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Half-metallicity, magnetic moments, and gap states in oxygen-deficient magnetite for spintronic applications

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The electronic structure near oxygen vacancies in half-metallic magnetite has been calculated using first principles methods. Oxygen vacancies are responsible for the existence of gap states occupied by majority and minority spin electrons. We discuss whether these defects modify the spin magnetic moments, the magnetization, the magnetic coupling between Fe ions, and the half-metallic behaviour of magnetite. These results, which contribute to remove stumbling blocks to magnetite-based spintronic devices, could be useful to analyze the conductivity, the magnetotransport and magnetic properties, the electron and optical spectra of actual magnetite electrodes. © 2012 American Institute of Physics. [doi:10.1063/1.3678028]

Transition metal oxides form a class of materials with a huge variety of magnetic and electronic properties, which can be tuned when these materials are grown as thin layers.^{1,2} Half-metallic oxides, i.e., oxides with a metallic behaviour for one spin direction and an insulating behaviour for the other one, should in particular give access to huge magnetoresistance effects when used as magnetic electrodes in spintronic devices. Several half-metallic oxides have been considered for this reason, and a high spin-polarization has been measured in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (Curie temperature $T_C = 370$ K),³ $\text{Sr}_2\text{FeMoO}_6$ ($T_C = 410$ K),^{4,5} CrO_2 ($T_C = 395$ K),^{6,7} and magnetite Fe_3O_4 between the Verwey temperature (120 K), and $T_C = 858$ K.⁸ The magnetoresistance measured in magnetite-based stacking is unfortunately far lower than the high value expected with half-metals.^{9–11} All the possible explanations must be considered successively to identify the genuine reason for these bad performances and to break the deadlocks standing in the way of magnetite-based devices. Several studies focused on the modification of the physical properties of magnetite induced by structural defects like antiphase boundaries^{12–15} and cationic vacancies^{16,17} or by interfaces with an insulating barrier.^{18,19} We propose to study a new scenario to explain the low performances of magnetite-based devices, namely the modification of the electronic structure induced by oxygen vacancies in this oxide.

Changes induced by oxygen vacancies can be important in magnetic oxides, partly because these defects decrease the number of magnetic atom-O-magnetic atom bridges responsible for the superexchange and double exchange interactions which govern the magnetic order. First principles calculations have also confirmed that oxygen vacancies modify the magnetization of some magnetic oxides.^{20–22} The effects of oxygen vacancies have been studied experimentally in insulating spinel ferrites^{23–30} but not in half-metallic magnetite.

Bulk magnetite crystallizes in the inverse spinel structure above 120 K: its ionic description consists in O^{2-} ions arranged in a distorted face-centered-cubic (fcc) lattice, which defines tetrahedral sites (A-sites) and octahedral sites

(B-sites) in which Fe^{2+} and Fe^{3+} ions settle down according to the formula $[\text{Fe}^{3+}]_A[\text{Fe}^{2+}, \text{Fe}^{3+}]_B\text{O}_4^{2-}$. According to Hund laws, Fe^{2+} and Fe^{3+} ions, respectively, have a magnetic moment of 4 and $5 \mu_B$ in this oxide. Fe ions in tetrahedral sites are antiferromagnetically coupled to those in octahedral sites, leading to a magnetic moment of $4 \mu_B$ per formula unit. In the perfect crystal, any oxygen atom is bounded to 1 Fe_A and 3 Fe_B atoms. When the magnetite crystal contains an amount of oxygen vacancies corresponding to the formula $\text{Fe}_3\text{O}_{4-\delta}$, the oxidation degree of Fe atoms is reduced, two electrons being restored to the crystal for each neutral oxygen atom removed from the lattice. Consecutive changes in the magnetic moments of Fe_A , Fe_B , and Fe_3O_4 formula unit are not easy to guess. One could expect that each oxygen vacancy is responsible for the reduction, from Fe^{3+} to Fe^{2+} , of two of the nearest neighbour Fe ions. However, the reduced Fe ions could be either the Fe_A and one of the three first neighbour Fe_B or two Fe_B ions. In the first case, the restored electrons have opposite spin states and the magnetization of the crystal does not change. In the second case, the two electrons belong to minority spin bands, and the magnetic moment per formula unit decreases to $4(1-\delta/2) \mu_B$. In this discussion, we made the assumption that the global magnetic coupling between Fe atoms is qualitatively the same near an oxygen vacancy as in bulk magnetite. In the two possible situations described above, the restored electrons should occupy localized states with energy inside an energy gap of bulk magnetite (vacancy induced gap states). In any cases, the density of states (DOS) of magnetite may be strongly distorted by oxygen vacancies, the presence of which could even suppress the half-metallic behaviour. In this letter, we used first principles calculations to describe the modification of the electronic structure induced by diluted oxygen vacancies in magnetite. We show how these point defects modify the electron states, the magnetic moment of the metallic ions, and the magnetization of the crystal. We check whether vacancy induced gap-states exist and whether these states suppress the half-metallicity.

The supercell we used was built from the conventional cubic cell of magnetite containing 56 atoms or 8 formula units, in which we have removed 1 oxygen atom ($\delta = 1/8$). We neglected the fact that the lattice parameter may change

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with the vacancy content and we used the parameter of bulk magnetite $a = 0.8397$ nm. We used the full potential linearized augmented plane wave code Wien2k (Ref. 31) and performed calculations within the local spin density approximation (LSDA), the LSDA+ U approximation,³² and with the hybrid functional PBE0 (Refs. 33 and 34) as implemented in Wien2k.³⁵ These two last approximations correct the spurious self-interaction and have given similar results for bulk magnetite.¹⁵ For the LSDA+ U calculations, we used the parameters $U = 4.5$ eV and $J = 0.56$ eV proposed by Anisimov³⁶ and Novák.³⁷ We used an energy cut-off of 25 Ry for the plane wave expansion of the Kohn-Sham wave functions in the interstitial area. The irreducible wedge of the first Brillouin zone was sampled with 60 Bloch vectors. The input data for the first iteration of each self-consistent calculation consist in the superposition of spin densities calculated for isolated atoms. These spin densities have been calculated using the spin populations which ensure an antiferromagnetic coupling between all the Fe_A and Fe_B atoms, except atoms close to a vacancy for which different initial spin populations have been tried. These different trials allowed rejecting metastable magnetic ordering and give access to the ground state which correctly describes the magnetic coupling between Fe atoms near the vacancy. The relaxation of the atomic positions was performed and stopped when the force applied on each atom was lower than 1.5 eV/Å. We checked that our conclusions on the physical properties of oxygen deficient magnetite remain valid for vacancy contents up to $\delta = 1/2$ (increasing δ only results in a widening of the gap-state peaks in the DOS curves). In the following, we only discuss in details the results obtained for $\delta = 1/8$.

Our calculations have shown that the relaxation of the atom coordinates mainly concerns Fe_A and Fe_B ions in the vicinity of the vacancy: the bounding lengths are reduced by 1% between the Fe_B atoms first neighbour of the vacancy and the oxygen atoms to which they are bounded and by 2.3% between the same oxygen atoms and Fe_B atoms second neighbour of the vacancy. The closest Fe_A ion is displaced along the [111] direction, by a distance of 0.22 Å away from the vacancy. The modifications of the electronic structure induced by oxygen vacancies are described in Fig. 1, in which we compared the majority and minority spin total DOS of Fe₃O_{3.875} (dark lines) and bulk Fe₃O₄ (red/light lines) calculated in the LSDA, LSDA+ U , and PBE0 approximations. For better clarity, we have chosen to align in this figure the main band edges which appear in the total DOS curves of Fe₃O_{3.875} and Fe₃O₄. Indeed, using the LSDA+ U and PBE0 approximations, the position of the Fermi level E_F with respect to band edges changes after removing an oxygen atom from the supercell. This shift of E_F would have been negligible at a smaller oxygen vacancy content. From Fig. 1, we can very easily identify the defect-induced electron states which appear in the energy gaps of bulk magnetite; these occupied gap-states are responsible for the important shift of the Fermi level observed in the LSDA+ U and PBE0 calculations. The modification of the electronic structure induced by oxygen vacancies is more important for the PBE0 than for the LSDA+ U approximation. In particular, the shift of the Fermi level of Fe₃O_{3.875} with respect to the unoccupied band edge of Fe₃O₄ is of 1.04 eV for the

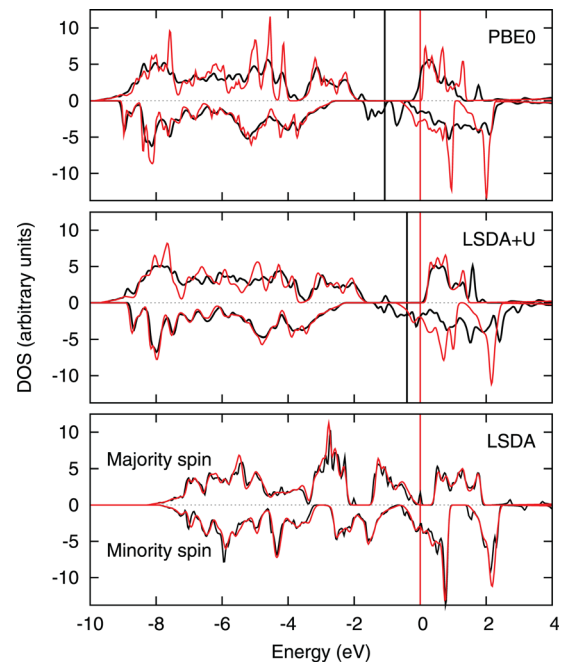


FIG. 1. (Color online) Total DOS of Fe₃O_{3.875} (dark curves) and Fe₃O₄ (red/light curves). From the bottom to the top, the different panels correspond to the LSDA, LSDA+ U , and PBE0 calculations. The DOS curves of Fe₃O_{3.875} have been shifted to align the main band edges to those of bulk magnetite. The Fermi level of Fe₃O_{3.875} and Fe₃O₄ are indicated by dark and red vertical lines.

PBE0 calculation and of 0.39 eV with LSDA+ U . These two approximations, however, give rather similar results for the energy of the occupied gap-states with respect to E_F : for majority spin, these states appear at 0.7 eV for PBE0 and at 0.65 eV for LSDA+ U below E_F . For minority spin, the energy range where occupied gap states can be found below E_F has a width of 0.8 eV for PBE0 and of 1.17 eV for LSDA+ U . The PBE0 and LSDA+ U results show that the half-metallic character of magnetite is not destroyed at the relatively small content of oxygen vacancies considered here. The minority spin DOS at E_F is however lower for Fe₃O_{3.875} than for perfect bulk magnetite. It means that the magnetoresistive properties of magnetite-based devices should keep very high values, even if oxygen vacancies reduce the conductivity of the magnetite electrodes. The majority spin energy gap at E_F is narrowed by occupied gap-states, from 1.98 eV in Fe₃O₄ to 1.25 eV in Fe₃O_{3.875} in the PBE0 calculation, and from 1.91 eV to 0.86 eV with the LSDA+ U approximation. This narrowing of the energy gap should be observed in optical spectra. The advanced approximations PBE0 and LSDA+ U give similar DOS curves (with differences which could be reduced by adjusting the value of U and J). This is not the case of the LSDA approximation, which does not correct the spurious self-interaction and does not efficiently describe the localization of Fe d -orbitals, thus giving narrower energy gaps even for bulk magnetite. The occupied gap-states induced by vacancies are only shown by few very small DOS peaks with this approximation; one of these peaks even destroys the half-metallic character of magnetite.

Partial-DOS curves allow understanding which atoms are involved in the defect-induced gap states. Fig. 2 describes the contribution to the total DOS of the Fe_A and of

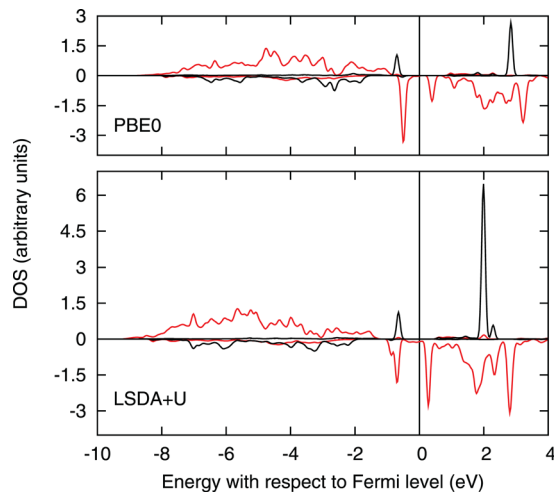


FIG. 2. (Color online) Contribution of the Fe_A (dark curves) and of one the 3 Fe_B (red/light curves) first-neighbour of the vacancy to the total density of states. The bottom and the top panels, respectively, correspond to the LSDA+ U and PBE0 calculations.

one of the three Fe_B atoms the closest from the vacancy. The PBE0 and LSDA+ U results show that the occupied majority spin gap-states near 0.7 eV below E_F mainly involve the closest Fe_A atom, while the minority spin gap-states at 0.5–0.8 eV below E_F belong to the Fe_B atoms first neighbour of a vacancy. This result confirms the ionic scenario in which the two electrons restored to the crystal per oxygen vacancy have different spin directions and are, respectively, captured by the closest Fe_A^{3+} and Fe_B^{3+} ions.

We found a similar ground state magnetic configuration for $\text{Fe}_3\text{O}_{3.875}$ than for Fe_3O_4 : the antiferromagnetic coupling between Fe_A and Fe_B atoms also holds in the vicinity of the vacancies, despite the suppression of some Fe-O-Fe bridges. The calculations also confirmed that the whole magnetization is the same for $\text{Fe}_3\text{O}_{3.875}$ and Fe_3O_4 . With the PBE0 hybrid functional, the absolute value of the spin magnetic moments of the Fe_A and Fe_B ions are, respectively, $0.54 \mu_B$ and $0.27 \mu_B$ lower close to the vacancy than in bulk magnetite. This lowering is of $0.41 \mu_B$ and $0.2 \mu_B$ with the LSDA+ U approximation. Again, the modification of the spin magnetic moments and the constant magnetization support the hypothesis that a majority spin electron restored by the oxygen vacancy is captured by the closest Fe_A^{3+} ion, while a minority spin restored electron belongs to one of the closest Fe_B^{3+} ions.

In conclusion, we have shown that electrons restored by oxygen vacancies to the magnetite crystal occupy gap states in the main energy gaps below E_F . Electrons occupying majority and minority spin gap states are, respectively, captured by the closest Fe_A and Fe_B atoms. These vacancy states are responsible for a decrease of the spin magnetic moments of the closest Fe atoms and for a narrowing of the energy gap (which should be observed in optical or photoemission experiments). These structural defects, however, do not modify the magnetization of the crystal and the ferrimagnetic ordering. The half-metallic behaviour is preserved in oxygen deficient magnetite, even if the minority spin DOS is smaller at E_F . Consequently, the hypothetical presence of oxygen vacancies could explain the relatively small conductivity of magnetite but not the disappointing magnetoresistance performances of magnetite-based spintronic devices.

The calculations presented in this article have been performed at the CALMIP/UPS Toulouse parallel computer centre.

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