Ab initio calculation of electric field gradient and magnetic hyperfine field in Fe-doped SnO$_2$

Qiaoli Zhang · Daqing Yuan · Ping Fan · Yi Zuo · Yongnan Zheng · Xiaqiang Ma · Juncheng Liang · Huanqiao Zhang · Shengyun Zhu

Abstract Ab initio calculations of the magnetic and electric hyperfine fields and the magnetic moments were performed for the Fe doped SnO$_2$ dilute magnetic semiconductors with the Wien2k code embodying the full-potential linearized augmented plane-wave method. The calculated results for the neutral system and the different charged state systems with and without the oxygen vacancy show clearly that the ground state is all magnetic and that the addition of electrons and the appearance of oxygen vacancy can increase the magnetic moment and the magnetic hyperfine field and reduce the electric hyperfine field. The energy level splitting of the Fe-3$d$ orbit can lead to enhancing the magnetic moment and, therefore, a very large magnetic moment of 5 $\mu_B$ is obtained for the Sn$_{15}$Fe$^{1-}$O$_{32}$ charged system.

Keywords Fe-doped SnO$_2$ · O vacancy · Ab initio calculation · Magnetic and electric hyperfine field · Magnetic moment

1 Introduction

Spintronics is an emerging technology in solid state devices, which exploits both the intrinsic spin of the electron and its associated magnetic moment in addition to its electronic charge. Dilute magnetic semiconductors (DMS) have attracted much attention because of their promising applications in spintronics. Tin dioxide (SnO$_2$) is an important semiconductor with wide-band-gap that makes it possible to become DMS by the doping of SnO$_2$ with transitional metals (TM). The giant magnetic moment (GMM) of 7.5 $\mu_B$ was discovered in Co-doped SnO$_2$, which encourages the investigation of different TM-doped SnO$_2$ [1]. The ferromagnetism (FM) of Fe-doped SnO$_2$ have been reported with a high Curie temperature
Q. Zhang et al.

of Tc = 850 K [2], which is the highest among the reported ones for TM-doped semiconductor oxides. The high temperature ferromagnetism was observed in many TM-doped SnO2 such as in Fe, Cr, V and Ni doped SnO2 [3, 4]. Fitzgerald et al. investigated the SnO2 doped with Cr, Fe, Co, Ni etc and no GMM was found [5]. No consensus has been reached experimentally on GMM in SnO2, and the origin of high temperature ferromagnetism in SnO2 based DMS is still an open question.

The first-principles calculations using the ultra-soft pseudopotential showed that large lattice distortion in Fe-doped SnO2 would induce the ferromagnetism and that the direct exchange interaction between the O–2p and Fe–3d electrons with antiparallel spins may bring about a competition between the ferromagnetic and anti-ferromagnetic super-exchange interactions [6]. Coey et al. and Fitzgerald et al. have investigated the pulsed-laser deposited Sn0.95Fe0.05O2 thin films by Mössbauer spectroscopy [3, 5]. The 57Fe Mössbauer spectra measured at room temperature showed that the magnetic hyperfine field at Fe is 51.6T that is larger than the one for the simple Fe oxides.

However, a consensus on the origin of the ferromagnetism in SnO2 has been kept still unknown. In order to shed light on the mechanism of FM in DMS, we have calculated the electric field gradient, magnetic hyperfine field and magnetic moment and investigated the microscopic electronic structure by performing large super-cell (SC) calculations for the Fe-doped SnO2 with the different Fe valence states and the effect of oxygen vacancy (V_O).

2 Ab initio calculation

SnO2, as the same as the well-known TiO2, has a tetragonal rutile structure with space group P42mm and unit cell parameters a=b=4.737 and c=3.185 [7]. In the unit cell, the Sn atoms are surrounded by the O atoms, leading to a slightly distorted octahedron with four O atoms at the tetrahedron base (O1)and two at the vertex (O2). A 2×2×2 super-cell with eight unit cells of SnO2 was constructed as shown in Fig. 1. This super-cell contains totally 48 atoms including 16 Sn atoms and one Sn atom among the 16 atoms is replaced by a Fe atom. The Fe concentration is 6.25 at % in Sn15FeO32. The valence state of Fe atoms is important to the ab initio calculation for Fe-doped SnO2 dilute magnetic semiconductors. To deal with the different valence states of the Fe atom in Fe-doped SnO2, two physical situations are considered: (i) the neutral system of Sn15Fe0O32 and (ii) the charged systems of Sn15Fe1−O32, Sn15Fe2−O32 and Sn15Fe2−O31–V_O. The Sn15Fe1−O32 and Sn15Fe2−O32 system are one electron and two electrons added super-cells, respectively. O vacancies have been observed to have great effect on the ferromagnetism in SnO2 [8, 9]. Then, the charged system of Sn15Fe2−O31–V_O formed by removing an oxygen atom was studied. There are three possible oxygen vacancy sites marked by 1, 2 and 3 as shown in Fig. 1: (1) a basal O site of Fe-contained octahedron (Sn15Fe2−O31–V_O1), (2) a vertex O site of Fe-contained octahedron (Sn15Fe2−O31–V_O2) and (3) an O site which is the farthest site from the Fe atom in the super-cell (Sn15Fe2−O31–V_O3).

The spin-polarized and un-polarized calculations were performed by using the Wien2k code, which embodies the full-potential linearized augmented plane-wave method [10]. The exchange and correlation effects were treated within the density-functional theory using the generalized gradient approximation (PBE-GGA) [11]. In the calculations the atomic sphere radii of Sn, O and Fe atoms were set at 2.0, 1.8, and 2.0 a.u., respectively. The parameter
Ab initio calculations of electric field gradient and magnetic hyperfine field in Fe-doped SnO$_2$

Fig. 1  Schematic drawing of $2 \times 2 \times 2$ super-cell of 48 atoms in SnO$_2$. Red and grey balls represent O and Sn atoms, respectively. One of the Sn atom is replaced by a Fe atom. Possible O vacancies are denoted by 1, 2 and 3.

$R_{mt}K_{\text{max}}$, which controls the basis function size of the basis set in the calculations, was chosen to be 7, where $R_{mt}$ is the smallest muffin-tin radius in the unit cell and $K_{\text{max}}$ is the cut-off energy for the plane wave. A grid with the $4 \times 4 \times 4$ k points in the first Brillouin zone was used in the k-space integration. The relaxation process was treated by the Newton dampened method, and the forces were calculated with a self-consistent potential in each displacement step and the calculations were done step by step until the force vanished. Lattice parameters for Sn$_{0.95}$Fe$_{0.05}$O$_2$ are $a=b=4.73$ and $c=3.181$ [5], which are close to that of the pure SnO$_2$. Therefore, the structure relaxations of the Fe-doped SnO$_2$ super-cell were calculated by fixing the lattice parameter at the value of the pure SnO$_2$ and the internal coordinates were fully relaxed until the forces on the ions are below 0.05 eV/Å.

3 Results and discussions

The calculated distances between the Fe atom and its nearest oxygen neighbors are listed in Table 1 for the studied super-cells with and without relaxation, respectively. The distance between the Fe atom and the O1 atom is larger than that between the Fe atom and the O2 atom for the neutral Sn$_{15}$Fe$^0$O$_{32}$ and the charged Sn$_{15}$FeO$_{32}$. The calculated distance is smaller than those for the un-relaxed SnO$_2$ system. The structural relaxations of the Sn$_{15}$Fe$^{2-}$O$_{31} - V_O$ are isotropic, which is different from the super-cell without an oxygen vacancy.

Then, the total energies of the super-cell for the non-magnetic (NM) and magnetic phases for the Fe-doped SnO$_2$ were calculated for the relaxed systems to identify the phase of the ground state. The results show that the total energies of the non-magnetic are higher than that of magnetic phase. This indicates that the ground state is magnetic.
Q. Zhang et al.

Table 1  Calculated distances between the Fe atom and the nearest O atoms for the Sn$_{15}$FeO$_{32}$ after structure relaxation (*Initial Un-relaxed initial system)

<table>
<thead>
<tr>
<th>System</th>
<th>d1(Fe−O1)</th>
<th>d2(Fe−O2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*SnO$_2$</td>
<td>2.051</td>
<td>2.057</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^0$O$</em>{32}$</td>
<td>1.925</td>
<td>1.922</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^1$−O$</em>{32}$</td>
<td>2.026</td>
<td>2.020</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^2$−O$</em>{32}$</td>
<td>2.047</td>
<td>2.027</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^2$−O$</em>{31}$(V$_{O1}$)</td>
<td>2.00</td>
<td>2.00 1.94</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^2$−O$</em>{31}$(V$_{O2}$)</td>
<td>1.924</td>
<td>1.924 1.924 1.924 1.938</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^2$−O$</em>{31}$(V$_{O3}$)</td>
<td>2.011</td>
<td>2.011 2.017 2.018 1.983 2.067</td>
</tr>
</tbody>
</table>

Table 2  Magnetic moments (µ$_B$) for Fe atoms $M^{Fe}$ and supercell $M^{Sc}$, magnetic hyperfine fields (MHF) and the electrifield gradients (V$_{ZZ}$) and their asymmetry parameters(η) 

<table>
<thead>
<tr>
<th>Supercells</th>
<th>$M^{Fe}$ (µ$_B$)</th>
<th>$M^{Sc}$ (µ$_B$)</th>
<th>V$_{ZZ}$ (10$^{21}$ V/m$^2$)</th>
<th>η</th>
<th>MHF(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$<em>{15}$Fe$^0$O$</em>{32}$</td>
<td>1.70</td>
<td>2.00</td>
<td>15.03</td>
<td>0.27</td>
<td>22.8</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^2$−O$</em>{31}$(V$_{O1}$)</td>
<td>3.75</td>
<td>4.99</td>
<td>10.36</td>
<td>0.20</td>
<td>−45.2</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^2$−O$</em>{31}$(V$_{O2}$)</td>
<td>3.62</td>
<td>4.36</td>
<td>−4.68</td>
<td>0.64</td>
<td>−45.1</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^2$−O$</em>{31}$(V$_{O3}$)</td>
<td>3.99</td>
<td>4.92</td>
<td>3.15</td>
<td>0.05</td>
<td>−49.4</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^2$−O$</em>{32}$</td>
<td>3.79</td>
<td>4.46</td>
<td>7.30</td>
<td>0.11</td>
<td>−43.9</td>
</tr>
<tr>
<td>Sn$<em>{15}$Fe$^1$−O$</em>{32}$</td>
<td>3.99</td>
<td>5.00</td>
<td>2.85</td>
<td>0.09</td>
<td>−45.5</td>
</tr>
</tbody>
</table>

Table 2 shows the magnetic moments, the electric field gradients and their asymmetry parameters and the magnetic hyperfine fields at the Fe site for the neutral and charged systems. It can be seen from Table 2 that the magnetic moments of the charged systems are much larger than the one of the neutral system, indicating that addition of electrons can increase the magnetic moment. The supcell magnetic moment of the Sn$_{15}$Fe$^2$−O$_{32}$ system is 4.46 µ$_B$, that is in agreement with the result of 4.00 µ$_B$ per super cell given by [6]. Also, the magnetic moments with O vacancy are much larger than the one for the neutral system, which demonstrates that the removing of the O atom can increase the magnetic moment. The rather large magnetic moment of 5µ$_B$ was obtained for the Sn$_{15}$Fe$^1$−O$_{32}$.

Since the electronic configuration of Fe is 3d$^6$4s$^2$, the local octahedral crystal field is symmetric. The Fe−3d states are split into the tripe-degenerated $t_{2g}$ state and the double-degenerated $e_g$ state [12]. The interaction between the Fe atom and the oxygen atom changes the energy levels $t_{2g}$ and $e_g$ states. Depending on the magnitudes of the splitting and pairing energies, the electrons may fill in the $t_{2g}$ and/or $e_g$ states. Then, the spin-split changes the level occupation of the electrons. Figure 2 shows the energy splitting of the density of states (DOS) of Fe−3d for the neutral system (a), charged system without (b) and with (c) oxygen vacancy. For the neutral system (Fig. 2)a, three electrons occupy the $t_{2g}$ state and one electron occupy the $e_g$ state and there are two unpaired electrons, which generate a magnetic moment of 2 µ$_B$. For the charged system with the addition of electrons (Fig. 2)b, three elections occupy the $t_{2g}$ state and two electron occupy the $e_g$ state. These 5 unpaired produce a large magnetic moment of 5 µ$_B$. For the the charged system with oxygen vacancy (Fig. 2)c, the $t_{2g}$ state and the $e_g$ state state are all occupied by two unpaired electrons, leading to the generation of a magnetic moment of 4 µ$_B$.
The magnetic hyperfine fields of the charged systems with and the O vacancy are obviously larger than that of the neutral system. The hyperfine fields of the charged systems are all higher than 45T. Both the calculated magnetic moments and magnetic hyperfine fields are in good agreement with the results given by Mössbauer spectroscopy [3, 5]. The addition of electrons and/or the removing of O atom can increase the MHF.

The absolute values of the electric field gradients of the charged systems with and without the O vacancy are smaller than the one that of the neutral system. This illustrates that the electric hyperfine fields can be suppressed by adding the electrons and/or removing the O atom.

4 Conclusion

Ab initio calculations of the magnetic and electric hyperfine fields and the magnetic moments have been performed for the Fe doped SnO\(_2\) dilute magnetic semiconductor. The obtained results show that the ground states of the Fe-doped SnO\(_2\) with and without O vacancies are all in ferromagnetic phase and that the addition of electrons and the removing of oxygen atoms can increase both the magnetic moments and magnetic hyperfine fields and reduce the electric hyperfine fields for the dilute magnetic semiconductors. The magnetic hyperfine fields are all higher than 45T for the charged systems with and without the oxygen vacancy and a rather large magnetic moment of 5\(\mu_B\) was obtained. The electric fields of the charged systems are obviously smaller than that of the neutral system. The present Ab initio calculations provide very useful information for the preparation of the SnO\(_2\) based dilute magnetic semiconductors (DMS).

Acknowledgments This work was supported by National Science Foundation of China under Grant No. 11305271. We are grateful to Prof. Heinz Hass, Instituto Tecnológico e Nuclear, Estrada Nacional Portugal and CERN/PH-IS, Geneve-23, Switzerland, and Prof. Stefaan Cottenier, Center for Molecular Modeling, Ghent University, Belgium, for many valuable discussions.
References