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Density functional theory description of the mechanism of ferromagnetism in nitrogen-doped SnO_2

Run Long, Niall J. English *

The SEC Strategic Research Cluster and the Centre for Synthesis and Chemical Biology, Conway Institute of Biomolecular and Biomedical Research, School of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin 4, Ireland

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ABSTRACT

Based on first-principles calculations, we have studied the occurrence of spin polarization in the magnetic metal oxide SnO_2 doped with nonmagnetic nitrogen (N) impurities. It was found that the local magnetic moments are localized mainly on the N dopant, causing a total moment of $0.95\mu_B$ per cell. The long-range magnetic coupling of N-doped SnO_2 may be attributed to a p–p coupling interaction between the N impurity and host valence states.

1. Introduction

Dilute magnetic semiconductors (DMS) have attracted much attention due to their potential application in spintronics. Most previous studies have focused on magnetic 3d transition-metal (TM) doped DMS, based on group III–V and II–VI host materials [1,2]. Recently, however, unexpected high-temperature ferromagnetism (FM) has been observed in a series of materials, which do not contain ions with partially filled d or f bands [3]; this has provoked a strong interest in investigating further the occurrence and nature of high-temperature ferromagnetism.

SnO_2 is a wide band-gap material which has been used as a transparent conducting electrode in solar cells [4] and gas sensors [5]. TM (Co, Fe, Cr, V, and Ni)-doped SnO_2 exhibits ferromagnetism above room temperature (RT) [6–10]. However, the origin of ferromagnetism observed in these different experiments is still under debate; Rahman et al. [11] have even showed that it is possible to induce magnetism in SnO_2 without doping of TM from first-principles. Recently, RT ferromagnetism was found in C-doped ZnO by replacement of O atoms by C atoms [12]. The group reported subsequently using first-principles calculations that N-doped ZnO can also display weak ferromagnetism [13]. Besides ZnO, Gu et al. [14] also reported that ferromagnetism was found in N-doped MgO within the tight-binding approximation and quantum Monte Carlo simulation. It would appear that the phenomenon of d^0 ferromagnetism may be a distinct possibility in a range of metal oxides.

In the present work, we have studied the electronic structure and magnetic properties of N-doped SnO_2 by density functional theory (DFT) calculations for a series of N-doped configurations. The calculated results show that each N atom induces a magnetic moment of $0.95\mu_B$ per cell and the N dopants tend to substitute the neighboring anions and favor FM spin-ordering. Long-range RT ferromagnetic behavior was found to be associated with holes mediated through p–p interaction between the impurities and host atoms. We corroborated this finding further by examination of the spatial spin distribution.

2. Methodology

All of the spin-polarized DFT calculations were performed using the projector augmented wave (PAW) pseudopotentials, as implemented in the VASP code [15,16]. The Perdew and Wang parametrization [17] of the generalized gradient approximation [18] was adopted for the exchange-correlation potential. The electron wave function was expanded in plane waves up to a cutoff energy of 400 eV and a Monkhorst–Pack k-point mesh [19] of $4 \times 4 \times 4$ was used for a $(2 \times 2 \times 2)$ 48-atom rutile SnO_2 supercell for geometry optimization and electronic property calculations. The cell and atomic relaxations were carried out until the residual forces were below 0.01 eV/Å. The optimized lattice parameters

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* Corresponding author.
E-mail address: niall.english@ucd.ie (N.J. English).

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were $a = b = 4.764$ Å and $c = 3.221$ Å, in good agreement with experimental values [20].

3. Results and discussion

3.1. Local magnetic order

Replacement of a single O atom by one N atom (N@O) in the supercell corresponds to a 2.08% N concentration. N@O favors a spin-polarized state and its total energy is 439 meV lower than that of nonspin-polarized states, indicating thereby that the ground state of N-doped SnO_2 is stable. Each N impurity introduces a total magnetic moment of $0.95\mu_B$ per cell, composed of $\sim 0.72\mu_B$ from N itself, $\sim 0.14\mu_B$ from its nearest-neighboring O atoms and $\sim 0.09\mu_B$ from its next nearest-neighboring Sn atoms. In essence, the substitution of an O atom by an N atom leads to a spontaneous magnetization of N inside SnO_2. The calculated total density (DOS) and projected DOS (PDOS) of 2p states of N, of the nearest-neighboring O atoms and of the 3d states of one of the next nearest-neighboring Sn atoms, are shown in Figs. 2(a) and (b), respectively. As shown in Fig. 2, the N 2p states are distributed mainly in the valence band due to the hybridization with O 2p states, leaving unoccupied ghost states in the forbidden gap. Fig. 2 shows also that N 2p states overlap slightly with O 2p and Sn 3d states above the Fermi level, E_F, resulting in an obvious splitting above E_F. The corresponding spin-density distribution is shown in Fig. 3(a). It shows clearly that the spin density in N-doped SnO_2 is localized mainly on the N atom and distributed slightly on its eight nearest-neighboring O atoms and the three first-neighboring Sn atoms. This means that magnetic orbital coupling extends to the nearest-neighboring O atoms from the N dopant center. Therefore, anions from the delocalized p orbitals contribute chiefly to the magnetic moment in N-doped SnO_2.

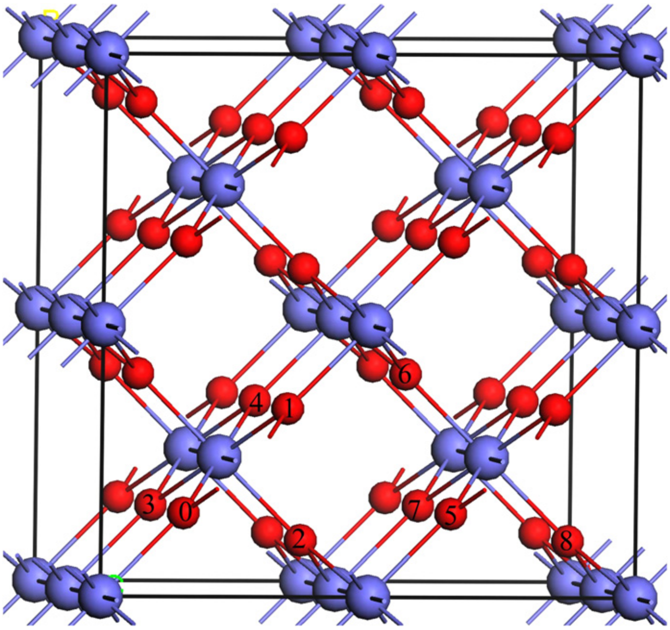

Fig. 1. 48-atom (2 × 2 × 2) supercell of rutile SnO_2 employed to define model B-doped SnO_2 structures. The large green and small red spheres represent the Sn and O atoms, respectively. The O atoms labeled by 0–8 are the sites to be replaced with N atoms.

3.2. Long-rang magnetic order

To examine long-range magnetic coupling of magnetic moments in N-doped SnO_2, we considered eight different configurations of two-N-atom anion doped SnO_2, corresponding to a dopant concentration of 4.2%. For convenience, the replaced oxygen atoms have been marked with numbers 0-8 in Fig. 1. The eight structures were obtained by two N atoms substituting two O atoms at $(0, 1)$, $(0, 2)$, $(0, 3)$, $(0, 4)$, $(0, 5)$, $(0, 6)$, $(0, 7)$, and $(0, 8)$ with different N–N distances, respectively.

Table 1 lists the energy difference between FM and antiferromagnetic (AFM) spin-ordering and the magnetic moments of these eight dopant configurations. The energy difference between the FM state and AFM state ($\Delta E = E(\mathrm{FM}) - E(\mathrm{AFM})$) spin-ordering indicates the lowest one to be the ground-state magnetic ordering. The calculated results show that the magnetic moments of the two N dopants favor significantly the FM state in the $(0, 1)$ configuration, and the energy of the FM state is 43 meV lower than that of the corresponding AFM state. Its magnetic moments in-

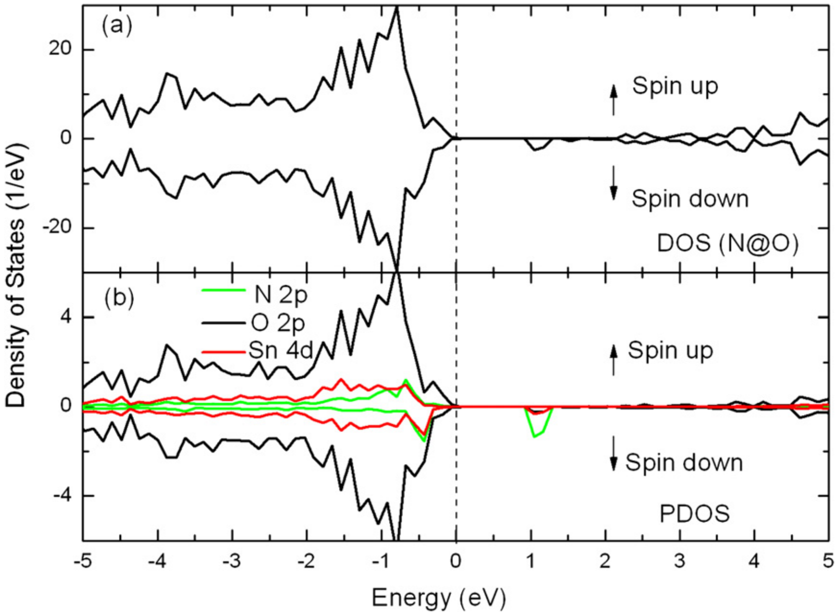

Fig. 2. (a) Total DOS of N-doped SnO_2 and (b) projected DOS for N 2p, the eight nearest-neighbor O 2p states and three nearest-neighbor Sn 4d orbitals. The Fermi level has been set to zero.