Electronic structure and interface states at the Fe₃O₄/MgO(100) interface

R Arras, L Calmels, B Warot-Fonrose
Université de Toulouse; UPS; CEMES; BP 94347, F-31055 Toulouse Cedex, France
E-mail: arras@cemes.fr

Abstract. Magnetite Fe₃O₄ is a ferrimagnetic material which could be used for its interesting properties in spintronic devices. In particular, magnetic tunnel junctions with magnetite electrodes and a MgO insulating barrier should behave like an ideal magnetic switch, because of the half-metallic character of Fe₃O₄ and because of the negligible lattice mismatch between these two oxides. We have calculated the electronic structure of the Fe₃O₄/MgO(100) interface and we show that the density of states is modified at this interface. We report in particular on the possible existence of a majority spin interface state which could play an important role in the magnetotransport properties of Fe₃O₄/MgO/Fe₃O₄ magnetic tunnel junctions.

1. Introduction
Above the Verwey transition (Tᵥ = 122 K [1]) and below the Curie temperature (T₉ = 858 K), magnetite Fe₃O₄ crystallizes in the inverse spinel structure with an experimental lattice parameter of 8.397 Å. In this crystal, oxygen atoms are arranged in a fcc lattice, with tetrahedral and octahedral sites partly occupied by Fe atoms. The iron atoms located on the octahedral and tetrahedral sublattices are coupled antiferromagnetically. Theoretical results based on the density functional theory (DFT) have shown that magnetite is a half-metal, with a spin polarisation of 100 % at the Fermi level [2]. Half-metallicity has been confirmed by spin- and angle-resolved photoelectron spectroscopy when experimental results are not affected by an hypothetical surface reconstruction [3]. MgO is an insulator which crystallizes in the rock salt structure with a lattice parameter of 4.212 Å. Fully epitaxial Fe₃O₄/MgO multilayers can easily be grown because the fcc oxygen sublattices of MgO and Fe₃O₄ have nearly the same lattice parameters. This is the case of the Fe₃O₄/MgO/Fe₃O₄ magnetic tunnel junction (MTJ), which possess a continuous oxygen sublattice with different chemical species occupying the cation sites on both sides of the interfaces. The originality of this MTJ comes from the half metallicity of the magnetic electrodes, which ensures interesting magnetotransport properties, and from the fact that it could work at a rather high temperature (T < T₉).

Several attempts have been done to obtain high quality Fe₃O₄/MgO/Fe₃O₄ junctions. These MTJs have been grown by pulsed laser deposition [4], by molecular beam epitaxy [5], and by sputtering [6]. Measurements have confirmed the good quality and the epitaxial growth of these MTJs with abrupt interfaces. The magnetoresistance of these junctions is however lower than the expected value, and the interpretation of their current-voltage characteristics is not obvious.
and requires first principles calculation of the electronic structure near the interface between magnetite and MgO.

In this article, we describe the density of states (DOS) and the iron atom spin magnetic moments in the vicinity of the Fe$_3$O$_4$/MgO(100) interface. We show that localized interface states can exist, which may modify the transport properties of the magnetic tunnel junction.

2. Computational details and supercell used in the calculations

The calculations have been done with the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) code Wien2k [7], within the Local Spin Density Approximation (LSDA). For the LSDA functional, we used the fit of the Monte-Carlo simulations of Ceperley and Alder [8] proposed by Perdew and Wang [9]. In order to build a supercell for the calculation of the electronic structure of the interface, we first had to calculate the distance between MgO atomic layers strained on the magnetite substrate. We have estimated the deformation $\epsilon_{[100]}$ of the MgO layer in the [100] direction, when MgO is strained on a Fe$_3$O$_4$(100) substrate. This deformation is given by $\epsilon_{[100]} = -2\frac{C_{12}}{C_{11}}\epsilon_{[001]}$, which correspond to a distance of 0.214 nm between successive MgO atomic layers [10]. The distance between Fe$_3$O$_4$ atomic layers is the same as in bulk magnetite, for which we have used the experimental lattice constant. The width of the supercell which has been used in the calculation is of 3.391 nm in the [100] stacking direction. It includes a 1.679 nm Fe$_3$O$_4$ layer (containing 16 atomic layers with either Fe atoms in octahedral sites and oxygen atoms, or Fe atoms in tetrahedral sites) followed by a 1.712 nm MgO layer (which contains 8 atomic layers). The distance between atomic layers at the interface is an average of the distances between atomic layers on both sides of the interface. The magnetite thin layer has the same proportion of oxygen atoms, iron atoms in tetrahedral and octahedral sites than in bulk magnetite. We have built the supercell in such a way that the fcc sublattice of oxygen atoms is continuous across the interface, which means that octahedral Fe and Mg atoms face each other at the interface, separated by an oxygen atom. In order to minimize the interstitial region, we have used an atomic sphere radius of 1.9 a.u. for iron atoms in tetrahedral site, of 2.3 a.u. for iron atoms in octahedral site, of 1.4 a.u. for oxygen atoms in the magnetite layer, of 1.7 a.u. for oxygen atoms in the MgO layer, and of 2.1 a.u. for all the magnesium atoms, except those at the interface which have a radius of 1.5 a.u. For the fundamental parameter $RK_{max}$ (product of the smallest atomic sphere radius by the largest wave-vector used in the plane wave expansion) we have used the value $RK_{max} = 4.21$, and we checked that this value gives a density of states (DOS) for atoms at the center of the magnetite and MgO layers identical to the DOS calculated for the bulk materials. The irreducible wedge of the Brillouin zone was sampled with a $k$-mesh of 42 points.

3. Electronic structure at the Fe$_3$O$_4$/MgO interface

3.1. Majority spin electrons

Figure 1 shows the majority spin DOS integrated over the atomic spheres of the first and second Fe$_3$O$_4$ atomic layers near the interface. It can directly be compared to the DOS calculated for a single formula unit of bulk magnetite, which is also shown in this figure.

The last curve in figure 1 represents the density of states for bulk MgO. We can see that the DOS calculated for a single Fe$_3$O$_4$ formula unit near the interface is very similar to that calculated in bulk magnetite. The main differences between these curves correspond to DOS peaks which appear at the same time in the majority spin gaps of bulk magnetite and of MgO. These peaks are more clearly visible in figure 2 which corresponds to a zoom for the energy range [-3.0 eV;2.0 eV] around the Fermi level. The 3 peaks which appear in the energy gaps are indicated by vertical arrows. The most intense of these peaks appears at the Fermi level, and corresponds to a majority spin interface state (bidimensional spin polarised electron gas).
Figure 1. Majority spin DOS for a single Fe$_3$O$_4$ formula unit near the interface (top curve), a single Fe$_3$O$_4$ formula unit far from the interface, and a MgO formula unit far from the interface (bottom curve).

Figure 2. Majority spin DOS for a single Fe$_3$O$_4$ formula unit near the interface (top curve) and far from the interface (bottom curve). The dashed lines indicate the energy gaps of bulk magnetite. Peaks in the DOS which appear in this gaps are indicated by vertical arrows.

3.2. Minority spin electrons

Figure 3 shows the minority spin DOS integrated over the atomic spheres of the first and second Fe$_3$O$_4$ atomic layers near the interface. It is compared to the corresponding DOS for bulk magnetite and for bulk MgO. This figure does not present an intense peak which could be attributed to a minority spin interface state.

Figure 3. Same as in figure 1 but for minority spin.
3.3. Iron atom spin magnetic moments

The iron atoms which are the closest from the interface in our calculation are located in tetrahedral sites and have a spin magnetic moment which is 13% lower than in bulk magnetite. The closest iron atoms in octahedral sites have nearly the same spin magnetic moment than in bulk \( \text{Fe}_3\text{O}_4 \).

4. Conclusion

We have calculated the electronic structure near the \( \text{Fe}_3\text{O}_4/\text{MgO}(100) \) interface. Our results mainly show that a majority spin interface state can exist at the Fermi energy which may be important for the interpretation of current-voltage characteristics of the \( \text{Fe}_3\text{O}_4/\text{MgO}/\text{Fe}_3\text{O}_4 \) magnetic tunnel junctions.

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