

Fe-doped SnO₂: A Quantum-chemical Approach

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We report first-principles results obtained on Fe impurity incorporation into the SnO₂ material. Different impurity concentrations have been taken into consideration when computing structural, electronic and magnetic properties of the material. DFT + *U* methodology within the GGA approach applied to a 96-atom supercell allowed us to establish the equilibrium geometry of the system, which consists of six defect-nearest oxygens shifting towards the Fe impurity. Antiparallel magnetic alignment between the electrons of the Fe 3*d* and impurity-neighbouring O 2*p* atomic orbitals forming the FeO₆ complex has been found.

Keywords: DFT+*U*, SnO₂, Impurity doping, Microstructure, Magnetism.

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1. INTRODUCTION

Tin dioxide (SnO₂) is a fascinating material with a lot of valuable applications in different fields. If doped with Fe impurities it becomes diluted magnetic semiconductor (DMS) showing permanent ferromagnetic behaviour. DMS, where transition metal (magnetic) impurities are doped into semiconductor material [1], has found increased interest in both scientific and industrial communities. In case of room temperature applications in spintronics, oxide-based DMS systems are gaining fast grow since such systems have not only high critical temperature but also large magnetic moments [2]. SnO₂ is one of compounds displaying the mentioned features.

In general, impurity doping in oxide crystals leads to a great deal of new properties in these materials [3]. These features sometimes are interrelated, i.e. atomic shifts in defective region and magnetism might be connected [4] or strong coupling between different atomic orbitals (AOs) might influence electronic conductivity in a given sample [5]. That is why it is important to understand as many properties as feasible in case of the impurity incorporation in SnO₂ material.

Iron is a typical magnetic atom and is ideal candidate to be used in order to understand better how a magnetic atom might influence the microstructure of SnO₂ and its possible relation to the magnetism. Density of states (DOS) have been analysed as well within the present work to find out the relationship between different electronic states at the equilibrium.

2. OUTLINE OF THE METHOD

Study is based on the density functional theory (DFT) [6] within the generalized gradient approximation (GGA) method [7]. VASP computer code [8] has been used throughout the work. The projector augmented wave (PAW) method [9] serves to describe the interaction between the core electrons and the valence electrons. The following valence configurations have been employed in the present research: 4*d*¹⁰5*s*²5*p*² for Sn, 3*p*⁶3*d*⁷4*s*¹ for Fe and 2*s*²2*p*⁴ for O atoms, respective-

ly. Perdew-Burke-Ernzerhof (PBE) developed [10] GGA functionals are utilised to describe the exchange correlation interactions. Additionally, we make use of the so-called *U*-term in order to correct some DFT deficiencies regarding the treatment of *d*-electrons. That means the intra-atomic interactions for the strongly correlated *d*-electrons are taken into account by the unrestricted Hartree-Fock approximation leading to the DFT + *U* method. In the present work, we use a scheme of the rotationally invariant approach to the DFT + *U* proposed by Dudarev et al. [11]. The corresponding values of *U* parameter were obtained previously: *U* = 4.0 eV for the Sn 4*d* electrons [12] and *U* = 3.8 eV for the Fe 3*d* electrons [13].

A cut-off kinetic energy of 480 eV has been used, which is obtained by converging the total energy of SnO₂ primitive unit cell to less than 1 meV atom⁻¹. Γ -centred Monkhorst-Pack (MP) grid with a 0.035 Å⁻¹ separation has been applied corresponding to a *k*-point mesh of 6 × 6 × 8 for the 6-atom primitive unit cell of the tetragonal, D_{4h}¹⁴ (P4₂/mnm) space group. The above-mentioned parameters were obtained through the atomic relaxation until all the forces were found to be < 0.008 eV Å⁻¹ and the equilibrium state of the system was achieved. To study effects produced by the Fe dopants, 6-atom primitive unit cell was expanded sixteen times, 2 × 2 × 4 extension, resulting in a 96-atom supercell. The *k*-point mesh of 3 × 3 × 2, maintaining the same MP grid with a 0.035 Å⁻¹ separation in the reciprocal space, has been exploited for integrations over the Brillouin zone for the large supercell. Band structure features and lattice parameters of pure SnO₂ have been successfully reproduced and are described in detail elsewhere [12, 14].

3. RESULTS AND DISCUSSION

Impurity-produced perturbation leads to atomic displacements in the region surrounding the Fe atom. Our computations show that only six defect-neighbouring O atoms have non-negligible shifts from their original positions within the crystalline lattice.

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These movements are towards the Fe atom. The four defect-nearest oxygens situated in the basal plane move by 0.09 Å whereas the oxygens along the vertex relax around 0.07 Å. In our mind, the main reason of defect-inward motions is the change in ionic radii due to the Fe \Rightarrow Sn substitution. Fe ion in six-fold neighbourhood has 0.61 Å radius while the host Sn ion has larger 0.69 Å ionic radius [15]. Thus, the doping procedure produces some extra space in the defective region around the point defect and the neighbouring oxygens try to fill in this space by defect-inward shifts.

A local magnetic moment occurs in the material because of the performed doping and it is equal to 2.00 μ_B . The main contribution to this value is done by the Fe atom itself, 2.29 μ_B , which is predominantly due to the Fe 3d electrons. Nevertheless, the six impurity-neighbouring O atoms also contribute towards the magnetic moment of the system. These contributions are due to the O 2p electrons and come from the four basal oxygens, $-0.036 \mu_B$ from each atom, as well as from the two vertex oxygens, $-0.057 \mu_B$ from each atom. It has to be stated that computed magnetic moment, 2.29 μ_B per Fe atom, is larger than in any other simple iron oxide. For instance, the net magnetic moment per iron in magnetite (Fe_3O_4) is $4/3 = 1.3 \mu_B$, whereas that in YIG ($\text{Y}_3\text{Fe}_5\text{O}_{12}$) material is $5/5 = 1.0 \mu_B$ [16]. Our results also show that the magnetic orientation of the O 2p electrons is antiparallel to that of the 3d electrons of impurity. In the SnO_2 structure, the impurity Fe atom has octahedral environment and the effect of environment on the Fe 3d electrons is determined by the amount of overlap between the Fe 3d and O 2p atomic orbitals (AOs). Obviously, the t_{2g} orbitals (d_{xy} , d_{xz} and d_{yz}) of iron are lowered in energy, while the e_g orbitals (d_{z^2} and $d_{x^2-y^2}$) are raised in energy. Thus, the Fe^{2+} ion exhibits high-spin configuration (Fig. 1) when doped in SnO_2 crystal. In such a configuration the electrons first occupy each orbital before any orbital becomes doubly occupied. Thus due to the Pauli principle the orientation is antiparallel and that is a necessary condition for the direct short range exchange interaction. So, we think that direct exchange interaction [17, 18] might be responsible for the magnetism occurring in the Fe-doped SnO_2 material where we find antiparallel magnetic orientation between the electrons in the Fe 3d and O 2p AOs, respectively. We would like to add that low-spin configuration (Fig. 2), in which the

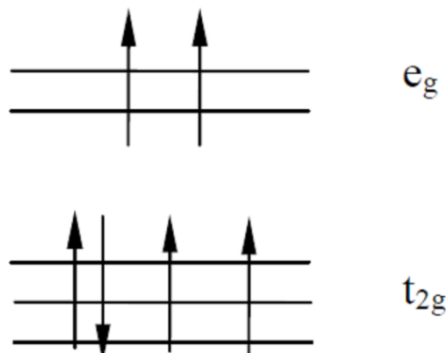


Fig. 1 – Electronic configuration for the high-spin case of the Fe^{2+} ion in the octahedral environment of the SnO_2 rutile structure



Fig. 2 – Electronic configuration for the low-spin case of the Co^{2+} ion in the octahedral environment of the SnO_2 rutile structure

electrons doubly occupy lower energy orbitals before occupying the higher energy states leads to the parallel alignment between the Fe 3d and O 2p electrons as it was recently shown in Co-doped SnO_2 [19].

Iron incorporation into the SnO_2 crystal produces changes upon the electronic band structure of the material. The density of states (DOS) pattern (Fig. 3) shows a local unoccupied level within the band-gap region. This state is composed mainly of the Fe 3d and O 2p AOs. That is why one can assume a strong hybridization effect between the Fe 3d and O 2p within the forbidden energy region. Actually, hybridization between the Fe 3d and O 2p states are also observed within the upper valence band (VB) region; in particular, in the energy interval between -6 eV and -3 eV as it can be seen from Fig. 3. The effect of hybridization might occur due to the local microstructure in the defective region, i.e. defect-inward shifts of the Fe-nearest oxygens. These distortions lead not only to the hybridization phenomenon but also to the spin polarization within the FeO_6 complex and consequently to the magnetic features described above.

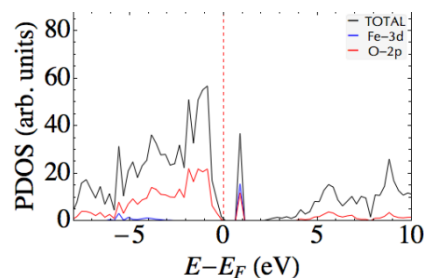


Fig. 3 – DFT + U computed total DOS of the Fe-doped SnO_2 material. Observed local in-gap state is due to the Fe 3d and O 2p AOs. Only upper valence band and conduction band is indicated. Vertical line denotes Fermi level

Different impurity doping rates have been considered by incorporating the second and the third iron atom into the SnO_2 crystalline lattice. It was found that defects tend to avoid each other and no clusterization effect takes place. Structural and magnetic properties of the SnO_2 doped with iron at higher concentrations are practically identical to those for low impurity doping rate described above. Each Fe atom creates a local magnetic moment with its six octahedrally situated neighbouring O atoms displacing themselves towards the point defect. The alignment between the Fe 3d electrons

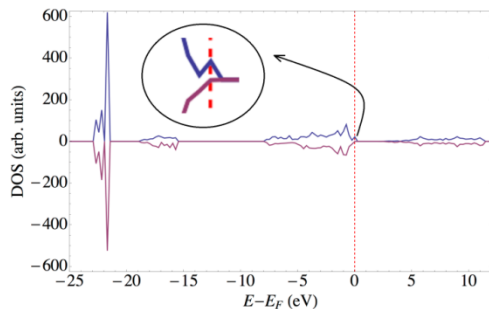


Fig. 4 – DFT + U computed total DOS of two Fe impurities incorporated into the 96-atom SnO_2 supercell. An empty band has been observed at the top of the upper VB. Vertical line denotes Fermi level

and the O $2p$ electrons contributing to the local magnetic moment is always antiparallel. However, at higher doping rates we observe some changes into the DOS pattern. Especially, as one can notice from Fig. 4, the Fe $3d$ – O $2p$ hybridized band moves from the band-gap region to lower energies and now are situated at the top of the upper VB. We interpret these results stating that Fe impurity generates unoccupied band at the top of the upper VB since there is a notable energy between the Fermi level and the last state corresponding to the upper VB. This energy interval is populated by holes and, in principle; one might expect the occurrence of p -type electrical conductivity within the crystal similar to that recently discovered in Sc-doped TiO_2 crystals [20].

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However, strictly speaking such a possibility is very low since these holes are not free to move through the lattice. Due to the hybridization phenomenon these holes are localized on the Fe atoms and we do not expect any changes upon the electrical properties of the material. Our results on electrical features are supported by the experimental spray pyrolysis technique measurements [21] arguing that starting from 2 mol. % iron doping concentrations the resistivity of the SnO_2 sample augments and the carrier concentration reduces.

4. CONCLUSIONS

Investigation of Fe-doped SnO_2 materials carried out by the DFT + U methodology demonstrates that overlap between the Fe $3d$ and impurity-neighbouring O $2p$ states lead to the hybridization phenomenon between the mentioned states. As a result, spin polarization occurs close to the Fe site. Iron exhibits high spin state in all considered models independently of its concentration. Only six Fe-nearest O atoms are coupled to the impurity most probably via short-range direct exchange interactions occurring within the FeO_6 complex. This complex is formed by the defect-inward dislocations which consist of four basal oxygen movements by about 0.09 \AA and two vertex oxygen displacements by approximately 0.07 \AA . According to the present study, atomic shifts in the defective region and magnetism are inter-related and are responsible for antiparallel magnetic alignment between the Fe $3d$ and O $2p$ electrons within the FeO_6 complex.