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Effect of oxygen vacancies on spin-dependent tunneling in Fe/MgO/Fe magnetic tunnel junctions

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First-principles calculations based on density functional theory are used to elucidate the effect of O vacancies, forming *F* centers, on spin-dependent tunneling in Fe/MgO/Fe(001) magnetic tunnel junctions. O vacancies produce occupied localized *s* states and unoccupied resonant *p* states, which is consistent with available experimental data. The authors find that O vacancies affect the conductance by nonresonant scattering of tunneling electrons causing a substantial reduction of tunneling magnetoresistance (TMR). Improving the quality of the MgO barrier to reduce O vacancy concentration would improve TMR in these and similar junctions. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2643027]

Magnetic tunnel junctions (MTJs) have aroused considerable interest due to the phenomenon of tunneling magnetoresistance (TMR), originating from the dependence of the tunneling current on the relative orientation of magnetization of the two ferromagnetic electrodes.[1] Recent theoretical predictions[2,3] followed by experimental demonstrations of large TMR values in MTJs based on epitaxial and textured Fe and CoFe electrodes and crystalline MgO barriers[4,5] have further triggered the interest in MTJs.

First-principles models of TMR so far have been largely limited to ideal MTJs. Some insight has been gained on the role of interface imperfections such as oxidation[6] and roughness,[7] and interface resonant states.[8] It is known, however, that defects in the insulator can also influence the properties of MTJs.[9] O vacancies are the simplest and most often encountered defect in oxides. Recently, an unambiguous evidence of the presence of localized defect states in the MgO barrier was reported by Mather *et al.*[10]

In this letter, we use first-principles calculations based on density functional theory to elucidate the effect of neutral O vacancies (*F* centers) on spin-dependent tunneling and TMR in crystalline Fe/MgO/Fe(001) MTJs. O vacancies produce occupied localized *s* states and unoccupied resonant *p* states, which is consistent with the experimental data.[10] We show that O vacancies affect the conductance by nonresonant scattering of tunneling electrons causing a substantial reduction of TMR.

First, we investigate the electronic structure of O vacancies in bulk MgO. We limit our consideration to *F* centers which, according to the earlier calculations,[11,12] have the lowest formation energy. We use a pseudopotential plane-wave method (VASP) (Ref. 13) within the local density approximation. Oxygen vacancies are introduced by removing a neutral O atom in 32, 64, and 216 atom supercells.[14] Atomic relaxations show that the MgO lattice is only slightly distorted in the vicinity of the vacancy.

Figures 1(a) and 1(b) show the calculated density of states (DOS) of an *F* center superimposed on DOS of bulk MgO for two different cells. The O vacancy produces a localized state lying close to the middle of the energy gap of MgO. This state is occupied by two electrons and has the *s* character on the *F* center site. This is evident from the partial DOS as well as from the spherically symmetric charge density on the vacancy site seen in Fig. 2(a). The charge density plot reveals hybridization between the vacancy *s* and *p* states of the nearest O ions. In addition to the *s* state, there is an unoccupied *p* state which appears on the *F* center site at the bottom of the MgO conduction band (Fig. 1). Figure 2(b) shows the charge density for this state indicating the hybridization with orbitals of the nearest-neighbor atoms. Since the *F* center *p* state lies within the continuum of the conduction band states, a nonzero charge density is present on atoms far away from the vacancy site. Our results are consistent with the earlier calculations of the electronic structure of O vacancies in MgO by Klein *et al.*[12]

These results conform with the scanning tunneling spectroscopy data of Mather *et al.*[10] Experimentally two defect levels are observed in the band gap of MgO [Fig. 3(c) in Ref. 10]—one centered about 1 eV above the valence band maxi-

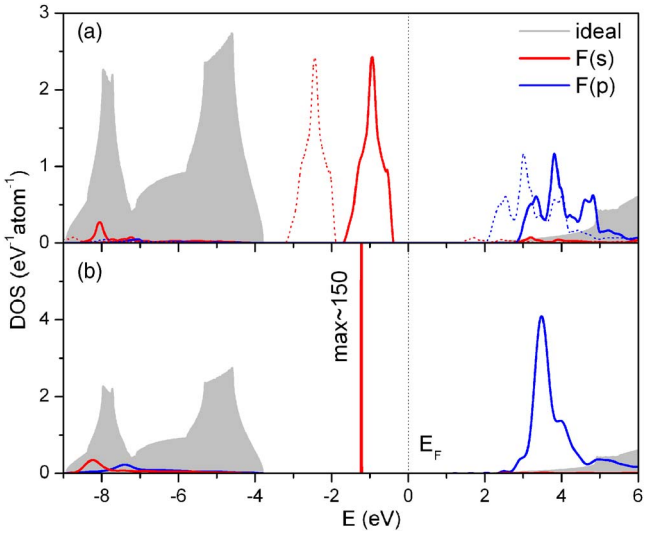

FIG. 1. (Color online) Density of states of bulk MgO (shaded area) and (a) *F* center *s* and *p* states for a $\frac{1}{32}$ cell (solid line). The dashed line indicates the approximate position of the levels corrected for self-interaction, (b) *F* center in $\frac{1}{216}$ cell. $E=0$ is the position of the Fermi level in Fe/MgO/Fe MTJs.

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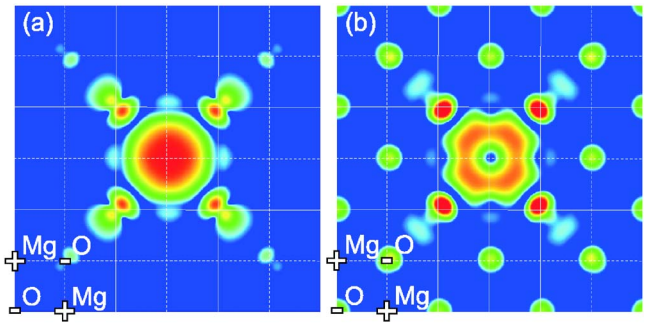

FIG. 2. (Color online) Charge density calculated in the energy window containing the defect level (a) *s* and (b) *p* states ($\frac{1}{216}$ MgO cell). Vacancy is in the middle, the positions of the Mg(+) and O(−) ions are indicated for one unit cell. Exponential scale is used with red indicating high and blue low charge density.

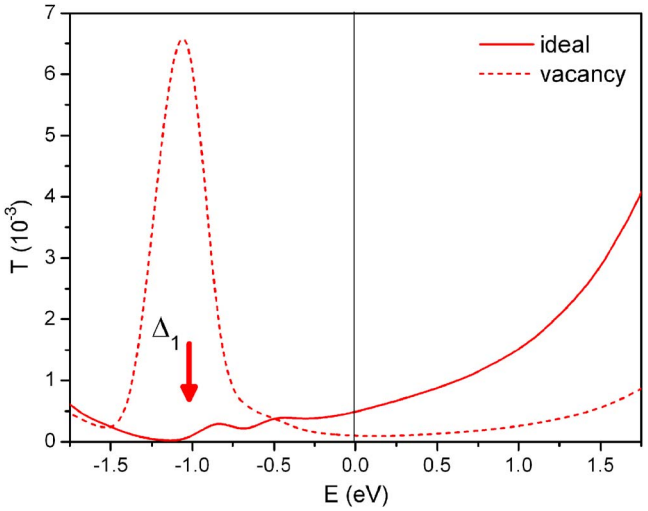

FIG. 3. (Color online) Majority-spin transmission probability vs energy per cell in Fe/MgO/Fe(001) with 5 ML of MgO for ideal MgO and MgO with O vacancies ($\frac{1}{8}$ cell). The arrow indicates the bottom of the majority Δ_1 band.

mum and another overlapping with the conduction band minimum. The former can be identified with the *F* center *s* state. The latter corresponds to the *F* center *p* state. It is unlikely that the occupied localized level represents a *V* center formed by a neutral Mg vacancy as suggested in Ref. 10, because the formation energy of a *V* center is larger than that of an *F* center.[11] For highly localized electrons on the *F* center self-interaction corrections become important. The self-interaction energy has been estimated to be $U_{ss}=1-1.5$ eV and $U_{sp}=0.5-0.8$ eV.[12] Figure 1(a) shows the approximate positions of the *F* center levels after the self-interaction has been subtracted, which agree well with the experimental data.[10]

Next we study the tunneling conductance in Fe/MgO/Fe(001) MTJs. We calculate the electronic structure self-consistently using the tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic sphere approximation.[15] The transmission probability as a function of the energy of a MTJ, representing a MgO barrier layer between two semi-infinite Fe leads, is obtained using the principal layer Green function technique used in Ref. 8. O vacancy is modeled by replacing an O atom by an empty sphere of equal radius. The TB-LMTO electronic structure is compared to VASP calculations for all systems showing excellent agreement. O vacancies in Fe/MgO/Fe MTJs are simulated by using a lateral supercell containing four or eight oxygen sites with one vacancy in the middle of the MgO slab.[16]

Figure 3 shows the majority-spin transmission as a function of energy for an ideal Fe/MgO/Fe MTJ (solid line) and for a MTJ with O vacancies (dashed line).[17] For the ideal MTJ, the majority transmission has a characteristic point at $E\approx-1$ eV with respect to the Fermi energy (E_F). Above this energy the transmission increases significantly due to the occurrence of the Δ_1 symmetry band in the electronic structure of Fe(001), which matches the evanescent state with the lowest decay rate in MgO.[18] In the energy interval $(-1,1.5)$ eV the Δ_1 band is present only in the majority-spin channel resulting in large values of TMR.[2,3]

O vacancies produce a pronounced peak in the transmission centered around $E=-1$ eV. This peak is due to the resonant tunneling of electrons via the *F* center *s* state. Another peak (not shown) occurs at $E=3.5$ eV due to the *p* resonant state. The width of the peak depends strongly on the vacancy density and on the coupling to the electrodes determined by MgO thickness.

The transmission at resonance is not of practical interest in this case because the resonant level is 1 eV below E_F. With correction for the self-interaction the resonant level moves even deeper down in energy as corroborated by the experimental data.[10] Therefore, for a moderate bias the transport mechanism is controlled by nonresonance scattering at O vacancies. We note that bringing a defect (impurity) level closer to the Fermi energy makes tunneling resonant which strongly affects TMR.[19]

It is evident from Fig. 3 that at and above E_F the transmission of a MTJ with vacancies is reduced by a factor of 5–7 depending on energy, as compared to the transmission of a perfect MTJ. This detrimental effect of O vacancies on the majority-spin transmission is due to scattering of tunneling electrons between states with different transverse wave vectors $\mathbf{k}_\parallel$. In a perfect Fe/MgO/Fe junction, the tunneling probability in the majority-spin channel is dominated by the Δ_1 evanescent state at the $\bar{\Gamma}$ point ($\mathbf{k}_\parallel=0$) because it has the longest attenuation length in MgO. Scattering to states with $\mathbf{k}_\parallel\neq 0$ reduces the transmission coefficient due to a shorter decay length of these states.

The reduction of majority-spin transmission in the presence of O vacancies can be understood by analyzing the decay rate of the Δ_1 state which has the lowest decay rate for both ideal and defective MgO crystals. Figure 4(a) shows the complex band structure[18] calculated for a *bulk* MgO crystal with and without O vacancies. The vacancy band, which produces the resonant peak in the transmission, splits the MgO gap into two parts. Away from resonance the decay rate of the defective MgO becomes larger than that for the ideal MgO. This implies that electron scattering from *F* centers effectively increases the decay constant. The decay rate of the metal-induced gap states in the MgO *slab* in the Fe/MgO/Fe MTJ can be estimated from the calculation the probability density $|\Psi|^2$ within the barrier.[2] Figure 4(b) shows $|\Psi|^2$ for the Δ_1 state at E_F. For ideal MgO the result agrees very well with the complex band structure. For defective MgO, $|\Psi|^2$ is a better estimate of the decay rate because the complex band structure calculation introduces an artificial periodicity of the O vacancies in the direction along the

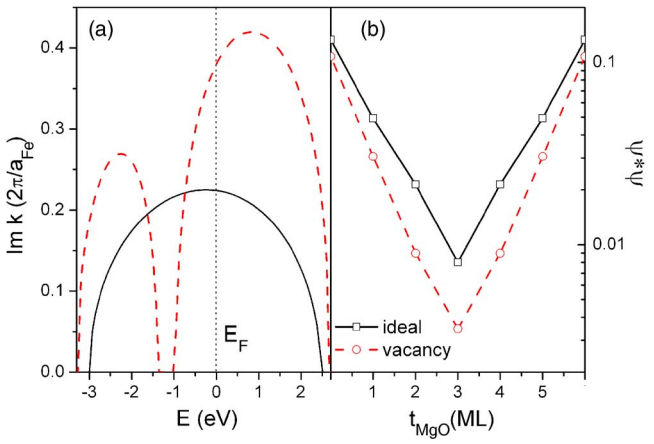

FIG. 4. (Color online) Decay rate for the Δ_1 state in ideal MgO (solid lines) and MgO with O vacancies in $\frac{1}{32}$ cell (dashed lines) obtained (a) from the complex band structure of bulk MgO and (b) from the probability density in Fe/MgO/Fe. The position of the Fermi energy in Fe/MgO/Fe MTJs is at $E=0$ eV.

current. The larger slope of the $|\Psi|^2$ graph for defective MgO indicates that the decay rate is about 24% larger than that for the ideal case. This implies seven times smaller transmission probability which is consistent with the actual results (Fig. 3).

The situation is different for minority-spin electrons because in ideal Fe/MgO/Fe MTJs the minority transmission is not dominated by the $\bar{\Gamma}$ point.[8] In this case nonresonance scattering by O vacancies contributes both destructively and constructively to the transmission. Our calculations show that off-resonance O vacancies do not have a pronounced effect on the minority-spin transmission in the parallel configuration and the transmission in the antiparallel configuration.

The overall effect of O vacancies is the significant reduction of TMR. For ideal junctions TMR is largely controlled by the enhanced transmission of the Δ_1 majority-spin band in the whole energy range $(-1,1.5)$ eV. The transmission through a defective MgO barrier displays clearly two distinct transport regimes—resonant when the electron energy is close to the position of the vacancy levels and nonresonant when the electron energy is far from the vacancy levels. At resonance the transmission asymmetry arises only from the difference in the majority and minority DOSs in the electrodes. Nonresonance scattering from vacancies diminishes the spin asymmetry by reducing the majority transmission.

Quantitative comparison of TMR below E_F is hindered by the appearance in the minority channel of interface resonant states[8] which interfere with the tail of the resonant transmission complicating the minority and antiparallel conduction. However, above E_F the tendency is very clear and indicative of what is expected in practice. In agreement with previous calculations[2,3,8] we find TMR$=(G_P-G_{AP})/G_{AP}$ of ideal MTJs $>1800\%$. In the presence of O vacancies TMR is reduced to $<800\%$. It is worth mentioning that any defects in the barrier, such as Mg vacancies, impurities, dislocations, etc., will act in a similar manner, scattering electrons out of coherence, thus reducing the resultant TMR.

In conclusion, we have found that O vacancies affect significantly the conductance in Fe/MgO/Fe MTJs due to nonresonant scattering of tunneling electrons, causing a substantial reduction of TMR. Improving the quality of the MgO barrier to reduce O vacancy concentration would improve TMR.

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