Ab Initio Study of the Ferromagnetic Response, Local Structure, and Hyperfine Properties of Fe-Doped SnO₂

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ABSTRACT: We present here an ab initio study of the structural, magnetic, and hyperfine properties of Fe-doped rutile SnO₂ for different concentrations and distributions of the Fe atoms and oxygen vacancies in the SnO₂ host. The calculated results are compared with experimental ones obtained by Mössbauer spectroscopy and X-ray absorption techniques. This comparison enables us to characterize the local structure around Fe atoms and to identify the different hyperfine interactions that are observed in samples prepared by different methods. It is concluded that oxygen vacancies are fundamental for the ferromagnetic response of Fe-doped SnO₂. The ab initio calculations show that two Fe ions sharing an oxygen vacancy are coupled ferromagnetically, forming a bound magnetic polaron (BMP), and that two neighbor BMPs are aligned antiparallel to each other. Electron doping plays a fundamental role mediating the magnetic coupling between the BMP inducing ferromagnetic alignment between the BMPs.

1. INTRODUCTION

Tin dioxide (SnO₂) is an n-type broad-band gap semiconductor oxide with outstanding optical, electrical, and mechanical properties. It is a versatile material especially attractive for gas sensor applications.1,2 Doping SnO₂ with transition metal ions is one of the most promising ways to extend light absorption into the visible range, thereby extending its photocatalytic response (see ref 3 and references therein). One of the mechanisms proposed to explain the observed ferromagnetism suggests that only small regions of the sample that contain defects (such as grain boundaries) become ferromagnetic. The defects, for example oxygen vacancies, produce an impurity band inside the oxide band gap, and a Stoner-type criterion could be used to predict the induced magnetism. The dopants would contribute to this picture but not as the determining factor.15,16

The interpretation of the experimental results were usually based on conjectures, and relatively little attention was given to the local structure around the dopants. However, the knowledge of the local environment of the dopant may be essential to understand the mechanisms giving rise to magnetic order in these compounds.

In this work we present the results of a theoretical investigation of Fe-doped rutile SnO₂ considering different locations (substitutional and interstitial sites), concentrations, and distributions of the Fe atoms in the host lattice. The effect

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of oxygen vacancies on the hyperfine parameters, magnetic moments, and the magnetic alignments for Fe-doped SnO$_2$ is studied as a function of oxygen vacancy concentration and dopant/oxygen vacancy distribution. The comparison with experimental studies enables us to characterize the local structure around the iron atoms in rutile unambiguously and supports the conclusion that oxygen vacancies induced by doping with metallic atoms are fundamental for the ferromagnetic response of these systems, explaining the diversity of magnetic moments observed experimentally in samples grown under different conditions.

This paper is organized as follows. The next section describes the computational method. In section 3, experimental results reported by other authors as well as our own results, concerning structure and Mössbauer parameters at the Fe sites in Fe-doped SnO$_2$, are reviewed. Section 4 contains the theoretical results and the comparison with experimental ones. In section 5 a long-range ferromagnetic order is considered.

### 2. COMPUTATIONAL DETAILS

The unit cell of rutile SnO$_2$ contains two Sn atoms at the positions (0, 0, 0) and (1/2, 1/2, 1/2) and four oxygen atoms at the positions $\pm(u_u, u_0)$ and $\pm(1/2 + u, 1/2 + u, 1/2)$ with $u = 0.3056$. The lattice parameters are $a = b = 4.7374$ Å and $c = 3.1864$ Å.$^{17}$ In this structure, the Sn atoms are surrounded by a slightly distorted octahedron of oxygen nearest neighbors (ONN) atoms, with a rectangular basal plane having four oxygen atoms at a distance 2.05 Å (O1) and two vertex atoms at 2.06 Å (O2) from Sn. For the oxygen atoms, there is also only one crystallographic site, and each oxygen atom is surrounded by three Sn atoms.

We have simulated the doped systems considering periodically repeated supercells (SCs), in which some Sn atoms are replaced by Fe atoms in the rutile SnO$_2$ host with and without oxygen vacancies. The SC considered here consists of eight unit cells of rutile SnO$_2$. The resulting 48-atom SC has dimensions $a' = 2a = b' = 2b = 9.4748$ Å and $c' = 2c = 6.3728$ Å. If only one Sn atom is replaced, the composition is Sn$_{15}$FeO$_{32}$, which represents about 6 at. % of Fe doping. SCs of dimensions $a' = b' = a, c' = 2c$ (25 at. %); $a' = b' = 2a, c' = 3c$ (4 at. %), and $a' = b' = 3a, c' = 2c$ (3 at. %) were also considered.

The ab initio spin-polarized electronic-structure calculations were performed using the ab initio code Wien2K,$^{18}$ which is an implementation of the full-potential augmented plane waves plus local orbitals (APW+lo) method.$^{19,20}$ The parameter $R_{K_{\text{MAX}}}$, which controls the size of the basis set, was set to 7.0 ($R$ is the smallest muffin tin radius and $K_{\text{MAX}}$ the largest wavenumber of the basis set). Integration in the reciprocal space was performed using the tetrahedron method taking up to 100 k-points in the first Brillouin zone. Atomic displacements around the iron atoms and oxygen vacancies have been obtained in the standard way described in ref 21. Exchange and correlation effects were treated within density-functional theory using the local spin density approximation (LSDA).$^{22}$ The LDA $+U$ formalism with the same value of $U$ ($5.4$ eV) for the 3d states of Ti and Fe was also applied for some selected systems. Since none of the resulting hyperfine properties and equilibrium (lowest energy) structures obtained using LDA $+U$ differs qualitatively from those obtained with LSDA, we will center our discussion in the results obtained with LSDA.

To check the accuracy of the calculated results, we have performed several additional calculations. For selected systems, we increased the basis from $R_{K_{\text{MAX}}} = 5.0$ to $R_{K_{\text{MAX}}} = 8.0$ and increased the number of k-points to 200. It is found that energy differences, magnetic moments, quadrupole splittings, isomer shifts, and interatomic distances could be obtained with adequate precision using the parameters mentioned in the previous paragraph.

### 3. REVIEW OF EXPERIMENTAL RESULTS

Before discussing the results of our calculations, we will review in this section the experimental results reported by other authors as well as our own, concerning structural and Mössbauer hyperfine parameters at the Fe sites in Fe-doped SnO$_2$, while focusing on those that could be compared with the calculations.

Spectroscopy based on the Mössbauer effect is an experimental technique enabling simple comparison with ab

### Table 1. Experimental Results Obtained in Mössbauer Spectroscopy Experiments for Fe-Doped SnO$_2$

| Sample                        | Method of Preparation                       | $IS$ (mm/s) | $\Delta Q$ (mm/s) | Ref  |
|-------------------------------|---------------------------------------------|-------------|-------------------|------|
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | hydrothermally synthesized                  | 0.38        | 0.77              | 23   |
| Sn$_{0.95}$Fe$_{0.05}$O$_2$    | sol–gel ($^{57}$Fe enriched)                | 0.36–0.37   | 0.69–0.83         | 8    |
| Sn$_{0.95}$Fe$_{0.05}$O$_2$    | simple hydrothermal                         | 0.41–0.46   | 1.56–2.07         |      |
| Sn$_{0.95}$Fe$_{0.05}$O$_2$    | pulsed-laser deposition                     | 0.38        | 0.73              | 26   |
| Sn$_{0.95}$Fe$_{0.05}$O$_2$    | chemically synthesized                      | 0.29        | 0.81              | 6    |
| Sn$_{0.95}$Fe$_{0.05}$O$_2$    | ball-milling                                | 0.37        | 0.85              | 4    |
| Sn$_{1−x}$Fe$_{x}$Sb$_{0.2}$  | sol–gel                                     | 0.41        | 0.83              | 27   |
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | $^{57}$Fe implanted SnO$_2$ at room temperature | 0.93        | 0.92              |      |
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | $^{57}$Fe implanted SnO$_2$ at 753 K         | 0.26–0.29   | 1.60–1.8          | 28   |
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | $^{57}$Fe implanted SnO$_2$ at 573 K         | 0.29–0.34   | 0.7–0.81          |      |
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | $^{57}$Fe implanted SnO$_2$ at room temperature | 0.35–0.39   | 0.95–1.05         | 29   |
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | $^{57}$Fe implanted SnO$_2$ at 753 K         | 0.95–1.01   | 1.96–2.03         |      |
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | $^{57}$Fe implanted SnO$_2$ at room temperature | 0.25–0.29   | 0.35–0.52         | 29   |
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | $^{57}$Fe implanted SnO$_2$ at 753 K         | 0.90–1.15   | 1.43–1.71         |      |
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | $^{57}$ Mn implanted SnO$_2$                | 0.48        | 0.91              | 30   |
| Sn$_{0.90}$Fe$_{0.1}$O$_2$     | $^{57}$ Mn implanted SnO$_2$                | 0.885       | 2.20              |      |

In the experiments, only the absolute value of $\Delta Q$ is obtained.
4. THEORETICAL RESULTS

All calculations were performed for bulk three-dimensional systems. Our spin-polarized and non-spin-polarized ab initio calculations showed that the spin-polarized solutions have lower energies than non-spin-polarized ones. Therefore, we will report only the spin-polarized cases.

4.1. System with One Substitutional Fe Atom (Sn15FeO32). To begin, we replaced one Sn atom of the rutile structure by a Fe one, and we let all atoms to move into the relaxed position. It is found that the presence of substitutional Fe in the rutile SnO2 host produces an almost isotropic structural distortion, shortening the Fe–ONN bond lengths. As can be seen in Table 2, the Fe–ONN bond lengths are reduced by 0.14 Å with respect to the Sn–ONN ones.

Table 2 also shows the calculated magnetic moments. It is found that they are almost independent of the local structural distortions and of the Fe concentration. Spin polarization occurs mainly at the Fe sites, but the ONN can be polarized up to 0.06 μB/ONN. The IS (Table 2) is referred to α-Fe, and in order to evaluate it, we used a calibration constant α = 0.25a03 mm/s.32,33 The value of the nuclear quadrupole moment Q of the 57Fe nucleus34 used to calculate the ΔQ was –0.16 b.

We found that the average Fe–ONN relaxed bond lengths (1.913 Å) predicted by the calculations are in poor agreement with the results of extended X-ray absorption fine structure (EXAFS, Fe–ONN bond lengths larger than 1.98 Å; see ref 26). Furthermore, our ab initio calculations predict an IS in the order of 0.1 mm/s (Table 2), which is far from the experimental results (Table 1), and the calculated ΔQ does not agree with the results obtained from the experiments (Table 1 and Figure 1). Therefore, we conclude that a substitutional doping model cannot account for the Mössbauer and EXAFS experimental results. Also, the EXAFS experiments show that the Fe coordination number is smaller than 6 (on the order of 4.8, see ref 26). For the above reasons we will explore a second scenario that includes the formation of oxygen vacancies along with substitutional Fe doping.

4.2. Study of the System Sn15FeO31 (One Oxygen Vacancy + Substitutional Fe). We studied the oxygen-deficient system Sn15FeO31 considering three possibilities for removing an oxygen atom from the SC: (i) from the Fe-contained octahedron removing O1 atom; (ii) from the Fe-contained octahedron removing O2 atom; (iii) from an Sn-contained octahedron removing O3 atom (see Figure 2). In all cases, it is found that the structural relaxations induced by the oxygen vacancies are larger than those produced by only doping (see Table 2). Comparing the total energies of the three cases (and even larger Fe–oxygen vacancies separations), it is found that the oxygen vacancies near the Fe dopants (sites O1 and O2) are more stable than those near Sn atoms and that the vacancy at O1 site is more stable than the vacancy at O2 site. Similar results have been obtained in the case of Fe doping in rutile TiO2.14,35–37 One important result is that the energy required to form an oxygen vacancy is smaller in the Fe-doped SnO2 system than in the pure one. This reduction is more important if the vacancies are close to the Fe ions. Therefore,

“Table 2. Predicted Average Equilibrium Bond Lengths (d) between the Fe Atom and the Neighbor Oxygen Atoms, Magnetic Moments in the Muffin-Tin Sphere of Fe (μimp) and in the Supercell (μSC), and Hyperfine Parameters ΔQ and IS at the Fe Sites”

|                  | SnO2   | Sn15FeO32 | Sn15FeO31 |
|------------------|--------|-----------|-----------|
|                  | μimp   | μSC       | μimp      |
|                  | 1.63/2.00 | 1.63/2.00 | 1.912     |
| ΔQ (mm/s)        | 2.43   | 0.91      | 0.91      |
| IS (mm/s)        | +0.13  | +0.48     | +0.32     |

The calculations correspond to the cases of one substitutional Fe atom with and without oxygen vacancies.
we predict that Fe-doped SnO$_2$ systems will have more vacancies than the undoped ones and that oxygen vacancies will tend to be close to the Fe atoms.

Table 2 shows that the presence of an oxygen vacancy close to the Fe atoms increases the magnetic moment of the Fe. This magnetic moment is originated mostly by the polarization of the Fe atoms. Regarding the hyperfine parameters at the Fe sites in Sn$_{16}$FeO$_{32}$, an oxygen vacancy located at O1, O2, or O3 sites produces an increase of the isomer shift up to 0.48, 0.32, and 0.20 mm/s, respectively (see Table 2). The values of the IS and the $\Delta Q$ obtained with an oxygen vacancy at O1 site are close to the parameters that characterize the interaction I1 and those obtained with vacancy at O2 site near the ones of I2. Finally, for the configuration with a vacancy at O1 site (associated with the Mössbauer interaction with higher relative fraction, I1) the structure is in good agreement with the distances obtained from EXAFS (1.985 Å, ref 38). As a conclusion of this section, the comparison between theory and experiments supports the idea that the two main interactions (I1 and I2) observed in Mössbauer experiments can be associated with Fe ions substitutionally located at the cationic sites and with oxygen coordination number smaller than six, which is in agreement with EXAFS results.

4.3. System with One Interstitial Fe ($\text{Sn}_{16}\text{O}_{32} + \text{Interstitial Fe}$). Some Mössbauer spectra reveal the existence of an interaction (I4) characterized by large isomer shift (IS, on the order of 0.9 mm/s) and quadrupole splitting ($\Delta Q$) of around 2.0 mm/s. This additional interaction appears only in samples prepared by high-energy methods like ball-milling and ion implantation. Since none of the previous calculations predict a high isomer shift, it is considered that this interaction may correspond to interstitial Fe atoms.

To study this problem, we first verified that the most stable position for an interstitial Sn or Fe atom is the octahedral site at the center of the (010) face (the atomic position is 0; 1/2; 1/2 in the unit cell). In this position, an interstitial atom has six ONN: two at 1.71 Å and the other four at 2.34 Å. After the structural relaxation, the closest O atoms relax outward from the interstitial site by 0.18 Å while the other four O atoms are pulled in toward the interstitial Fe site by 0.35 Å. The equilibrium interstitial Fe−ONN bond lengths are then very similar to those corresponding to Fe in the substitutional site without oxygen vacancies.

The formation energy of an interstitial Fe is in the order of 6.0 eV, by 3.0 eV larger than for the substitutional position. Finally, our calculations predict a null magnetic moment at the Fe interstitial sites.

In the equilibrium structure, the calculated IS and $\Delta Q$ at the Fe site are 0.61 and 0.82 mm/s, respectively, both smaller than those corresponding to I4. From the study on the role of oxygen vacancies it is found that the preferential site for an oxygen vacancy is close to the interstitial Fe ion. Similar to the substitutional case, the presence of the oxygen vacancies reduces the energy necessary to locate Fe in the interstitial site, but this energy is also larger than that for the substitutional Fe. Depending on the location of the vacancy, a magnetic moment may appear. This magnetic moment is mainly originated by the polarization of Fe interstitial atoms. Concerning the IS, when vacancies are present, the IS increases up to 0.70 mm/s (see Table 3). Although the IS corresponding to an interstitial iron is higher than the corresponding one of the substitutional case, the calculated $\Delta Q$ is far away from the experimental one that characterizes I4 (0.90−1.0 mm/s). Therefore, to assign this particular interaction, more studies are needed considering different configurations of substitutional and interstitial Fe and oxygen vacancies.

4.4. Systems with Two Substitutional Fe Atoms ($\text{Sn}_{14}\text{Fe}_{2}\text{O}_{32}$). In the previous sections, only one Fe atom per unit cell was considered, so that the Fe spins were forced to be ferromagnetically aligned. To study the case of an antiferromagnetically aligned between two Fe atoms, we performed calculations with two Fe atoms, initially without oxygen vacancies, for different Fe atom distribution. The purpose is to find the preferred configurations and the dependence of the magnetic moments on the Fe distribution. Figure 3 shows the three Fe−Fe configurations studied. The other possible configurations in the SC with larger Fe−Fe separations were not considered.

Our results show that the lowest energy is obtained when the Fe atoms are located at the shortest possible distance from each other. This corresponds to Fe atoms located along the c-axis of the rutile structure (configuration a, Figure 3). Table 4 shows the energies for the FM and AF cases and the magnetic moments of each configuration. As seen in Table 4, for two of the three configurations the most stable phase is the antiferromagnetic one. In consequence, the possibility to obtain a stable ferromagnetic semiconductor with a large magnetic moment depends on the distribution of the Fe atoms in the SnO$_2$ lattice.

When two Fe atoms are considered, the IS values at the Fe sites are on the order of 0.15 mm/s for all the configurations.
studied. These values are similar to that for one isolated Fe atom and in poor agreement with the experimental results. This discrepancy was expected as we were not including oxygen vacancies here. The oxygen vacancies will be considered in the next section.

4.5. Systems with Two Substitutional Fe and Oxygen Vacancies \((Sn_{14}Fe_2O_{32-d})\). It is very difficult to determine experimentally the location of oxygen vacancies, and the computational modeling is required. The study of the magnetic behavior when two Fe atoms and oxygen vacancies are introduced is far more complicated than in the previous cases since the concentration and distribution of Fe atoms and vacancies will affect the magnetic interactions. The magnetic and hyperfine properties of the material will be an average of different Fe-defect configurations.

We considered the three configurations shown in Figure 3 with one or two oxygen vacancies. Configuration a has the two Fe ions linked by two Fe-O-Fe paths \((d(Fe-Fe) = 3.19 \text{ Å in the unrelaxed structure})\). Configuration b has the two Fe linked by only one Fe-O-Fe path \((d(Fe-Fe) = 3.70 \text{ Å in the unrelaxed structure})\). Configuration c has the Fe atoms linked by three separate Fe-O-Sn-O-Fe chains \((d(Fe-Fe) = 4.74 \text{ Å})\). It is found that one oxygen vacancy in configuration a prefers to be in one of the two Fe-O-Fe paths (sites a1 or a2 in Figure 3) and two oxygen vacancies prefer to occupy both Fe-O-Fe paths. In configuration b an oxygen vacancy prefers to be in the Fe-O-Fe path (site b1 in Figure 3), and if there are two oxygen vacancies, one prefers to be in the Fe-O-Fe path and the other as a nearest neighbor of one of the Fe atoms. Finally, for configuration c, the oxygen vacancy prefers to be near one of the Fe atoms. If a second oxygen vacancy is present, the stable configuration is obtained when the oxygen vacancies are located as a nearest neighbor of each Fe atom.

Energetically, if a vacancy is located in sites a1 or a2, it is estimated that \(\Delta E = E^{anti} - E^{ferro} = -0.1 \text{ eV}\). Therefore, the lowest energy configuration is the antiferromagnetic one, but the energy difference between the ferromagnetic and antiferromagnetic states is smaller than those of the system without oxygen vacancies. If there are two vacancies in a1 and a2, the lowest energy clearly corresponds to a ferromagnetic state (see Table 4). Another ferromagnetic state was obtained for one vacancy at site b1. Configuration c with one or two oxygen vacancies gives ferromagnetic alignment with \(\Delta E\) higher than that of the configuration without vacancies.

As is shown in Table 4, the magnetic moments at the Fe sites increase when one or two oxygen vacancies are present. We conclude that oxygen vacancies play an important role in the magnetic properties, enhancing the magnetic moments and favoring the ferromagnetic coupling between Fe atoms.

Regarding the hyperfine parameters, we find that the IS values increase in the presence of oxygen vacancies. In configuration a, two Fe atoms share two oxygen atoms (a1 and a2 in Figure 3, configuration a) of the rectangular basal plane of their coordination octahedra (O1 site). If only one of these oxygen atoms is removed, the resulting IS and \(\Delta Q\) are

| configuration | IS (mm/s) | \(\Delta Q\) (mm/s) | \(\mu^{\text{IS}}\) (\(\mu_B\)) | \(\mu^{\text{IC}}\) (\(\mu_B\)) | \(\Delta E\) (eV) | magnetic order |
|---------------|-----------|-----------------|-----------------|-----------------|----------------|----------------|
| a             | NV        | 0.15            | 1.26            | ±1.80           | 0.0            | -0.136         | AF             |
|               | 1 V       | 0.38            | 0.65            | ±3.52           | 0.0            | -0.095         | AF             |
|               | 2 V       | 0.50            | 0.65            | 3.40            | 8.5            | 0.082          | FM             |
| b             | NV        | 0.14            | 2.50            | 1.63            | 0.0            | -0.068         | AF             |
|               | 1 V       | 0.32/0.31       | 1.30/2.02       | 2.43/2.48       | 6.0            | 0.054          | FM             |
| c             | NV        | 0.12            | 2.24            | 1.63            | 4.0            | 0.013          | FM             |
|               | 2 V       | 0.32            | 1.34            | 2.38            | 6.0            | 0.027          | FM             |

\(^a\)NV, 1V, and 2V indicate the cases without oxygen vacancies or one or two oxygen vacancies in the SC. In the case of Configuration b with one oxygen vacancy the results for the IS, the \(\Delta Q\), and \(\mu^{\text{IS}}\) refers to each inequivalent Fe site of the structure.
close to experimental ones corresponding to I1. If two oxygen atoms are removed, a further increment of IS is found. In configuration b, the two Fe atoms share one oxygen atom (b1 in Figure 3, configuration b) that is of type O1 for the Fe site placed in the center of the unit cell and is apical oxygen O2 for the Fe atom located at a vertex of the unit cell. Removing this shared oxygen atom, the two nonequivalent iron atoms remain with almost the same IS and with different $\Delta Q$ (see Table 4).

The average values of IS and $\Delta Q$ for these iron are in very good agreement with the experimental hyperfine parameters of I2. In configuration c, the two Fe atoms do not share oxygen nearest neighbors. The oxygen atoms labeled c1 and c2 in Figure 3 (configuration c) are at the apical (O2) position of two different Fe octahedral coordination. If both atoms are removed, the IS and $\Delta Q$ are in the range of experimental hyperfine parameters of I2.

The calculated values of the IS and $\Delta Q$ for the substitutional cases with one and two oxygen vacancies are included in Figure 1 (open symbols). If an apical oxygen O2 atom is removed, the IS and $\Delta Q$, have values close to experimental ones corresponding to I2, whether the iron atom has or does not have another Fe atom as nearest neighbor (configuration b or c, blue symbols in Figure 1). In the cases where oxygen O1 is removed, the calculated hyperfine parameters (red symbols in Figure 1) are close to the experimental values corresponding to I1.

### 4.6. Systems with One Interstitial and One Substitutional Fe Atom

We consider the interstitial and substitutional Fe atoms with and without oxygen vacancies. The two interstitial + substitutional configurations considered here are (a) An interstitial Fe atom (Fe(int)) located at position (0, 1/2, 1/2) and the substitutional Fe atom (Fe(subst)) located at (1/2, 1/2, 1/2) and (b) Fe(int) located at (0, 1/2, 1/2) and the Fe(subst) at (0, 0, 0). These configurations correspond to the smaller Fe(subst)—Fe(int) separation distances. The predicted IS and $\Delta Q$ values are shown in Table 5. When one oxygen vacancy is introduced, the oxygen vacancy prefers to be located as a nearest neighbor of both Fe atoms. In this situation, the IS for Fe(subst) is similar to those of the experimentally observed interactions I1 and I2.

In ref 30, the authors analyze $^{57}$Mn $\rightarrow$ $^{57}$Fe implanted in SnO$_2$ films and report that the Mössbauer spectra presents two doublets, one with IS $= 0.48$ mm/s and $\Delta Q = 0.91$ mm/s and the other with IS $= 0.89$ mm/s and $\Delta Q = 2.20$ mm/s. Comparing with Table 3 (calculated values for one interstitial Fe atom), there is poor agreement between experimental and calculated results, but there is good agreement with the situation where the interstitial Fe has a substitutional iron near neighbor (see Table 5, configuration b with one oxygen vacancy).

### 5. LONG-RANGE FERROMAGNETIC ORDER

In section 4.5 we discussed on the effect of oxygen vacancies on the magnetic alignment considering two Fe atoms and one or two oxygen vacancies. We showed that the presence of one or two oxygen vacancies in the Fe–O–Fe paths clearly favors ferromagnetic ordering. Such an ferromagnetic entity (the Fe atoms and oxygen vacancy) was described as a bound magnetic polaron (BMP). In order to explore the long-range ferromagnetic order, we considered two BMPs inside a larger SC of 108 atoms ($3a \times 2a \times 3c$ SC, see Figure 4a). The distance between the BMPs is 4.74 Å. Note that the BMP corresponds to two Fe atoms in configuration b with the oxygen vacancy in the position b1. Two possible BMP alignments were considered: ferromagnetic (Figure 4a) or antiferromagnetic (Figure 4b). It is found that the energy difference between both alignments is $\Delta E = -0.05$ eV, i.e., the antiferromagnetic alignment is favored. Thus, although an increase in iron concentration would favor a neighboring situation with the increase in the number of BMP, the antiferromagnetic BMP alignment would reduce the magnetization, which is in very good agreement with the experimental results. In consequence, the origin of the ferromagnetic contribution is still unexplained, and another mechanism must be considered to explain the ferromagnetic response of Fe-doped SnO$_2$.

At this point it is important to return to the experiments. It was reported that the codoping of SnO$_2$ with Fe and Sb$^{5+}$ ions increases the saturation magnetization. This experimental result led us to study the effect of extra electron doping on the ferromagnetic alignment. The electron doping was simulated in two different ways: adding one electron to the 108-atom SC or replacing one indigenous Sn atom by a donor impurity. For both approaches we found that the ferromagnetic coupling

| configuration | IS (mm/s) | $\Delta Q$ (mm/s) | $\mu^\text{eff}$ ($\mu_B$) | $\mu^\text{SC}$ ($\mu_B$) |
|---------------|-----------|--------------------|-------------------------|-------------------------|
| a NV Int      | 0.50      | 1.43               | $+0.36$                 | $-0.76$                 |
| Sus           | 0.45      | 0.73               | $-0.66$                 |                         |
| 1V Int        | 0.40      | 0.88               | $-0.17$                 | $-3.77$                 |
| Sus           | 0.52      | 0.64               | $+3.45$                 |                         |
| b NV Int      | 0.65      | 0.72               | $-1.69$                 | $-2.56$                 |
| Sus           | 0.68      | 0.42               | $-3.63$                 |                         |
| 1V Int        | 0.46      | 1.12               | $+0.95$                 | $-2.00$                 |
| Sus           | 0.60      | 1.95               | $-2.56$                 |                         |
between BMP is the most stable configuration with $\Delta E = E_{\text{anti}} - E_{\text{ferro}}$ on the order of +0.3 eV. A Bader analysis reveals that 20% of the added charge is localized in the four Fe atomic spheres and the remaining in the interstitial region. This result shows that electron doping plays a fundamental role in mediating the nonlocal magnetic coupling between two BMP.

6. CONCLUSIONS

We have shown here a theoretical investigation of Fe-doped rutile SnO$_2$. Our calculations, assuming different structural scenarios, allow us to assign the two main interactions (I1 and I2) observed in the M"ossbauer experiments reported in the literature to Fe$^{3+}$ replacing Sn$^{4+}$ in the rutile structure with oxygen vacancies close to the dopant. Other interactions were found in some experiments. These additional interactions have lower intensity than I1 and I2. The third interaction (I3) is characterized by a low IS (on the order of 0.20 mm/s). Based on the low IS it can be assigned, in principle, to Fe atoms replacing Sn with an oxygen vacancy far away from the first shell of oxygen neighbors. The interaction I4, characterized by a high IS value (on the order of 1.0 mm/s), can be tentatively assigned to Fe ions located at interstitial sites with iron and oxygen vacancies in its close vicinity. The fact that the energy necessary to locate an iron atom at an interstitial site is large compared with the substitutional configuration allows us to understand why this high intensity interaction is only observed in samples obtained by high-energy methods such as ion implantation or high-energy ball milling. From our results it is clear that the overall hyperfine properties of Fe-doped SnO$_2$ are a statistical average of different defect configuration. In order to reach a better understanding of the interactions I3 and I4, different configurations (considering different concentrations and distributions of Fe atoms and oxygen vacancies) must be considered.

An important result of our calculations is that doping lowers the formation energy of vacancies, so that doped systems will have more vacancies than the undoped ones. The strong interaction between oxygen vacancies and Fe atoms increases the local magnetic moment of the Fe atom. We also found that the oxygen vacancies enhance the ferromagnetic coupling between Fe atoms. Fe ions are coupled ferromagnetically when they are mediated by an oxygen vacancy forming a BMP. In cases where there are no free carriers, BMPs are coupled antiferromagnetically. Carrier doping produces the ferromagnetic alignment between BMPs. Therefore, oxygen vacancies would be responsible for forming BMPs and free carriers for inducing the ferromagnetic coupling between BMPs.

The overall magnetic properties of Fe-doped rutile SnO$_2$ are an average over many possible defect configurations, and therefore ferromagnetism in this system is a complex phenomenon, which involves the interplay between oxygen vacancies and doping atoms. Our results support the hypothesis that oxygen vacancies play an important role in the magnetic properties of Fe-doped rutile SnO$_2$ and can explain the diversity of magnetic behaviors experimentally observed for samples grown in different conditions. Similar conclusions were obtained in the case of Fe-doped rutile TiO$_2$, $^{35}$Zn-ferrite, and other doped metallic oxides such as Fe-doped In$_2$O$_3$ and Co-doped ZnO.$^{31}$ In all these systems it was demonstrated that oxygen vacancies in the Fe$^{3+}$-Fe (or Co$^{3+}$-Co) paths clearly favor ferromagnetic ordering.

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**REFERENCES**

(1) Batzill, M.; Diebold, U. The Surface and Materials Science of Tin Oxide. *Prog. Surf. Sci.* 2005, 79, 47–154.
(2) Göpel, W.; Schierbaum, K. D. SnO$_2$ Sensors: Current Status and Future Prospects. *Sens. Actuators B* 1995, 26, 1–12.
(3) Das, S.; Jayaraman, V. SnO$_2$: A Comprehensive Review on Structures and Gas Sensors. *Prog. Mater. Sci.* 2014, 66, 112–255.
(4) Punnoose, A.; Hays, J.; Thuber, A.; Engelhard, M. H.; Kukkadapu, R. K.; Wang, C.; Shuttthanandan, V.; Thevuthasan, S. Development of High-Temperature Ferromagnetism in SnO$_2$ and Paramagnetism in SnO by Fe Doping. *Phys. Rev. B* 2005, 72, 054402.
(5) Punnoose, A.; Hays, J.; Gopal, V.; Shuttthanandan, V. Room-Temperature Ferromagnetism in Chemically Synthesized Sn$_{1-x}$Co$_x$O$_2$ Powders. *Appl. Phys. Lett.* 2005, 85, 1559–1561.
(6) Coey, J. M. D.; Douvalis, A. P.; Fitzgerald, C. B.; Venkatesan, M. Ferromagnetism in Fe-Doped SnO$_2$ Thin Films. *Appl. Phys. Lett.* 2004, 84, 1332–1334.
(7) Fitzgerald, C. B.; Venkatesan, M.; Douvalis, A. P.; Huber, S.; Coey, J. M. D. SnO$_2$ Doped with Mn, Fe or Co: Room Temperature Dilute Magnetic Semiconductors. *J. Appl. Phys.* 2004, 95, 7390–7392.
(8) Nomura, K.; Barrero, C. A.; Sakuma, J.; Takeda, M. Room-Temperature Ferromagnetism of Sol-Gel-Synthesized Sn$_{1-x}$Fe$_x$O$_{2-d}$ Powders. *Phys. Rev. B* 2007, 75, 184411.
(9) Rodríguez Torres, C. E.; Errico, L. A.; Golmar, F.; Navarro Mudarra, A. M.; Cabrera, A. F.; Duhalde, S.; Sánchez, F. H.; Weissmann, M. The Role of the Dopant in the Magnetism of Fe-Doped SnO$_2$ Films. *J. Magn. Magn. Mater.* 2007, 316, e219–e222.
(10) Srivastava, S. K.; Lejay, P.; Barbara, B.; Palîhé, S.; Madigou, V.; Bouzerar, G. Possible Room-Temperature Ferromagnetism in K-Doped SnO$_2$: X-Ray Diffraction and High-Resolution Transmission Electron Microscopy Study. *Phys. Rev. B* 2010, 82, 193203.
(11) Espinosa, A.; García-Hernández, M.; Menéndez, N.; Prieto, C.; de Andrés, A. Ferromagnetism in SnO$_2$-Based Multilayers: Clustering of Defects Induced by Doping. *Phys. Rev. B* 2010, 81, 064419.
(12) Hong, N. H.; Poiriot, N.; Sakai, J. Ferromagnetism Observed in Pristine SnO$_2$. *Thin Films. Phys. Rev. B* 2008, 77, 033205.
(13) Chang, G. S.; Forrest, J.; Kurmaev, E. Z.; Morozovska, A. N.; Glüchau, M. D.; McLeod, J. A.; Moeves, A.; Surkova, T. P.; Nguyen Hoa, H. Oxygen-Vacancy-Induced Ferromagnetism in Undoped SnO$_2$. *Thin Films. Phys. Rev. B* 2012, 85, 165319.
(14) Mudarra Navarro, A.; Errico, L. A.; Rodriguez Torres, C.; Cabrera, A. F.; Bilovol, V.; Rentería, M.; Weissmann, M. In Rutile: Properties, Synthesis and Applications; Nova Science: Hauppauge, NY, 2012.
(15) Khalid, D. M.; Setzer, A.; Ziese, M.; Esquinazi, P.; Spemann, D.; Pöpel, A.; Goering, E. Ubiquity of Ferromagnetic Signals in Common Diamagnetic Oxide Crystals. *Phys. Rev. B* 2010, 81, 214414.
(16) Coey, J. M. D.; Stamenov, P.; Gunning, R. D.; Venkatesan, M.; Paul, K. Ferromagnetism in Defect-Ridden Oxides and Related Materials. *New J. Phys.* 2010, 12, 053025.
Magnetic Behaviour of Fe-Doped TiO2 Anatase Nanoparticles: Requejo, F. G.; Weissmann, M.; Stewart, S. J. Local Structure and Between Oxygen Vacancies and Ferromagnetism in Fe-Doped TiO2 Cabrera, A. F.; Errico, L. A.; Weissmann, M. Study of the Relation
Magnetism in Transition-Metal-Doped TiO2 And TiO2 Implanted SnO2 Films by 57Fe and 119Sn CEMS. Sawatzky, G. A. Density-Functional Theory and NiO Photoemission Representation of the Electron-Gas Correlation Energy. Rodriguez Torres, C. E.; Cabrera, A. F.; Renteria, M.; Sanchez, F. H.; Weissmann, M. Appearance of Room-Temperature Ferromagnetism in Cu-Doped TiO2 Films. 57Mn Implanted SnO2 Film. Hyperfine Interact. 2009, 200, 114, 15−20. Madsen, G. K. H.; Blaha, P.; Schwarz, K.; Stojstod, E.; Nordstrom, L. Efficient Linearization of the Augmented Plane-Wave Method. Phys. Rev. B 2001, 64, 195134. Duhlalde, S.; Vignolo, M. F.; Golmar, F.; Chiolli, C.; Rodríguez Torres, C. E.; Errico, L. A.; Cabrera, A. F.; Renteria, M.; Sanchez, F. H.; Weissmann, M. Appearance of Room-Temperature Ferromagnetism in Cu-Doped TiO2 Films. Phys. Rev. B. 2005, 72, 161313(R). Perdew, J. P.; Wang, Y. Accurate and Simple Analytic Representation of the Electron-Gas Correlation Energy. Phys. Rev. B 1992, 45, 13244−13249. Anisimov, V. I.; Solovyev, I. V.; Korotin, M. A.; Czyzyk, M. T.; Sawatzky, G. A. Density-Functional Theory and NiO Potoemission Spectra. Phys. Rev. B 1993, 48, 16929−16934. Zboril, R.; Mashlan, M.; Petridis, D. Iron(III) Oxides from Thermal Processes- Synthesis, Structural and Magnetic Properties, Mössbauer Spectroscopy Characterization, and Applications. Chem. Mater. 2002, 14, 969−982. Sorescu, M.; Diamandescu, L.; Tarabasani-Mihaila, D.; Teodorescu, V. S.; Howard, B. H. Hydrothermal Synthesis and Structural Characterization of (1−x)Fe2O3−xSnO2 Nanoparticles. J. Phys. Chem. Solids 2004, 65, 1021−1029. Liu, J. F.; Lu, M. F.; Chai, P.; Fu, L.; Wang, Z. L.; Cao, X. Q.; Meng, J. The Magnetic and Structural Properties of Hydrothermal-Synthesized Single-Crystal Sn1−xFexO2 Nanograins. J. Magn. Magn. Mater. 2007, 317, 1−7. Bilovol, V.; Mudarra Navarro, A. M.; Rodríguez Torres, C. E.; Sánchez, F. H.; Cabrera, A. F. Magnetic and Structural Study of Fe Doped Tin Dioxide. Physica B 2009, 404, 2834−2837. Nomura, K.; Barrero, C. A.; Kuwano, K.; Yamada, Y.; Saito, T.; Kuzmann, E. 57Fe Mossbauer Study of Fe and Sn Doped SnO2 Powders. Hyperfine Interact. 2009, 191, 25−32. Nomura, K.; Reuther, H. Nano-Structure Analysis of Fe Implanted SnO2 Films by 57Fe and 119Sn CEMS. Hyperfine Interact. 2009, 191, 159−165. Gunnlaugsson, H. P.; Nomura, K.; Malholt, T. E.; Shayeestehaminzadeh, S.; Johnston, K.; Mantovan, R.; Masenda, H.; Ncube, M.; Bharuth-Ram, K.; Gislon, H.; Langouche, G.; Naidoo, D.; Olafsson, S.; Weyer, G. Characterization of Fe States in Dilute 57Mn Implanted SnO2 Film. Hyperfine Interact. 2014, 226, 389−396. Shirane, G.; Cox, D. E.; Ruby, S. L. Mössbauer Study of Isomer Shift, Quadrupole Interaction, and Hyperfine Field in Several Oxides Containing 57Fe. Phys. Rev. 1962, 125, 1158−1165. Eriksson, O.; Svane, A. Isomer Shifts and Hyperfine Fields in Iron Compounds. J. Phys.: Condens. Matter 1989, 1, 1589−1599. Mudarra Navarro, A. M.; Rodriguez Torres, C.; Errico, L. A. Calibration of the Isomer Shift of the 14.4 keV Transition of 57Fe. Hyperfine Interact. 2011, 202, 117−121. Dufeck, P.; Blaha, P.; Schwarz, K. Determination of the Nuclear Quadrupole Moment of 57Fe. Phys. Rev. Lett. 1995, 75, 3545−3548. Mudarra Navarro, A. M.; Rodríguez Torres, C. E.; Bilovol, V.; Cabrera, A. F.; Errico, L. A.; Weissmann, M. Study of the Relation Between Oxygen Vacancies and Ferromagnetism in Fe-Doped TiO2 Nano-powders. J. Appl. Phys. 2014, 115, 223908. Errico, L. A.; Weissmann, M.; Renteria, M. Theoretical Study of Magnetism in Transition-Metal-Doped TiO2 And TiO2: 45603 DOI: 10.1021/jp512521q J. Phys. Chem. C 2015, 119, 5596−5603