the solute diffusivity values. The effect of solute-host swap [29] on the solvent migration has also been studied, comparing the KMC results of self-diffusivity with or without this process.

2. Theory

It is clear that simple interstitial and vacancy-mediated mechanisms cannot explain the anomalous diffusion behaviour of Fe, Co and Ni in α -Ti. In fact, the activation energy barrier would be too small in the first case, and too high in the second [12]. These solutes can be accommodated at both interstitial and lattice sites as confirmed by high temperature Mössbauer spectra [10, 11]. Therefore, they may be able to move through the dissociative diffusion mechanism [12]. As introduced above, this mechanism can be broken down into three processes in the case of metals: interstitial diffusion, vacancy-mediated substitutional diffusion and the combination-dissociation process.

At the atomic scale, the interstitial diffusion consists on the migration of solute along the interstitial voids between the host atoms. It is usually a fast diffusion because of relative high number of interstitial sites available for the solute walk and weak bonding between interstitial solute and solvent

atoms relative to substitutional solute. However, Frank and Turbull have estimated that pure interstitial diffusion of Cu in Ge is 100 time higher than apparent diffusion [12]. Similar behaviour is expected in case of fast-diffusers in hcp-Ti.

In the case of vacancy-mediated substitutional diffusion, the solute moves by swapping with vacant lattice sites. The migration depends on the vacancy concentration and the ability of the jumping atom to squeeze between the neighbouring atoms. The migration of substitutional atom is much slower than interstitial solute due to lower availability of vacant sites to jump into.

The combination-dissociation process involves all the three types of point defects: vacancies (V), interstitial solutes (A_i) and substitutional solutes (A_s). When an interstitial atom encounters a vacancy, it can jump into it becoming substitutional (combination). On the other hand, it is also possible that a substitutional solute moves to an interstitial site creating a vacancy-interstitial pair (dissociation). These two mechanisms are described as,



The combination-dissociation process was modeled for simple fcc crystals by Miller in the 1969 [13], and it is represented schematically in Figure 1. The transition v_1 identifies the substitutional atom moving to an interstitial site, creating a vacancy-interstitial pair. Once the vacancy-interstitial pair is formed, the interstitial solute can move away via interstitial transitions, k_1 , or move to re-orient the pair, k_2 . The pair can also be separated, w_1 , or re-orientated, w_2 , by vacancy-host exchange. It is also possible that the interstitial atom recombines with the vacancy occupying lattice site through v_2 transition. The vacancy annihilation by interstitial solute can slow down the

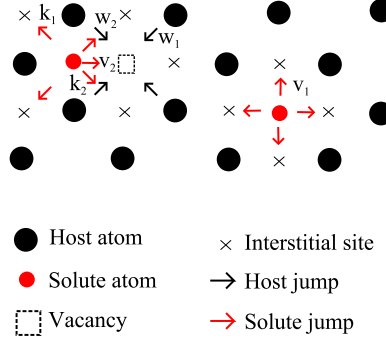


Figure 1: Schematic representation of solute (red arrows) and host (black arrows) transitions in the case of interstitial-vacancy pair diffusion mechanism in fcc crystal [13]: v_1 is the dissociation solute-vacancy, v_2 is the interstitial-vacancy combination, k_1 is the interstitial hop with dissociation of the pair, k_2 is the interstitial hop with reorientation of the pair, w_1 is the host-vacancy exchange with dissociation of the pair, w_2 is the host-vacancy exchange with reorientation of the pair.

extreme fast solute migration along the interstitial sites. On the other hand, the dissociation transition can increase the vacancy concentration influencing the self-diffusion coefficients. Under these considerations, the anomalous behaviour of fast-diffusers can be attributed to the combination-dissociation process.

Another explanation for the behaviour of Fe, Co and Ni in hcp-Ti has been suggested by Frank and Turnbull [12]. They have argued that the reaction rate of the combination-dissociation process is very small with respect to other processes, and it has no noticeable impact on diffusion. Instead, they suggested that majority of solute atoms are stationary at the substitutional lattice sites, and the migration occurs only when solute atoms are located at interstitial sites. In other words, the substitutional solutes has high solubility but low diffusivity. Vice-versa, the interstitial diffusivity is very high, but

there are few interstitial solutes. Therefore, it is expected that only a small fraction of atoms like Fe, Co and Ni are located at interstitial sites in α -Ti and migrate interstitially, while the remaining substitutional atoms migrate rarely. As a results, the overall diffusivity, D^{Eff} , is approximated as [12],

$$D^{\text{Eff}} \approx D_i \frac{C_i^{\text{eq}}}{C_s^{\text{eq}}}, \quad (2)$$

where D_i is the interstitial diffusion coefficient, C_i^{eq} and C_s^{eq} are the equilibrium concentrations of interstitial and substitutional solutes, respectively. The contribution of substitutional solute atoms to the effective diffusivity is negligible.

The above cannot explain why the diffusivity of the host may be affected by the presence of Fe, Co and Ni. A possible mechanism to explain the increase of self-diffusion in presence of Fe, Co, and/or Ni is the solute-host swap described by Warburton [30]. Warburton have modified the Miller's model, assuming that the only possible transitions are the solute dissociation and combination, and host-vacancy swap with reorientation of the pair (respectively v_1 , v_2 and w_2 in Figure 1). Therefore, the solute can exchange position with host atom after a sequence of dissociation-reorientation-combination transitions. As a result, the migration of Ti atoms does not necessarily require the presence of vacancies. Modelling can shed light on this matter.

3. Methodology

Density functional theory (DFT), in conjunction with kinetic Monte Carlo, was used to investigate the effect of the diffusion mechanism presented in Section 2 on the migration of solutes in dilute binary hcp-Ti-X (X=Fe, Co, Ni).

The computational details such as supercell size, plane wave cutt-off, k-points mesh are reported in the supplementary materials.

The migration through different lattices (substitutional and/or interstitial) proceeds via a sequence of transitions. These transitions are thermally activated processes with frequencies given by [31],

$$w = \nu^* \exp \left(-\frac{\Delta H_m}{k_b T} \right), \quad (3)$$

where k_b and T are respectively the Boltzmann's constant and absolute temperature, ν^* is the attempt frequency and ΔH_m is the migration energy, defined as the energy difference between the saddle point and initial state.

The stable lattice sites (interstitial and substitutional types) can be mapped using DFT calculations. This technique allows to investigate the stabilities of point defect, such as interstitial and substitutional atom, not only from a classical point of view, but also considering the electronic structures of the species considered. This can lead to unexpected results, as reported by Pasianot *et al* [29].

The saddle point energy necessary to calculate the migration energy was investigated using the nudged elastic band (NEB) method [32]. This method allows to determine the minimum energy path (MEP) starting from an initial and final state. The transition path is initially guessed by a set of images of the system connected by an imaginary spring. The images are then relaxed perpendicular to the path and kept equidistant. The effective frequency ν^* was approximated using Vineyard equation [33],

$$\nu^* = \frac{\prod_{i=1}^{3N} \nu_i}{\prod_{j=1}^{3N-1} \nu'_j}. \quad (4)$$

The $3N$ normal vibrational frequencies at saddle point, ν_i , and $3N-1$ ones at initial state, ν'_j , can be estimated using DFT phonon calculations.

The KMC method was used to study stochastic phenomena knowing the processes involved. It contains a list of stochastic events that can occur in a given system. At each timestep, a transformation is simulated by randomly choosing one of the events based on their frequency of occurrence. Time is incremented based on a function of the cumulative frequency of all possible events. The final diffusion behaviour depends on the list of possible events. Therefore, KMC is the perfect instrument to test the validity of a theory. Four different KMC simulations were developed to test the different mechanisms involved in fast-diffusers migration in α -Ti. The KMC simulations were informed with the transition frequencies obtained by DFT calculations and the calculated diffusivities were compared with experimental data available in the literature [5, 4, 6].

3.1. Interstitial diffusion

In case of the interstitial diffusion, the solute occupies and moves through interstitial sites. Conventionally, there are eight symmetrical positions in which an extra atom can rest in hcp structure: octahedral, tetrahedral, crowdion, split dumbbell along c axis, basal octahedral, hexahedral, basal crowdion and split dumbbell within the basal plane. The geometry and symmetry of these sites can be found in [34]. The interstitial formation energy, E_i , describes the tendency of a solute to sit at interstitial or substitutional sites. E_i is the energy difference of a system where the solute is at the interstitial site under investigation ($E\{M_N + I_1\}$), and a system where the solute

occupies a substitutional site ($E\{M_{N-1} + S_1\}$),

$$E_i = E\{M_N + I_1\} - E\{M_{N-1} + S_1\} - \frac{1}{N}E\{M_N\}; \quad (5)$$

where N is the total number of solvent atoms, and M , I and S identify the solvent, interstitial solute and substitutional solute, respectively. The last term is added to balance the energies of the two systems which contain different number of atoms. Negative values of E_i indicate that solute tends to sit at the interstitial site and vice-versa.

The interstitial migration in dilute systems can be considered random and only the interstitial solute jump frequencies are required for the KMC simulations. For each element, the transition network was mapped and reported in Section 4. The interstitial diffusivity values were obtained after 500 simulations of 10^9 solute transitions each.

3.2. Substitutional diffusion

The substitutional diffusion mechanism is governed by vacancy jumps towards the nearest neighbours. For the KMC simulation, we considered three cases. The first case is that the vacancy and solute are far away and they do not interact, and only the vacancy-solvent exchanges are possible. The second case is that solute and vacancy are first nearest neighbours and they can exchange position. The transition frequencies of solvent-vacancy swaps are also different from the first case since they depend on the solvent position with respect to the solute-vacancy pair. The last case is that solute and vacancy are not first nearest neighbours, but some of the solvent-vacancy jumps can lead to the formation of solute-vacancy pair and lead to the first case.

In the first case, the vacancy is surrounded by six nearest solvent atoms in the basal plane, and three atoms in the above basal plane and three atoms in the below basal plane. The vacancy can exchange position with one of the six solvent in the basal plane (w_{\parallel}^v), or one of the six atoms in the adjacent basal planes (w_{\perp}^v) (see Figure 2-a).

In the second case, two types of substitutional solute-vacancy pair can be formed, the in-plane pair where the pair lays on the same basal plane (\parallel), and out-of-plane pair where vacancy and solute are in adjacent basal planes (\perp), see Figure 2-b and Figure 2-c. The binding energies of substitutional solute-vacancy pairs (ΔE_b^s) are defined as the energy difference between a system with solute-vacancy pair and a system where solute and vacancy are at infinite distance,

$$\Delta E_b^s = E\{M_{N-2} + S_1\} - E\{M_{N-1} + S_1\} - E\{M_{N-1}\} + E\{M_N\}. \quad (6)$$

where $E\{M_{N-2} + S_1\}$ is the energy of a crystal with a substitutional solute-vacancy pair, and the other terms were previously described. Based on this definition, the positive values of ΔE_b^s indicate a repulsive force between the vacancy and the solute. On the contrary, ΔE_b^s is negative when the solute prefers to sit next to a vacancy. Since it has been reported that fast-diffusers can accommodate at off-lattice sites in open metals [29], the substitutional configurations were studied comparing the fully relaxed energies of a supercell with the solute replacing a solvent atom at lattice site, and supercell with vacancy at the first-nearest neighbour lattice site to the interstitial solute. It is expected that this last configuration relaxes to the substitutional configuration, however Pasianot and co-workers have found that Fe tends to sit in off-set position in Zr [29]. Similar calculations were performed in this work,

and when needed, the energies of off-set positions were used in equation 6 to calculate the binding energy. The 8-frequency model was adopted to describe the solute transistons [35]. The transition frequencies are illustrated in Figure 2-b for in-plane pair, and in Figure 2-c for out-of-plane pair. In the case of in-plane pair, the possible transitions are one solute-vacancy exchange (w_{\parallel}), two pair-rotation vacancy-solvent swaps in the adjacent basal plane (w_a) and two pair-rotation vacancy-solvent swaps within the basal plane (w_b), and seven dissociative vacancy-solvent swaps (w_c). Similarly, in the case of out-of-plane pair, the possible events are one solute-vacancy exchange (w_{\perp}), two pair-rotation vacancy-solvent swaps in the adjacent basal plane (w'_a) and two pair-rotation vacancy-solvent swaps within the basal plane (w'_b), and seven dissociative vacancy-solvent swaps (w'_c).

To conclude in the last case, the host-vacancy swaps leading to the formation of vacancy-solute pair are approximated by w_d if an in-plane vacancy-solute pair is formed and w'_d if an out-of-plane vacancy-solute pair is formed as illustrated in Figure 2-e and Figure 2-d, respectively. For the other cases, where the solute-vacancy is not formed as result of solvent-vacancy swap, the jumps are approximated with w_{\parallel}^v and w_{\perp}^v .

Compared to interstitial diffusion, the walk of substitutional atom is not random, and the diffusion needs to be simulated in a rigid lattice, repeated infinite times along the three directions. Since the vacancy concentration in this small box is much higher than real value, the diffusion coefficients (D_s) need to be scaled using the equilibrium vacancy concentration, C_{eq} ,

$$D_s = D_{scaled} = \frac{D_{not-scaled}}{C_{scaled}}. \quad (7)$$

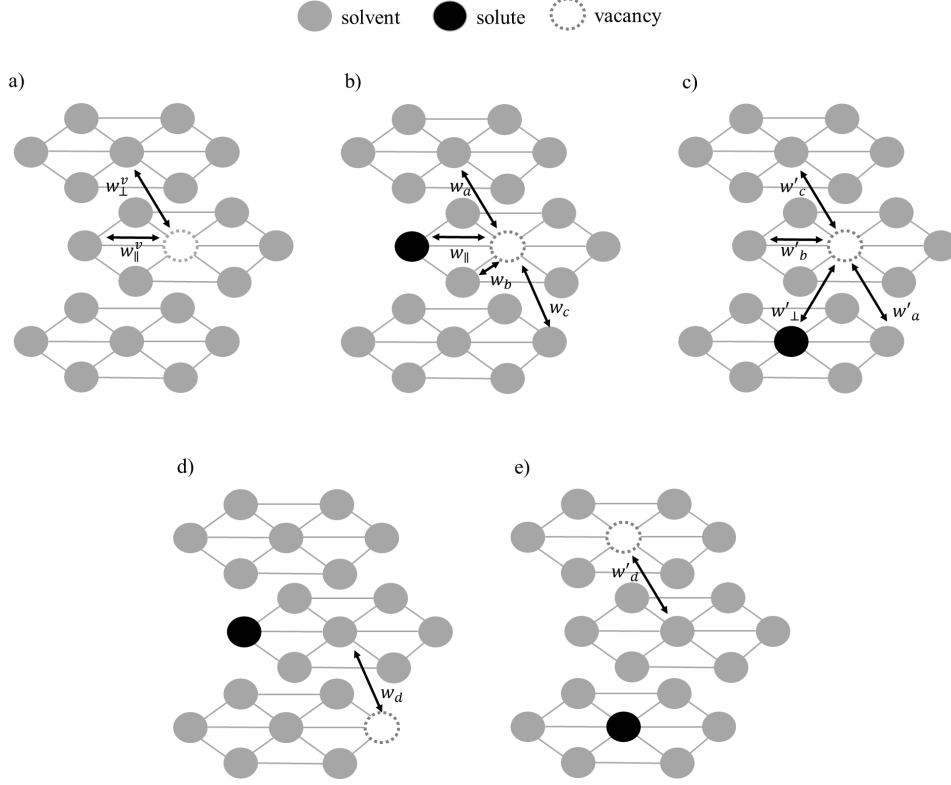


Figure 2: Schematic representation of transition frequencies involved in substitutional solute diffusion: a) solvent-vacancy transitions when vacancy and solute are not interacting, b) solvent- and solute-vacancy transitions in presence of in-plane vacancy-solute pair, c) solvent- and solute-vacancy transitions in presence of out-of-plane vacancy-solute pair, e) solvent-vacancy swap leading to in-plane solute-vacancy pair, and d) solvent-vacancy swap leading to in-out-of solute-vacancy pair.

$$C_{scaled} = \frac{N_v}{N_s} \frac{1}{C_{eq}}, \quad (8)$$

where N_v and N_s are respectively the number of vacancies and lattice sites in the simulation box, and C_{eq} is the vacancy concentration depending on

the vacancy formation, E_v , [36]

$$C_{eq} = \exp\left(-\frac{E_v}{k_b T}\right) \left[1 + z C_x \exp\left(-\frac{\Delta E_b^s}{k_b T}\right)\right], \quad (9)$$

where z is the number of nearest neighbour and C_x is the atomic fraction of solute atoms. The diffusivities were obtained after 100 KMC simulations of 10^6 solute transitions each. The solvent diffusion coefficients were also evaluated tracking the host migrations.

3.3. Combination-dissociation process

The combination-dissociation process was tested modifying the KMC code simulating the interstitial mechanism including the dissociation and combination events. Since this work focuses on evaluation of the impact of this process on the migration, the vacancy hops were omitted and the walk was considered random. This is not far from reality since the diffusion barriers of vacancy-mediated migration are higher than interstitial migration energies. After a dissociation event, the solute atom is still close to the vacancy, enhancing the probability to move back to the lattice site. This was taken into account multiplying the transition frequency of the combination by the probability (P) of interstitial-vacancy pair,

$$P = \exp\left(-\frac{(E_v + \Delta E_b^i)}{k_b T}\right). \quad (10)$$

ΔE_b^i is the binding energy of interstitial solute-vacancy pair, and it is calculated as,

$$\Delta E_b^i = E\{M_{N-1} + I_1\} - E\{M_N + I_1\} - E\{M_{N-1}\} + E\{M_N\} \quad (11)$$

where $E\{M_{N-1} + I_1\}$ is the energy of a system with interstitial solute-vacancy pair and $E\{M_{N-1}\}$ is the energy of system with one vacancy, and the other

terms were already described. Negative values of ΔE_b^i indicate attraction between these two defects, and vice-versa. In this case, 500 simulations of 10^9 solute transitions were performed.

3.4. Frank-Turnbull theory

The Frank-Turnbull theory [12] was verified using the equation 2 to evaluate the effective diffusion of Fe, Co and Ni in α -Ti. This equation was used in conjunction with results of KMC simulations of the interstitial mechanism, while the interstitial-substitutional concentration ratio was approximated using,

$$\frac{C_i^{eq}}{C_s^{eq}} = \exp \left(-\frac{E_i}{k_b T} \right), \quad (12)$$

where E_i is the highest values of interstitial formation energy calculated for each solute. This means that C_i^{eq}/C_s^{eq} ratio is approximated with the highest probability to find the solute at substitutional site rather than interstitial site at 0 K.

3.5. Solute-host swap

The KMC simulation of the vacancy-mediated mechanism was modified to include the transition frequencies of solute-host exchanges schematically displayed in Figure 3, in order to estimate the effect of solute-host swap on self-diffusion. Similar to the simple vacancy-mediated mechanism, 100 simulations of 10^6 solute transitions each were performed.

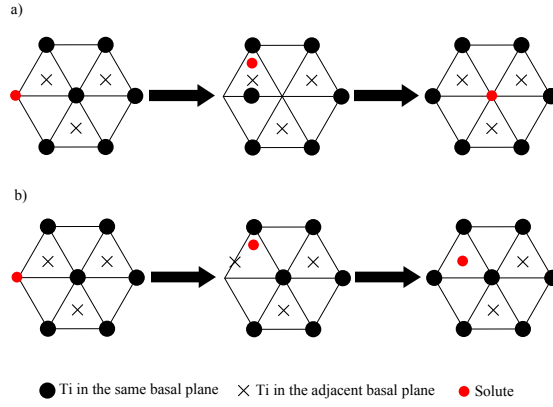


Figure 3: Scheme of solute-host swap a) in-plane and b) out-of-plane transitions without the presence of vacancy.

4. Results

4.1. Interstitial behaviour

The stability of Fe, Co and Ni at conventional interstitial sites of hcp-Ti were investigated with *ab initio* calculations as described in Section 3.1. Fe and Ni are stable at octahedral, crowdion, basal octahedral, split and basal split sites, while basal octahedral, basal split, crowdion and octahedral sites are the stable sites for Co. A comparison of the interstitial energy of these sites with the previous works of Pasianot and Pérez [26], and Zhang *et al* [25] is presented in Table 1. Our results are very similar to the ones obtained by Zhang *et al*, and small differences may be due to the higher-size supercell (96 atoms) and higher energy cut-off (400 eV) used by Zhang. The higher mismatch with Pasianot and Pérez can be attributed to the the fact that they have used the norm-conserving TM-type of potentials that are considered less accurate than PAW potential as underlined by Zhang and coauthors [25].

However, the calculated minimum energy paths show that these interstitial sites are not always the minima, but distorted configurations are more stable (see for example Figure 4). This behaviour has also been observed by Zhang and colleagues [25]. Three non-classical interstitial sites were found to be stable for Co and Fe (here identified by S1, S2, S3), and two non-classical interstitial sites for Ni (called in this work S1, S2) (see Figure 5). The reduced coordinates (RC) with respect to lattice sites (0,0,0) and (1/3,1/3,1/2) within the primitive lattice [$a_1 = (a; 0; 0)$; $a_2 = (a/2; \sqrt{3}a/2; 0)$; $a_3 = (0; 0; c)$] and interstitial energies of these sites are reported in Table 2. Similar interstitial sites have been reported by Zhang *et al* [25]. Bernstein *et al* [9] have also reported the presence of more stable no-symmetrical interstitial sites. The interstitial sites, they founded are similar to the S2 sites in case the of Fe and Co and to S1 for Ni. In Table 3, the formation interstitial energies are re-calculated using the definition in [9, 25], and compared with the values reported in Bernstein [9] and Zhang [25] papers. The energies are similar and the difference can be attributed to the different calculation settings used. Bernstein and his colleagues have performed the DFT calculations using a 10-valence-electrons potential, higher energy cut-off (400 eV) and larger cell size (190-atom cell) compared to the calculations presented in this work. Zhang and co-authors have used an energy cut-off of 450 eV with a supercell of 96 atoms.

All possible interstitial transitions were then mapped from the stable interstitial sites. Fe can perform two S1→S3 transitions within the basal plane, six S1→S2 transitions along *c*-axis and two S1→S1 transitions within the basal plane from S1 site. From S2 site, there are six possible S2→S1

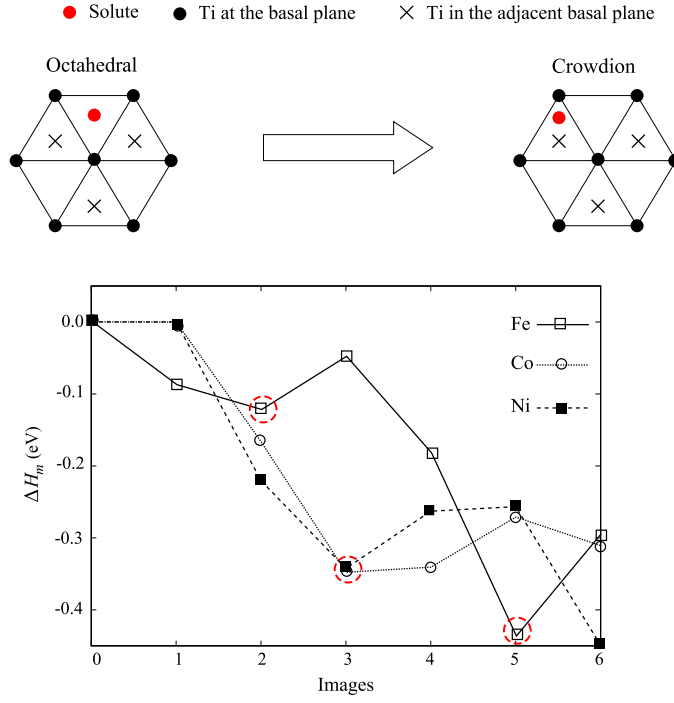


Figure 4: Minimum energy path of Fe (open squares), Co (open circles) and Ni (filled squares) transitions between octahedral and crowdion sites. The migration energy is calculated with respect to the octahedral sites. The minima are indicated by dashed red circle line.

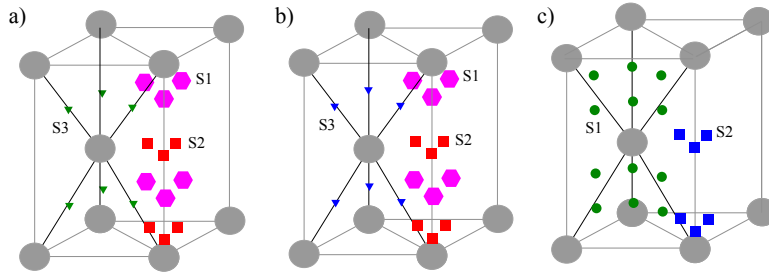


Figure 5: Schematic representation of fast-diffusers stable interstitial sites in hcp unit cell: a) Fe has six S1, six S2 and six S3 equivalent sites; b) Co has six S1, six S2 and six S3 equivalent sites; c) Ni has twelve S1 and six S2 equivalent sites.

	E_i^O (eV)	E_i^{BO} (eV)	E_i^C (eV)	E_i^{BC} (eV)	
Fe	0.714	0.926	0.419	0.629	This work
	0.76	0.97	0.6	0.75	[25]
	0.85	0.97	0.71	0.80	[26]
Co	1.045	1.127	0.597	0.860	This work
	0.91	0.96	0.78	0.77	[25]
	1.13	1.28	1.14	1.15	[26]
Ni	1.497	1.528	1.187	1.410	This work
	1.58	1.57	1.57	1.46	[25]
	2.19	1.92	2.05	1.94	[26]

Table 1: Comparison of formation energies of Fe, Co and Ni octahedral (E_i^O), basal octahedral (E_i^{BO}), crowdion (E_i^C) and basal crowdion (E_i^{BC}) with previous work [25, 26].

	RC^{Fe}	E_i^{Fe} (eV)	RC^{Co}	E_i^{Co} (eV)	RC^{Ni}	E_i^{Ni} (eV)
S1	Fe	(0.51,0.75,0.22)	Co	(1/6,1/6,1/4)	Ni	(0.22, 0.20, 0.16)
	Ti	(-0.17,1.08,-0.11)			Ti	(-0.13, -0.15, -0.12)
	Ti	(0.36,1.36,0.55)			Ti	(0.39, 0.40, 0.60)
S2	Fe	(0.5,0.78,0.04)	Co	(0.49,0.79,0.05)	Ni	(0.44, 0.83, 0.13)
	Ti	(-0.26,1.03,-0.10)			Ti	(-0.27, 1.01, -0.13)
	Ti	(0.33,1.35,0.51)			Ti	(0.37, 1.37, 0.54)
S3	Fe	(0.17,0.17,0.25)	Co	(0.47,0.78,0.21)		
	Ti	(-0.10,-0.10,-0.10)				
	Ti	(0.44,0.44,0.59)				

Table 2: The reduced coordinates (RC) respect to lattice sites (0,0,0) and (1/3,1/3,1/2) with primitive lattice [$a_1 = (a; 0; 0)$; $a_2 = (a/2; \sqrt{3}a/2; 0)$; $a_3 = (0; 0; c)$] and interstitial energies (E_i) of Fe, Co and Ni interstitial sites in α -Ti. The position of the nearest Ti atoms are also reported.

transitions along c -axis and two S2→S2 transitions within the basal plane. From S3 site, there are two S3→S2 transitions within the basal plane. These

	E_i^{S1} (eV)	E_i^{S2} (eV)	E_i^{S3} (eV)	
Fe	0.870	0.799	0.548	this work
		0.95		[9]
	~ 0.62	~ 0.735	~ 0.735	[25]
Co	0.703	0.579	0.565	this work
		0.89		[9]
	~ 0.75	~ 0.71	~ 0.75	[25]
Ni	1.043	0.993		this work
		1.04		[9]
	~ 1.56	~ 1.33	~ 1.28	[25]

Table 3: Comparison of formation interstitial energies calculated in this work and ones obtained by Bernstein *et al* [9] and Zhang *et al* [25]. The calculations were performed using the equation reported in [9, 25].

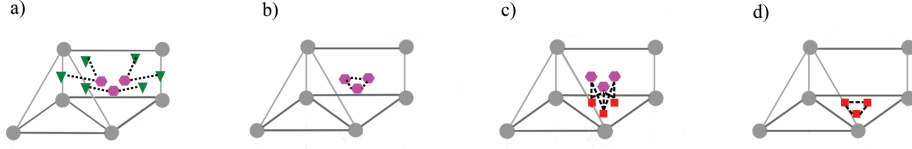


Figure 6: Schematic representation of transition pathways between the stable Fe interstitial sites in α -Ti: a) $S3 \leftrightarrow S1$, b) $S1 \leftrightarrow S1$, c) $S2 \leftrightarrow S1$ and d) $S2 \leftrightarrow S2$ transitions.

transitions are schematically displayed in Figure 6, and the migration energies and effective frequencies are reported in the supplementary materials.

Cobalt has two $S1 \rightarrow S1$ transitions within the basal plane, four $S1 \rightarrow S2$ transitions and two $S3 \rightarrow S1$ transitions within the basal plane from S1 sites, six $S3 \rightarrow S2$ transitions along c -axis and two $S3 \rightarrow S3$ transitions within the basal plane from S3 site. Two transition from S2 to nearest S2 are also

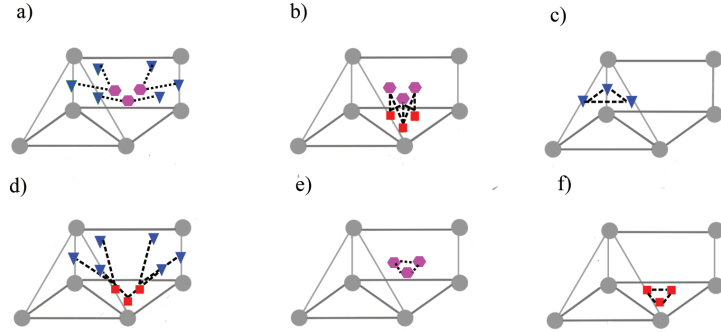


Figure 7: Schematic representation of transition pathways between the stable Co interstitial sites in α -Ti: a) $S1 \leftrightarrow S3$, b) $S2 \leftrightarrow S3$, c) $S1 \leftrightarrow S1$, d) $S2 \leftrightarrow S1$, e) $S3 \leftrightarrow S3$ and f) $S2 \leftrightarrow S2$ transitions.

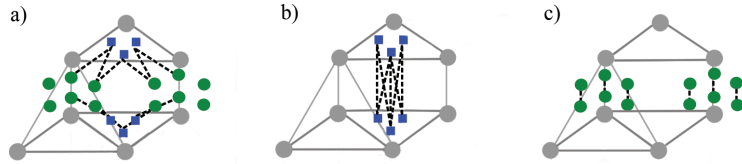


Figure 8: Schematic representation of transition pathways between the stable Ni interstitial sites in α -Ti: a) $S2 \leftrightarrow S1$, b) $S2 \leftrightarrow S2$ and c) $S1 \leftrightarrow S1$ transitions.

possible. All the transitions are schematically shown in Figure 7 and their migration energies and effective frequencies are presented in the supplementary materials.

Nickel only has two stable interstitial sites, S1 and S2 (see Figure 5). From S1, Ni can move to the nearest S1 site along the c -axis ($S1 \rightarrow S1$) or to one of the two S2 sites ($S1 \rightarrow S2$). From S2, there are four $S2 \rightarrow S1$ and six $S2 \rightarrow S2$ possible transitions. The migration energies and effective frequencies are reported in the supplementary materials, while the transitions are schematically shown in Figure 8.

4.2. Substitutional behaviour

The study of substitutional behaviour of fast-diffusers was conducted looking at possible off-lattice configurations following the procedure presented in Section 3.2. Fe and Co have off-lattice configurations that are more stable than simple substitutional sites, while Ni sits at lattice sites. Referring to the site (0,0,0) and the primitive lattice defined as $[a_1 = (a; 0; 0); a_2 = (a/2; \sqrt{3}a/2; 0); a_3 = (0; 0; c)]$, the off-site position of Fe is (0.28, -0.14, 0) and it is (0.26, -0.13, 0) for Co. The binding energies of substitutional solute-vacancy pair were evaluated by equation 6 and they are reported in Figure 9. The data shows attraction between the vacancy and solute for both in-plane and out-of-plane configurations for all elements. The substitutional formation energies obtained using the formulation in [9, 25] are compared with previous work of Bernstein *et al* [9], Zhang *et al* [25] in Table 4. Although, they do not report the off-lattice positions, the energies formation for in-lattice position are similar to one calculated in this work. Similar to the interstitial case, the difference may be due to the calculations set-up: different electronic potential, higher energy cut-off and larger supercell.

For each element, the migration energies and the effective frequencies of the transitions required to describe the substitutional vacancy-mediated diffusion (see Section 3.2) are reported and compared with previous work [25] in Table 5. Zhang and co-authors consider two distinct paths for the pair-rotation vacancy-solvent swap (named in this work w_b), taking into account the fact that along one of these paths there are a solvent atoms in the adjacent basal planes ([25] refer to this as path 3), while this is not the case for the other pair-rotation vacancy-solvent swap (path 4 in [25]). We calculated very

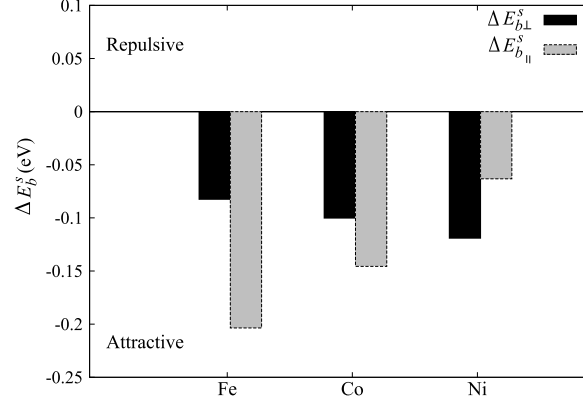


Figure 9: Binding energy of out-of-plane (black bar) and in-plane (grey bar) substitutional solute-vacancy pairs (ΔE_b^s) for Fe, Co and Ni in α -Ti, calculated with 54-atom supercells. Positive values of ΔE_b^s indicate that the solute atom is repulsed by the vacancy, while negative values indicate attraction between vacancy and solute.

	$E_{f,s}$ (eV)	$E_{f,s}^{\text{off}}$ (eV)	
Fe	0.607	0.293	this work
	0.37		[9]
	0.41		[25]
Co	0.187	0.005	this work
	0.10		[9]
	0.26		[25]
Ni	-0.091		this work
	-0.21		[9]
	-0.16		[25]

Table 4: Comparison of substitutional formation energies on ($E_{f,s}$) and off ($E_{f,s}^{\text{off}}$) lattice site calculated in this work with the result of Bernstein *et al* [9] and Zhang *et al* [25]. The calculations were performed using the equation reported in [9, 25].

similar values of migration energies in the case of Fe-vacancy pair rotation along these two paths, respectively 0.168 for the path 3 and 0.145 eV for path 4. Therefore, it was chosen to consider the transition along path 4 equal to the one along path 3. This was also done to use the same transitions considered by the 8-frequency model. On the other hand, the solute-vacancy dissociative and pair-formation transitions were considered in our work, while they are neglected in Zhang paper [25]. The migration energies are very similar with the values reported by Zhang *et al* [25], especially in the case of solute transitions. Despite using a different set of transitions, the activation energies for vacancy-mediated diffusion calculated in this work are very similar to the one obtained by Zhang *et al* [25] as shown in Table 6. The values of vacancy formation energy, migration energies and the effective frequencies of w_{\parallel}^v and w_{\perp}^v in pure Ti were evaluated in a previous work as $E_v = 1.976$ eV, $\Delta H_m^{\parallel} = 0.423$ eV, $\nu_{\parallel}^* = 7.456$ THz, $\Delta H_m^{\perp} = 0.413$ eV and $\nu_{\perp}^* = 7.233$ THz [24].

4.3. Combination-dissociation process

In order to investigate the combination-dissociation process, the binding energies of interstitial-vacancy pair were studied. The first-nearest-neighbour interstitial site to the vacancy is unstable and the solute moves to the off-lattice position in the case of Fe and Co, and to the lattice site in the case of Ni as shown in Section 4.2. On the other hand, the vacancy can form a stable pair with the second-nearest S2 site for all three solutes (see Figure 10). The relative ΔE_b^i values of Fe, Co and Ni are reported in Figure 11. Interstitial Fe and Ni are shown to be attracted by the vacancy, while Co prefers not to sit next to the vacancy. The migration energies and effective frequencies of combination ($S2 \rightarrow L$) and dissociation ($L \rightarrow S2$) events from the second-

	ΔH_m (eV)	ν^* (THz)	ΔH_m (eV)	ν^* (THz)	ΔH_m (eV)	ν^* (THz)	
	Fe		Co		Ni		
w_{\perp}	0.575	2.349	0.702	6.307	0.767	1.557	this work
w_{\perp}	0.71	-	0.78	-	0.83	-	[25]
w_{\parallel}	0.824	14.378	0.741	10.706	0.674	2.994	this work
w_{\parallel}	0.68	-	0.75	-	0.69	-	[25]
w'_a	0.081	5.031	0.004	3.433	0.133	4.313	this work
w_a	0.202	4.809	0.058	3.252	0.077	3.906	this work
$w_a-w'_a$	0.09	-	0.13	-	0.03	-	[25]
w'_b	0.389	6.409	0.018	3.221	0.164	4.388	this work
w'_b	0.13	-	0.23	-	0.009	-	[25]
w_b	0.168	5.351	0.377	6.063	0.259	6.447	this work
w_b	0.56	-	0.38	-	0.23	-	[25]
w'_c	0.519	4.898	0.533	6.649	0.591	11.379	this work
w_c	0.468	6.037	0.527	4.671	0.484	5.340	this work
w'_d	0.254	5.745	0.172	5.705	0.390	8.295	this work
w_d	0.179	7.455	0.290	6.114	0.390	5.241	this work

Table 5: Migration energy (ΔH_m) and effective frequency (ν^*) of fast-diffusers transitions involved in the substitutional vacancy-mediated mechanism compared with previous work [25].

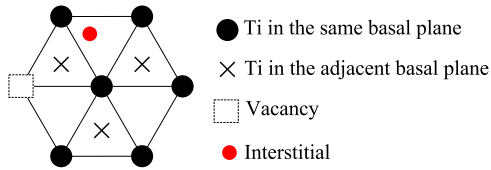


Figure 10: Projection on the basal plane of interstitial-vacancy pairs when the interstitial is at the next-nearest neighbour site.

nearest neighbour were studied and reported in the supplementary materials.

Solute	Q_{\perp}^s (eV)	Q_{\parallel}^s (eV)	Q^s (eV)	
Fe	2.678	2.664		this work
Fe			2.57	[25]
Co	2.731	2.729		this work
Co			2.54	[25]
Ni	2.876	2.855		this work
Ni			2.73	[25]

Table 6: Values of Fe, Co and Ni activation energy of vacancy-mediated compared with previous work [25].

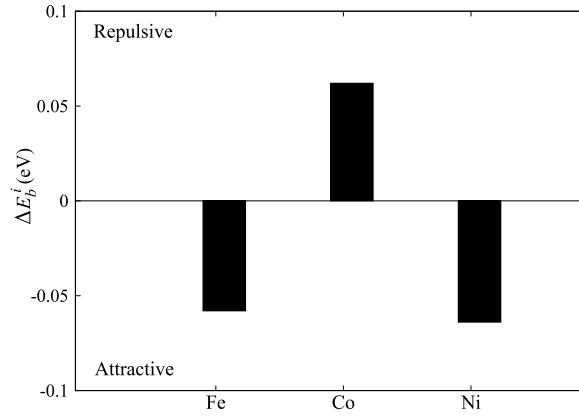


Figure 11: Binding energy of interstitial-vacancy pair (ΔE_b^i) of Fe, Ni and Co at the next-nearest neighbour S2 site. Negative sign indicates attraction between interstitial solute and vacancy and vice-versa.

4.4. Solute-host swap

The migration energies and effective frequencies of the two solute-host swaps (see Figure 3) were also evaluated and they are reported in the supplementary materials. In total there are twelve solute-host transitions, six in the adjacent basal plane and six in the same basal plane.

4.5. Kinetic Monte Carlo results

The KMC method was used to verify that simple interstitial and vacancy-mediated mechanisms cannot explain the anomalous diffusion of fast-diffusers in Ti. The KMC results are displayed in Figure 12 and compared with experimental data (D^{Exp}) [6, 4, 5], while the diffusion parameters are summarised in the supplementary materials. As expected, the substitutional diffusion is too slow with respect to experimental data, and the diffusion barriers in this case are too high as a result of the vacancy formation energy. On the other hand, the interstitial transitions are too fast compared to the experimental diffusion data, suggesting that there is a second process involved, which decreases these diffusivity values.

The combination and dissociation events were added in the KMC model simulating the interstitial migration in order to evaluate the impact of combination-dissociation process on the diffusivities. The KMC results labeled D_{cd} are compared to the simple interstitial diffusivities and experimental data [4, 5, 6] in Figure 13. The D_{cd} values are very similar to D_i , indicating that this mechanism has no influence on the migration of Fe, Co and Ni in α -Ti, and therefore it cannot explain the anomalous behaviour of these solutes.

Finally, the effective diffusivities of fast-diffusers were calculated using the formula by Frank and Turnbull [12] (see equation 2) informed with D_i data. The interstitial-substitutional concentrations ratio were approximated by equation 12 with E_i of S1 for each solute (see Table 2). The effective diffusion coefficients are consistent with the experimental data as shown in Figure 14. In the case of Co, the D^{Eff} data matches the experimental values very well [4]. On the other hand, the computational data overestimates the

experimental values in the case of Fe [5], and underestimate the Ni experimental values [6]. This may be due to the choice of using E_i . In fact, Fe has smaller E_i values with respect to Ni. Therefore, in the case of Fe the correction introduced by the C_i^{eq}/C_s^{eq} factor is overestimating the experimental data. Vice-versa, the E_i^{Ni} values are larger leading to a smaller value of C_i^{eq}/C_s^{eq} . It is also important to notice that these energies are calculated at 0 K, and in this work we omitted the effect of temperature on defect formation energies. Nevertheless, these results confirm the idea of Frank and Turnbull that the majority of atoms are stationary at substitutional lattice sites, and the anomalous behaviour of fast-diffusers in Ti is due to the few atoms moving interstitially. The diffusion parameters calculated are reported in the supplementary materials. The activation energies are around 1 eV, similar to the experimental data [5, 6, 4]. In addition, the D^{Eff} values show the same anisotropic behaviour (see Figure 15) reported by Nakajima and co-workers [6, 4, 5]. In their work, Nakajima *et al* have found that fast-diffusers have D_{\perp}/D_{\parallel} ratio greater than one, opposite to what normally observed in the case of self-diffusion, substitutional solute diffusion [8] or interstitial solute diffusion in α -Ti, such as C [37] and O [38]. In addition, the effective diffusivities calculated with the KMC method are more consistent with the experimental data compared to the values obtained by Zhang *et al* [25], as shown in Fig. 16.

Although the theory of Frank and Turnbull describes the migration of fast-diffusers in α -Ti well, it cannot explain the enhancement of self-diffusion in presence of these elements. This phenomenon is a result of another process: the solute-host swap [29, 30]. As described in Section 3, the solvent diffusion

coefficients were calculated with (D_{sh}) and without (D_{vm}) the solute-host swaps as shown in Figure 17, with a concentration of solute atoms of 1.9%. Enhancement is obvious in the case of Ni and Fe, while it is limited in the case of Co. The activation energies of solute-host swap in case of Fe and Ni are close to energy required for the Ti to move in a vacancy site. The ΔH_m of Fe-Ti swap within the basal plane and Ni-Ti swap in the adjacent plane are respectively 2.563 eV and 2.513 eV (see supplementary materials), while the energies for vacancy-solvent transitions are circa 2.4 eV as reported in [24]. Therefore, these transitions compete with the vacancy-host exchanges speeding up the self-diffusion. In the case of Ni, the enhancement affects the diffusion in both directions because the jump in the adjacent basal plane determines a displacement along both directions. In the case of Fe, only parallel self-diffusion is affected because the Fe-Ti swap within the basal plane has no component along the c -axis. On the other hand, Co-Ti swaps have significantly higher activation energy, above 2.6 eV (see supplementary materials), than vacancy-host exchange, leading to minimum enhancement of self-diffusion.

5. Discussion

5.1. Interstitial and substitutional behaviour

The dissociative solubility of Fe, Co and Ni in both interstitial and substitutional sites of α -Ti is confirmed by the *ab initio* calculations. These results reflect the experimental works of Yoshida and co-workers [11, 10], who have found interstitial and substitutional Fe atoms in α -Zr and α -Ti. The energies of symmetric interstitial sites calculated in this work are consistent with

previous works of Zhang *et al* [25], and Pasianot and Pérez [26]. However, the fast-diffusers seem to prefer distorted interstitial sites instead of the eight traditional classical sites. This behaviour has been already noticed for Fe, Cr, Be, Ni in Zr [39, 40], and Fe, Ni and Co in Ti [9, 25]. The interstitial formation energies reported here are in good agreement with these previous *ab initio* studies [9, 25], indicating that Fe, Co and Ni prefer to sit substitutionally within the α -Ti lattice, but a significant fraction of these solute atoms may occupy this low-energy non-classical interstitial sites. Our findings also indicate that Ni has no off-lattice configuration and it sits at the lattice sites. On the other hand, off-lattice sites are more stable in the case of Co and Fe. Different studies show that Fe have similar behaviours in Zr and Ti, as it prefers off-lattice positions [29, 39, 26]. This may be due to volumetric factors and electronic structure considerations. Because of their small atomic size relative to Ti, these three solutes cause a contraction of the crystal lattice similar to the one caused by the introduction of a vacancy. In the case of Ni, the relative volume difference between a supercell with one vacancy and a supercell with the substitutional atom is |0.05|%. This difference is higher in the case of Fe and Co, |0.12|% and |0.14|% respectively. On the other hand, the off-lattice configurations of Fe and Co introduce distortions similar to the vacancy, and the relative volume differences of Fe and Co are respectively |0.06|% and |0.03|%. The dissociative solubility in interstitial and substitutional sites plays a key role in the anomalous fast diffusion behaviour and the self-diffusion enhancement.

5.2. Diffusion mechanism

The KMC results confirm the fact that the fast diffusion of Fe, Co and Ni in α -Ti cannot be a result of simple interstitial or substitutional vacancy-mediated mechanisms [12]. In the first case, the diffusion is too fast and overestimates the experimental data. On the other hand, the substitutional diffusion is very slow and can be neglected, because it requires the presence of a vacancy which is a rare event. The combination-dissociation process [13] was also shown to have a very small impact on the migration of fast-diffusers. Similar to the vacancy-mediated mechanism, it requires that the interstitial encounters a vacancy, or it requires the formation of the vacancy after a dissociation reaction, which are both rare events. These facts corroborate the idea of Frank and Turnbull [12] that the anomalous diffusion of these solutes in α -Ti is a result of few atoms moving through interstitial sites, while the majority of them sits at lattice sites without contributing to the overall solute migration. Compared to previous studies [25], the KMC results of diffusivity values are more consistent with the experimental data as shown in Fig. 16. Other researchers have highlighted the importance of the Frank and Turnbull mechanism in other systems such as Fe, Cr, Be, Ni, Hf, Sn and self-diffusion in Zr at high temperature [40, 27]. Such behaviour is experimentally confirmed by the work of Behar and co-workers [41] on the Pd diffusion in Ti. Pd has similar solubility value to Au in α -Ti [41, 42], however it diffuses two orders of magnitude faster than Ti [41], while Au has similar diffusion behaviour to the solvent [42]. The anomalous diffusion of Pd can be explained by the fact that 30% of Pd atoms sit at interstitial sites as shown by their channelling experiments [41], while only substitutional solutes have been found in the

case of Au [42].

The anomalous anisotropy behaviour of Fe, Co and Ni is also a result of the interstitial migration. In fact, the number of interstitial transitions along c -axis are higher than within the basal plane. For example, Fe can perform six transitions along c -axis and only two transitions within the basal from S2 sites. Co shows a similar behaviour with the addition of four other transitions in the adjacent basal plane. Ni only has six transitions contributing to the parallel diffusion, while all the other transitions occur along the c -axis.

However, the fast migration of few atoms through interstitial sites cannot explain the self-diffusion enhancement due to the fast-diffusers. Our results indicate that this acceleration can be attributed to the solute-host swap mechanism [29, 30]. In the case of Ni and Fe, the self-diffusion enhancement due to this mechanism is evident. The migration energies of Ni and Fe solute-host swaps are similar to the sum of the migration energy of the vacancy-solvent exchange and the vacancy formation energy. On the other hand, the Co-Ti swaps considered in this work have higher migration energy, and therefore the solvent diffusion is less affected. It is important to bear in mind, that the data reported in this work can only be considered qualitative in nature. The magnitude of the effect of Ni and Fe additions on the self-diffusivity of Ti is smaller than expected. Mishin and Herzig [43] suggest that additions of these elements should significantly accelerate self-diffusivity in Ti. Quantitative information can only be obtained after an accurate investigation of all the possible solute-host transitions. This is beyond the scope of this current study, and it will hopefully be the subject of further work. It is also important to notice that a real comparison with experimental data can-

not be conducted since systematic studies on the influence of fast-diffusers on the solvent diffusion are not present in the literature. Nevertheless, these results support the idea that fast-diffusers impact solvent diffusion by allowing host atoms to swap with solute atoms without the presence of vacancy.

6. Conclusions

In this study, the anomalous diffusion of Fe, Co and Ni in α -Ti was investigated using KMC and first principles calculations. Our results support the idea proposed by Frank and Turnbull. The diffusion coefficients calculated for simple interstitial migration overestimate the experimental data, while the simulation of substitutional diffusion underestimate them. The simulations reported in this work also show that the combination-dissociation process has a small impact on the overall diffusion, and it can be neglected. Only the interstitial migration of a few atoms contributes to the diffusion, while the majority of atoms sit substitutionally within the lattice without contributing to diffusion. This effect is captured by Frank and Turnbull theory, introducing an interstitial-substitutional concentration ratio in order to correct the interstitial diffusivity values. The corrected diffusivities are in good agreement with the experimental values. The anomalous diffusion behaviour of the fast diffusers can also be attributed to the non-classical interstitial sites that these solute atoms may occupy. Finally, we find that host atoms may be able to swap with solute atoms without the need of vacancies, thank to their ability to dissolve both at non-classical interstitial and substitutional sites in α -Ti. The KMC simulations show that this mechanism can explain the enhancement of solvent diffusion.

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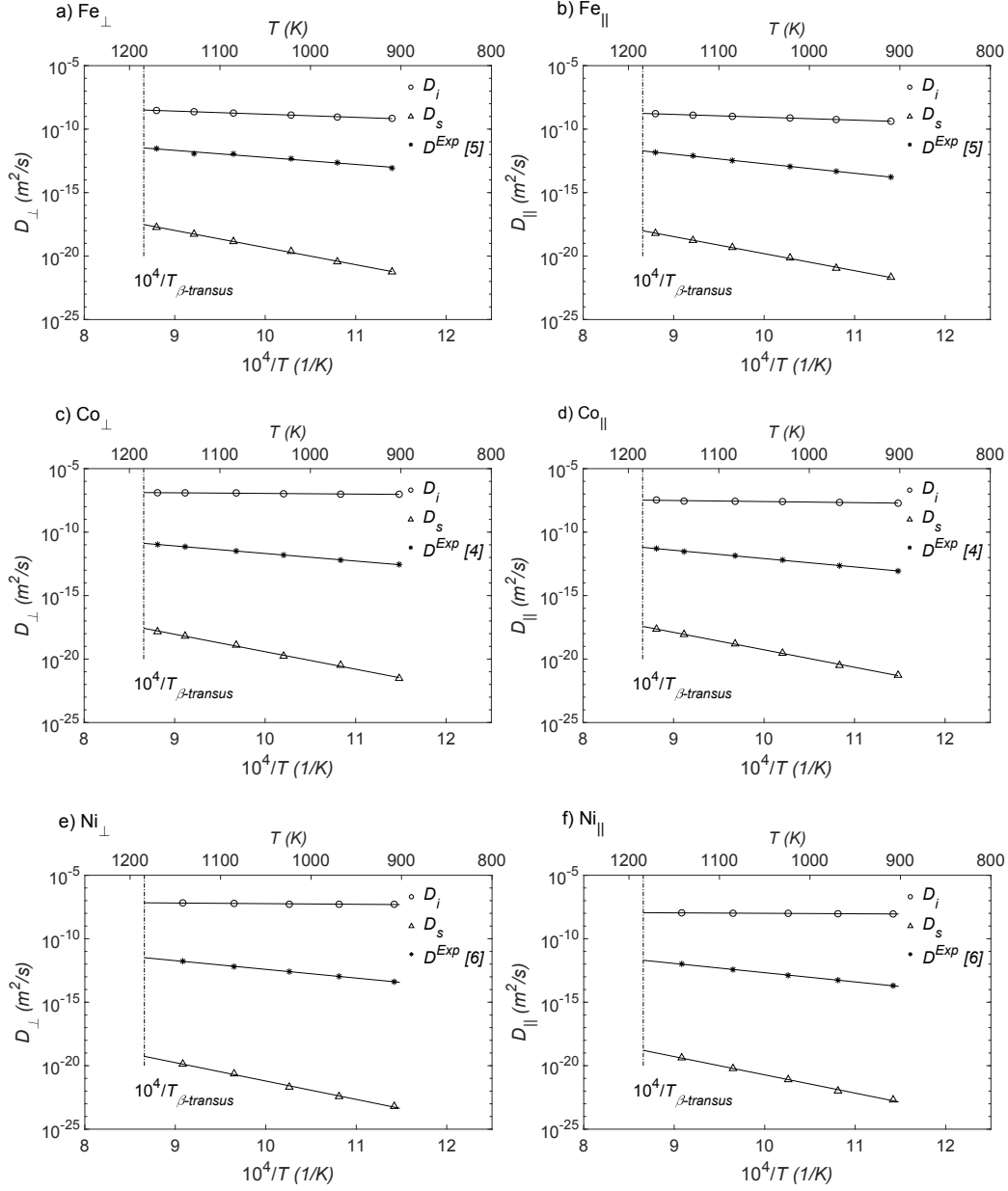


Figure 12: Perpendicular (\perp) and parallel (\parallel) diffusivities of fast-diffusers in the case of interstitial (D_i) and substitutional mechanism (D_s) calculated by KMC simulations and compared with experimental data (D^{Exp}) [5, 4, 6].

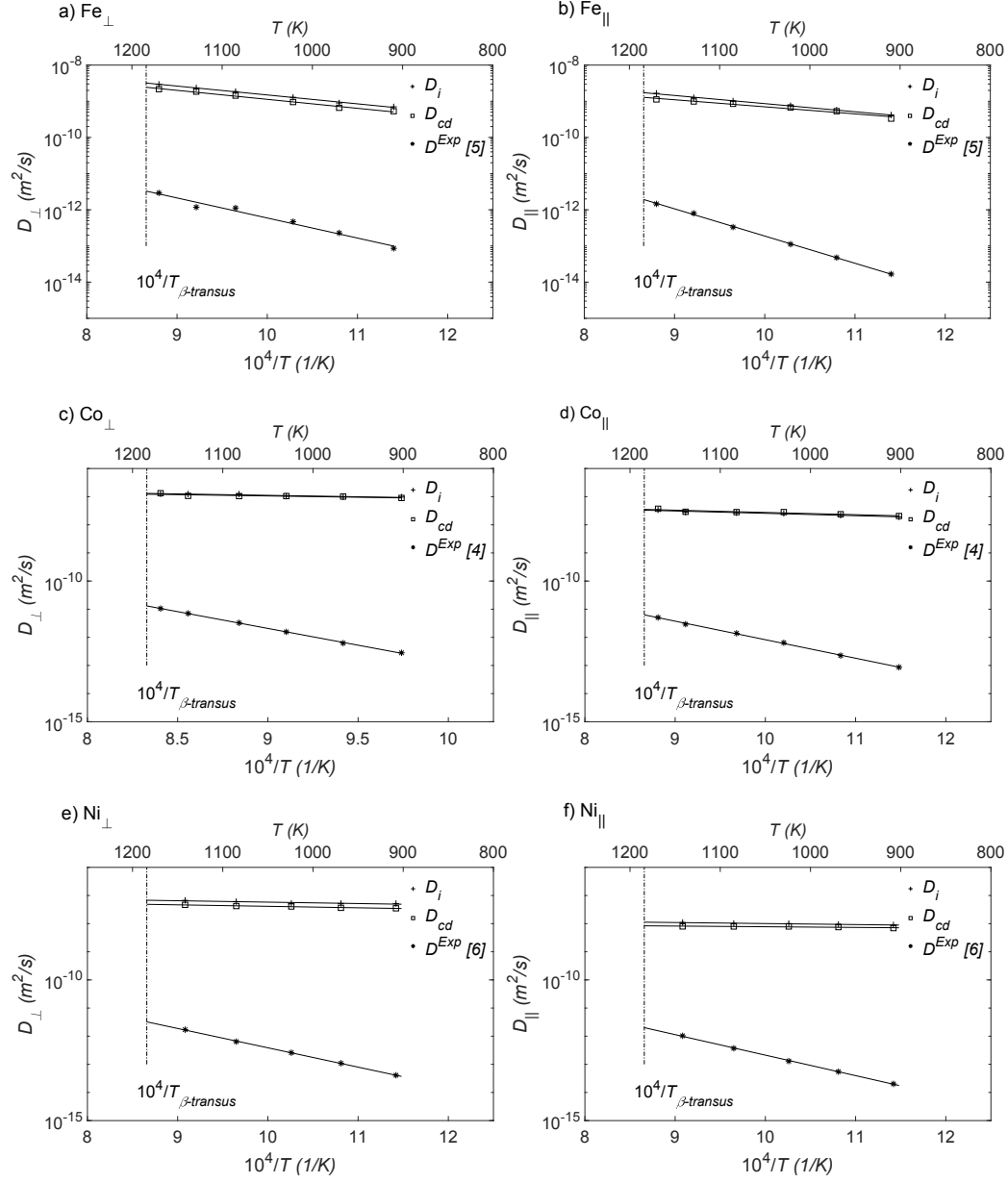


Figure 13: The effect of combination-dissociation process [13] on fast-diffusers migration along the perpendicular (\perp) and parallel (\parallel) to the basal plane calculated including the combination and dissociation events (D_{cd}) and compared with simple interstitial diffusivities (D_i), and experimental data (D^{Exp}) [4, 5, 6].

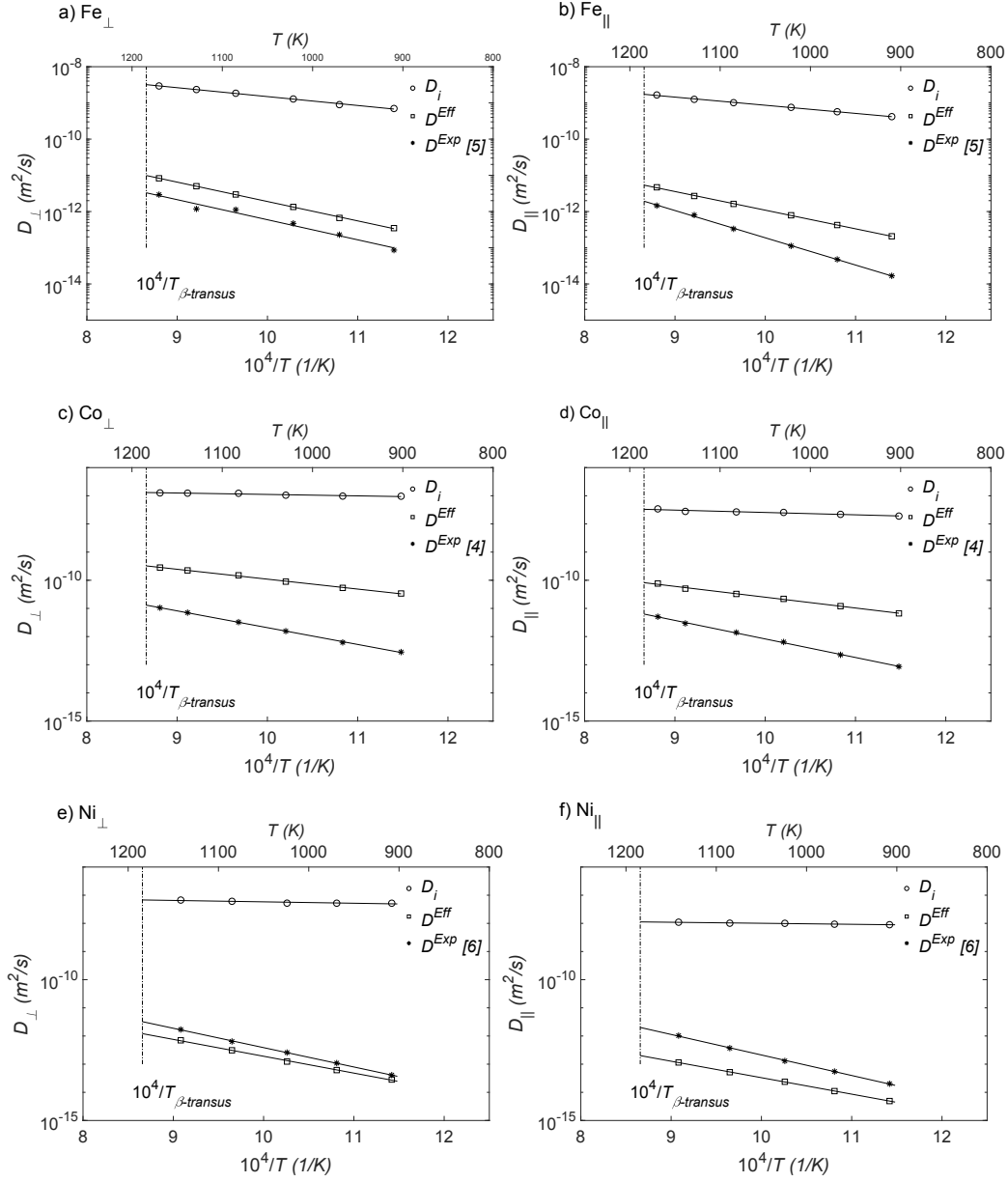


Figure 14: Effective perpendicular (\perp) and parallel (\parallel) to the basal plane diffusivities of Fe, Co and Ni in Ti calculated by Frank-Turnbull equation [12] (D^{Eff}) and compared with simple interstitial diffusivities (D_i), and experimental data (D^{Exp}) [5, 6, 4].

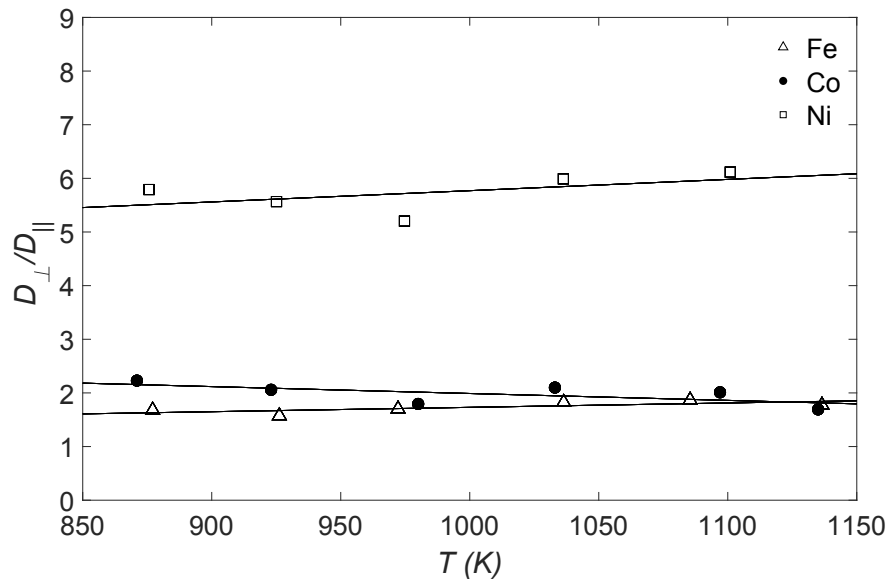


Figure 15: Comparison of calculated D_{\perp}/D_{\parallel} ratio of Fe, Co and Ni in α -Ti.

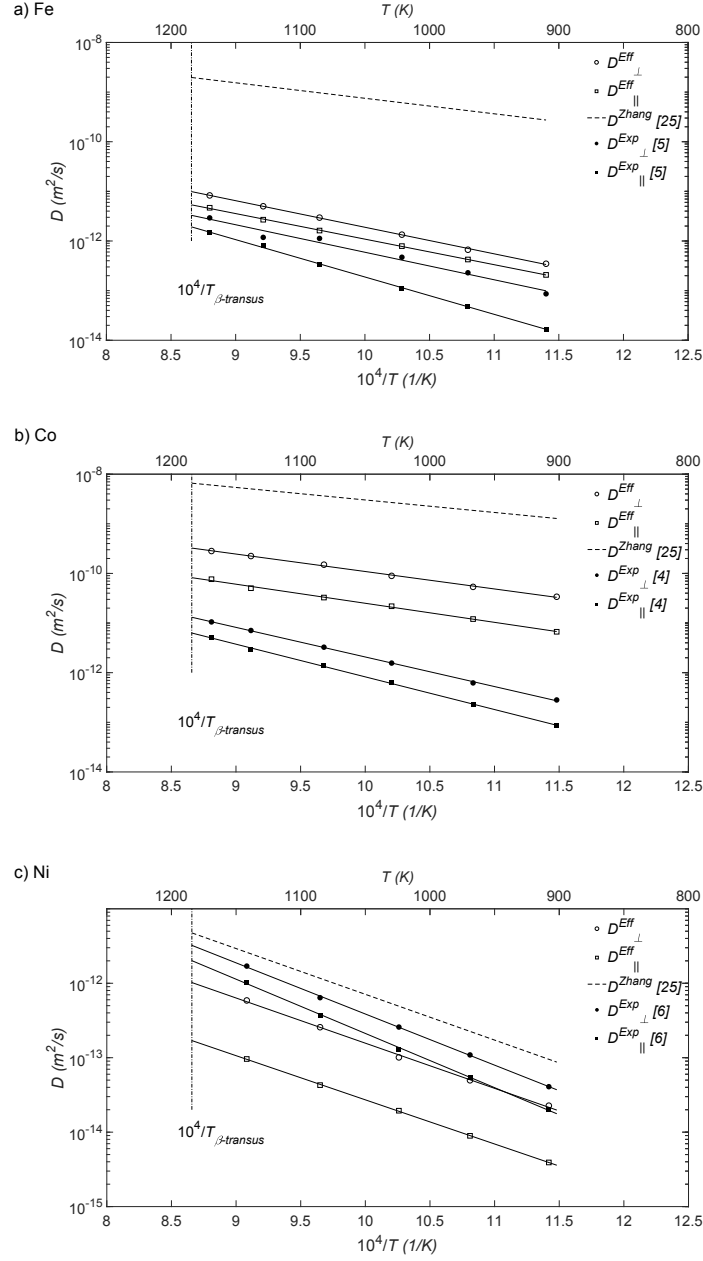


Figure 16: Comparison of KMC effective diffusivities with the experimental data and the computational result of Zhang *et al* [25].

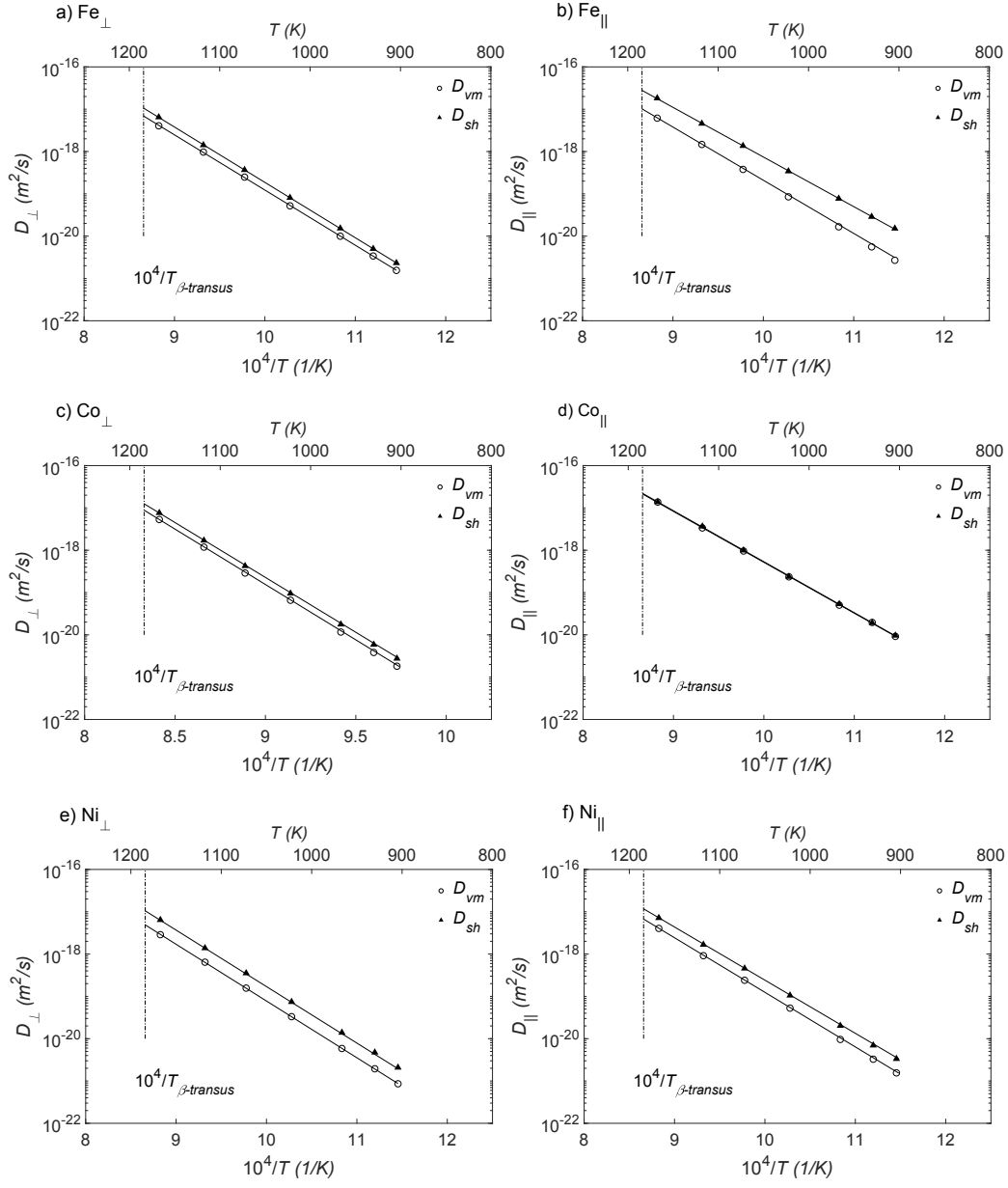


Figure 17: Solvent perpendicular (\perp) and parallel (\parallel) diffusivities in presence of fast-diffusers applying simple vacancy-mediated migration (D_{vm}) and solute-host swap mechanism [30, 29] (D_{sh}), the solute concentration is 1.9%.