



# On the origin of precipitation of transition metals implanted in MgO

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**Abstract.** Transition metals implanted in a stable oxide can either precipitate out at grain boundaries or can remain embedded in bulk. For MgO, experimentally it has been observed that some of the implanted Fe atoms precipitate out, while few Fe atoms in 2+ and 3+ charge states remain embedded in the lattice. Using first-principles calculations based on density functional theory, we show that formation energy, dopant site, barrier of transition and diffusivity, all these factors collectively determine the chance of precipitation of the implanted ion in the host lattice. Our calculations revealed that at 600 K (typical annealing temperature) while neutral iron in MgO would migrate 1  $\mu\text{m}$  in few microseconds, it takes several years for the charged Fe ions to migrate the same distance. On the other hand, Ni ions in all its charge states (neutral, 1+, 2+, and 3+) would migrate 1  $\mu\text{m}$  in just few microseconds, at 600 K. While explaining the experimentally observed precipitation of implanted Ni and few Fe atoms in MgO, this work provides a new scheme for predicting the stability of an implanted ion against precipitation in any stable rock-salt structured oxide.

## 1 Introduction

Implantation of metallic ions in refractory oxides have attracted immense attention [1] as the oxides find applications in switching and memory devices, spintronics and as dilute magnetic semiconductors [2]. Many studies suggest that the final state of the implanted ions depend on its charge state, nature of the host and the ions' local environment in the host lattice. Besides this, diffusion of the ions in the lattice also plays an important role in altering a solid's properties, and hence, controlling diffusion of the dopant in the host has always been an integral part of materials design [3].

In this paper, we explain two important experimental findings on precipitation of implanted Fe and Ni in MgO. Several studies on implanted Fe in MgO have revealed that some of the Fe atoms precipitate out, while the rest Fe can remain embedded in the host lattice [1–4]. For Ni on the other hand, available experiments show that Ni atoms implanted in MgO at room temperature get distributed in the matrix evenly, however, upon annealing Ni precipitates out [5] with an average particle size of 8–10 nm [6].

As mobility of the impurity atoms often results in undesired precipitation in binary oxides, a detailed knowledge of the diffusion of transition metal (TM) impurities in MgO is indispensable to explain the observed precipitation of Fe and Ni in MgO. However,

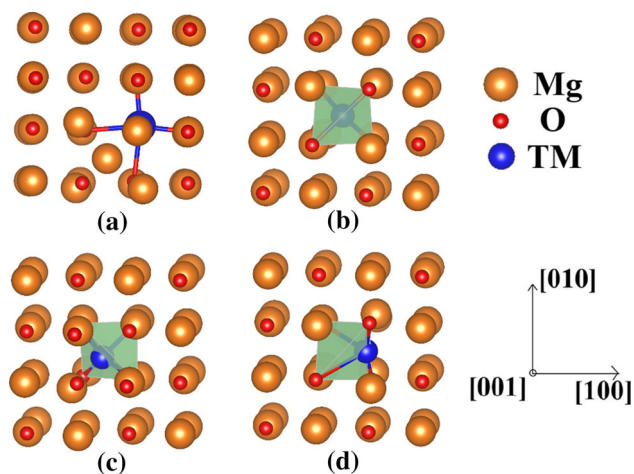
to shed light on the diffusion process, it needs one to first characterise the state of the dopants by thoroughly investigating their charge states and preferred sites in the host lattice.

Available experimental studies on Fe in MgO also claim Fe to be mostly in 3+ charge state with a possibility of acquiring 2+ and neutral states as well [3,4]. Nevertheless, a comprehensive study pertaining to the preferred defect sites, charge states and their role in the diffusion process of the implanted TM ions in MgO is lacking in the available literature and needs utmost attention. Using first-principles density functional theory (DFT) here we relate the thermodynamic stability and diffusivity of Fe and Ni, implanted in MgO, to their observed charge states in the host: we investigate (i) site preference of Fe and Ni ions in MgO, (ii) their stability in few particular charge states, and (iii) diffusion of Fe and Ni in MgO, not only to understand the experimentally observed precipitation of these two TM ions but also to provide a way to predict the stability of an implanted ion in a host oxide against precipitation.

## 2 Methodology

A cubic super cell containing 32 formula units of MgO with a dopant concentration of 3.1% has been considered for studying the thermodynamic stability and diffusion of Fe and Ni dopants in the oxide. Density func-

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**Fig. 1** Atomic structure of TM dopants (Fe or Ni) in MgO: (a) TM replaces host cation and the host cation sits in the tetrahedral interstitial; TM dopant sits at the (b) middle (c) corner and (d) edge of the oxygen tetrahedra

tional theory as implemented in Vienna Ab initio Simulation Package (VASP) [7, 8] is used for all our calculations with projector-augmented wave (PAW) method [9] and a plane wave basis set. The valence states of Mg contain 8 electrons in its 2*p* and 3*s* shells and O has 6 electrons. Fe and Ni possess 14 and 16 electrons respectively in their 3*p*, 3*d* and 4*s* shells. As the focus of this work was to study the trend pertaining to the thermodynamic stability of TM dopants in oxides, performing advanced calculations such as DFT+U or HSE were beyond the scope of this paper. We used generalized gradient approximation (GGA) to treat the exchange correlation interaction with the Perdew, Burke, and Ernzerhof (PBE) functional [10]. All the structures were fully relaxed using the conjugate gradient scheme and relaxations were considered converged when force on each atom was smaller than 0.02 eV/Å. A plane wave cut-off of 500 eV and a k-point mesh of 5 × 5 × 5 were used for achieving converged results within 10<sup>-4</sup> eV per atom. The density of states (DOS) for the doped systems were calculated by the linear tetrahedron method with Blöchl corrections and using a denser k-grid.

### 3 Results

Here we first briefly summarise our results on the preferred site and charge states of Fe and Ni, followed by our simulations on diffusion barriers of these two dopants in various charge states in MgO.

#### 3.1 Thermodynamic stability of Fe and Ni in MgO

To explore whether Fe and Ni atoms occupy interstitial sites or replace the lattice cations, energies of two different configurations were compared: (1) Fe or Ni atom substituting lattice Mg atom (wyckoff 4a(0.5, 0, 0.5)) and pushing it to the center of the nearest oxygen

tetrahedra (Fig.1a) (hereafter referred to as replacement) and (2) Fe or Ni atom occupying tetrahedral interstitial site (wyckoff 8c(0.25, 0.25, 0.25)) (Fig. 1b) (referred as interstitial). If the first configuration comes out to be more stable, the lattice Mg atom will be replaced by Fe or Ni and will be pushed into the adjacent interstitial site; the Mg atom can then migrate out of the matrix forming substitutional doping. If the second configuration is more stable, Fe or Ni will occupy the interstitial site of MgO as an added atom. It should be noted that, while calculating the substitutional formation energy, the host cation replaced by the dopant is generally removed from the lattice site. However, such approaches generally represent a system when doping is achieved by conventional chemical routes such as mixing compounds to maintain the overall stoichiometry of the host lattice [11]. However, in case of TM doping in the oxide by ion beam implantation, there could be more metal in the oxide when the implanted dopants are stabilized as interstitials [11].

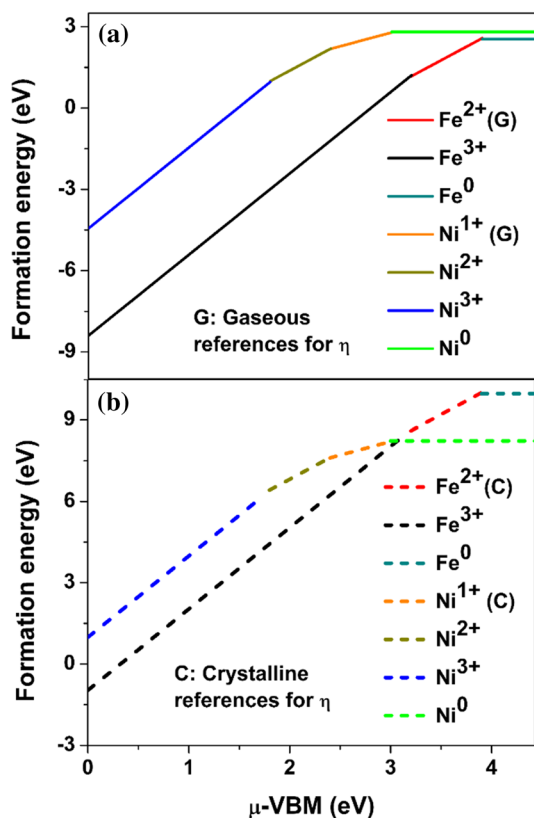
The charge states preferred by Fe and Ni, implanted in MgO, can be found in terms of the dopant formation energy  $E_f^q$  [12–15]

$$E_f^q = E_D^q - E_B - \eta + q(\mu + E_{ref} + \Delta V) + E_{corr}^q \quad (1)$$

Here  $E_D^q$  and  $E_B$  represent the total energies of defect supercell with charge  $q$  and the defect free host supercell, respectively.  $\eta$  is the chemical potential of the transition metal atom species. The ‘+’ sign indicates addition of the TM defect in host.  $E_{ref}$  is a suitable reference energy, taken to be the valence band maximum (VBM) [11] of the oxide.  $\mu$  is the electronic chemical potential of the system that varies from VBM up to the band-gap of MgO obtained from our DFT calculation.  $\Delta V$  is the correction necessary to realign the reference potential of the defect supercell with that of the defect free supercell [16] and  $E_{corr}^q$  is the first-order monopole correction to the electrostatic interaction and the finite size of the supercell.

We showed that both Fe and Ni prefer to occupy tetrahedral interstitial sites in MgO irrespective of their charge states. However, neutral Ni occupies not the center but one corner of the oxygen tetrahedron (wyckoff 32f (0.81, 0.688, 0.688))(Fig. 1c). Neutral Fe on the other hand prefers to sit in between two oxygen atoms forming the tetrahedron (wyckoff 48 g (0.25, 0.9, 0.25)) (Fig. 1d). Fe ion occupying the edge of the oxygen tetrahedra in MgO is also supported by an earlier Mössbauer spectroscopic analysis of Fe in MgO [3].

Figure 2 shows formation energy of Fe and Ni in various charge states as a function of electronic chemical potential. Both the gaseous and crystalline metal energy references for the chemical potential of Fe and Ni are taken into account, where gaseous reference to chemical potential indicates Fe and Ni energies in atomic state. While formation energies obtained with gaseous reference is necessary to access the thermodynamic driving force of TM atoms when implanted, crys-



**Fig. 2** Formation energy of the neutral and charged Fe and Ni atoms in MgO as a function of electronic chemical potential  $\mu$ . Chemical potential ( $\eta$ ) of Ni and Fe in (a) gaseous and (b) crystalline references

talline energy of Fe and Ni as reference is more relevant when chance of precipitation of the implanted ions is to be investigated. Our calculations shows that only  $Fe^{3+}$  has negative formation energy which indicates that Fe should be observed only in 3+ charge state. Besides this, our calculated formation energies also suggest that Fe in neutral and 2+ charge states, and Ni in all charge states should precipitate out. Hence in order to have a thorough understanding of the implanted Ni and Fe in MgO, we further proceeded to probe the diffusion behaviour of these ions in the host lattice.

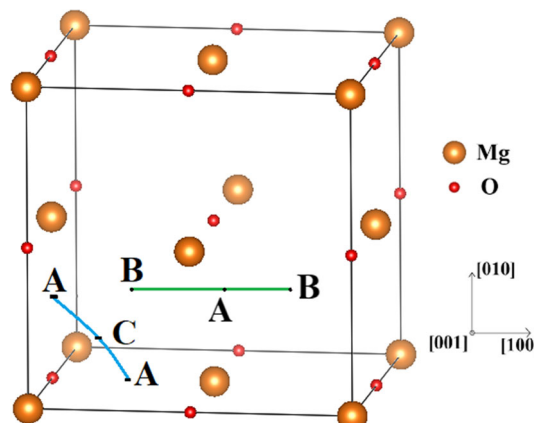
### 3.2 Barrier of transition and diffusion coefficient

Hopping of Fe and Ni from one interstitial site to the next interstitial site leads to their precipitation at the grain boundary. DFT provides a reliable way of calculating this transition barrier which is essential for estimating the time TM dopants take to diffuse out of MgO. Using Climbing Image Nudged Elastic Band (CI-NEB) method [17], barrier of transition between nearest interstitial sites have been calculated for both Fe and Ni in various charge states as listed in Table 1. Two possible diffusion paths are shown in Fig. 3; while  $Fe^0$  occupies the A site, rest of the ions occupy B site. Among the two possible pathways for diffusion of neutral Fe, we find that it is more likely for  $Fe^0$  to fol-

**Table 1** Attempt frequencies  $\nu$  and transition barriers  $E_{ij}$  (from  $i$ th to  $j$ th interstitial) for Fe and Ni in MgO

Attempt frequencies ( $\nu$ )	Dopant	$E_{ij}$ (eV)	Time ( $t_D$ )
$\nu_{Fe} = 13.28$ THz	$Fe^0$	0.15	$7.72 \times 10^{-8}$ Sec
	$Fe^{2+}$	2.16	94 Years
	$Fe^{3+}$	2.21	246 Years
$\nu_{Ni} = 12.95$ THz	$Ni^0$	0.02	$3.2 \times 10^{-9}$ Sec
	$Ni^{1+}$	0.08	$1.02 \times 10^{-8}$ Sec
	$Ni^{2+}$	0.11	$1.83 \times 10^{-8}$ Sec
	$Ni^{3+}$	0.59	$1.96 \times 10^{-4}$ Sec

Debye temperature  $T_D^{MgO} = 750$  K and Debye frequency  $\nu_D^{MgO} = 15.62$  THz.  $t_D$  is the time required for ions to diffuse 1 micrometer at  $T = 600$  K

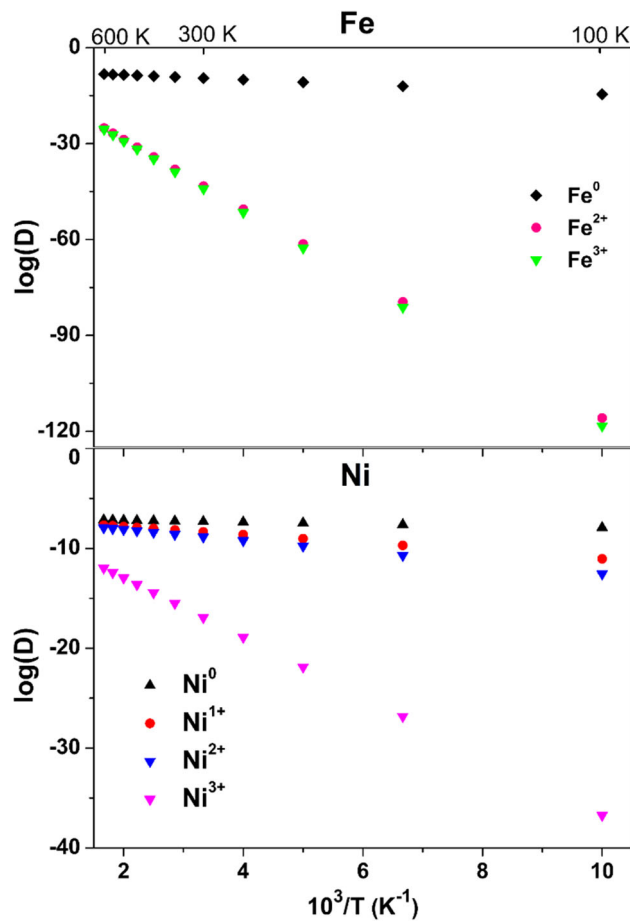


**Fig. 3** Diffusion paths for Fe and Ni dopants in MgO unit cell.  $Fe^{2+}$ ,  $Fe^{3+}$ , and Ni in all charge states follow B–A–B path for diffusion.  $Fe^0$  has two possible paths for diffusion: A to another equivalent A site (i) via C or (ii) through B. The barriers for transition for  $Fe^0$  via the paths A–C–A and A–B–A came out to be 0.15 eV and 1.29 eV respectively, indicating that A–C–A path is preferred for diffusion

low the path A–C–A as the barrier height of transition is substantially low (0.15 eV) compared to A–B–A path with a sufficiently high (1.29 eV) transition barrier. However, for  $Fe^{3+}$  and  $Fe^{2+}$ , barrier heights for transition are more than 2 eV. Ni, on the other hand, has very low barriers for diffusion in all charge states, with a maximum barrier height being 0.59 eV for  $Ni^{3+}$ . In general, a heigh barrier of transition is indicative of the fact that the ion under consideration is stable in the host lattice. Activation energies of  $Fe^{3+}$  and  $Fe^{2+}$  in interstitial site are comparable to the experimentally reported activation energies for substitutionally doped TM dopants (1.81 eV for  $Fe^{3+}$  and 2.10 eV for  $Ni^{2+}$ ) [18]. However, the activation energies of  $Fe^0$  and Ni in all charge states are significantly lower. For calculating the diffusion coefficients we have adopted a method proposed by Wu et al [19]. Transition frequencies  $\lambda_{ij}$  are first computed from

$$\lambda_{ij} = \nu_{ij} \exp(-E_{ij}/k_B T) \tag{2}$$

Here  $\nu_{ij}$  is the attempt frequency and  $E_{ij}$  is the barrier of transition between sites  $i$  and  $j$ .  $k_B$  and  $T$  are



**Fig. 4** Diffusivity of charged Fe and Ni dopants in MgO as a function of temperature

Boltzmann constant and temperature respectively. For diffusion of Fe and Ni,  $\nu_{ij}$  can be approximated using the relation

$$\nu_{ij} = \nu_D \sqrt{m_{matrix}/m_{TM}} \tag{3}$$

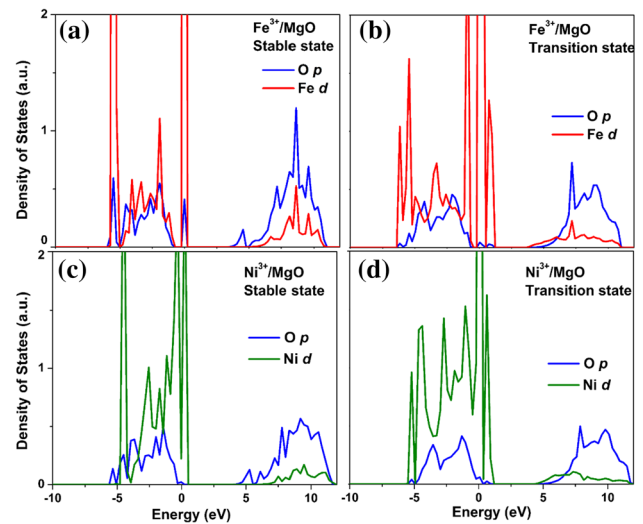
where  $\nu_D$  is the Debye frequency of the host which can be easily calculated from its Debye temperature ( $T_D = \nu_D h/k_B$ ).  $m_{matrix}$  and  $m_{TM}$  refer to the masses of MgO and TM (Fe, Ni) dopants respectively, and  $h$  is the Planck’s constant. Attempt frequency values for Fe and Ni in MgO are listed in Table 1.

Considering equal probabilities for diffusion along all three directions, the diffusion coefficients ( $D$ ) can be calculated from

$$D = \frac{1}{6} \lambda_{ij} \alpha^2 \tag{4}$$

where  $\alpha$  is the length of diffusion. For our calculations, alpha is length of A–B–A path or A–C–A path.

Our DFT calculated diffusion coefficients for neutral and charged Fe and Ni in MgO are shown in Fig. 4.  $Fe^{3+}$  has the lowest diffusivity among all and is comparable to that of  $Fe^{2+}$ , which suggests that both  $Fe^{3+}$  and  $Fe^{2+}$  share similar diffusion behaviour. On the other



**Fig. 5** Density of states plots for  $Fe^{3+}$  and  $Ni^{3+}$  in MgO in initial and transition states.  $d$  states for Fe and Ni and  $p$  states for neighboring oxygen atoms are shown

hand, diffusivity of Ni in all charge states and Fe in neutral state are several orders higher than  $Fe^{3+}$  and  $Fe^{2+}$ , even at 600 K which suggests that a much slower diffusion of Fe in 2+ and 3+ charge states should be expected than  $Fe^0$  and Ni ions.

We also estimate the time required for ions to diffuse 1 micrometer (typical grain size) at 600 K (typical annealing temperature) from the speed of diffusion which can be calculated as

$$S = \frac{1}{6} \alpha \lambda_{ij} \tag{5}$$

assuming that it takes  $6/\lambda_{ij}$  seconds for the ions to traverse the transition path length of  $\alpha$ . The time required to diffuse 1 micrometer by various ions are listed in Table 1. While Ni in all charge states and Fe in neutral state can diffuse 1 micrometer in less than a second, it takes several years for Fe in 2+ and 3+ charge states to diffuse the same length. Upon annealing, Ni (in all charge states) and neutral Fe being unstable in MgO, precipitate out of MgO very quickly. However,  $Fe^{2+}$  despite being unstable can remain in MgO, as it takes several years for  $Fe^{2+}$  to diffuse out to the grain boundary.

### 3.3 Electronic structure

To study if barrier of diffusion of the TM dopants in MgO also gets reflected from their respective electronic density of states (DOS), orbital resolved DOS for doped MgO have been calculated. Figure 5 shows the  $d$ -states of Fe and Ni both in 3+ charge states and the  $p$  states of neighbouring O-atoms. From Fig. 5a–b it is clearly evident that from the initial to transition state, the peaks shift to the higher energy region and the hybridization between  $p$  and  $d$  states also decreases, indicating the lower stability of the later configuration. The plot also

reveals the changes in the bonding between Fe and Ni  $d$  with O  $p$  in the transition states. The decrease in TM  $d$  and O  $p$  hybridization from initial to transition state, is more in Fe than in Ni, which in turn explains higher diffusion barrier for Fe<sup>3+</sup>. A comparison between Fe<sup>3+</sup> and Ni<sup>3+</sup>, both in their respective initial positions, reveals that hybridization between Ni  $d$  and O  $p$  states is substantially low compared to the same between Fe<sup>3+</sup> and neighbouring O atoms. This clearly indicates that in terms of overall stability, Fe<sup>3+</sup> is more stable than Ni<sup>3+</sup>, as already seen from our defect formation energy calculations.

## 4 Conclusions

This work intends to shed light on the possible factors that decide the stability of an implanted ion in a host oxide. Using first-principles calculations based on DFT we show that, charge state, dopant site, barrier of transition and diffusivity of an implanted ion, have huge impacts on the stability of the dopant in the host lattice. We have substantiated our claim by explaining Fe and Ni precipitation in MgO, which have already been observed experimentally. From our dopant formation energy calculations we explained why few particular charge states of an implanted dopant will be preferred over others and hence observed in the host lattice. We have also shown that rather than substituting the host cations, implanted ions (such as Fe and Ni in MgO) might occupy interstitial sites of the host oxide as well. Our calculations revealed that what favours the precipitation of Ni and neutral Fe is not only their instability but also their high diffusivity in MgO. At 600 K it takes Ni ions and Fe in neutral state less than a second to diffuse 1 micrometer. Fe<sup>2+</sup> on the other hand despite being unstable can remain in MgO as the required barrier for diffusion is high and it will take several years for Fe<sup>2+</sup> to diffuse 1 micrometer in MgO. From our density of states calculations, we further discussed the different behaviour of these two dopant species based on the extent of hybridization between the dopants and the neighboring oxygen atoms and the changes in the local bonding environments the dopants undergo from stable to transition states. Our study can pave a new way forward to predict the relative stability of implanted ions in a host oxide against precipitation.

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## Author contributions

The authors contributed equally to the paper.

**Data Availability Statement** This manuscript has no associated data or the data will not be deposited. [Authors'

comment: The work presented here is entirely computational and theoretical. The data are expressed in figures and graphs in the manuscript.]

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