Large reduction of the magnetoresistance in Fe/MgO/Fe tunnel junctions due to small oxygen concentrations at a single FeO interface layer: A first-principles study

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The tunneling magnetoresistance (TMR) of Fe/MgO/Fe junctions is strongly diminished by small O concentrations in a single partially oxidized FeO interface layer, as is found by first-principles transport calculations. By modeling the electronic transport through the disordered FeO layer within a supercell approach, the effect is traced back to a significant reduction of specular contributions to the conductances of the parallel configuration of the lead magnetizations. These findings bring theoretical TMR ratios closer to their experimental counterparts and highlight the importance of ordered interfaces for large TMR ratios.

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In magnetoelectronics, a field of research with increasing importance,[1,2] one focus is put on spin-dependent ballistic transport in magnetic tunnel junctions (MTJs, a trilayer of ferromagnetic electrodes separated by an insulating barrier). The conductances for the parallel (G_P) and the antiparallel (G_{AP}) configuration of the electrode magnetizations define the tunnel magnetoresistance (TMR) quantified here as the "optimistic" TMR ratio

$$\delta \equiv \frac{G_P - G_{AP}}{G_{AP}}. \tag{1}$$

For applications, magnetoelectronic devices with TMR ratios larger than 100% at room temperature are demanded. Up to now, this objective could not be reached by MTJs with amorphous barriers, e.g., Al_2O_3.[3–5] More promising are epitaxial MTJs which are expected to provide sufficiently high TMR ratios. Indeed, transport calculations for Fe/MgO/Fe, in which perfect crystallinity, epitaxy, and stoichiometry are assumed, predict TMR ratios that exceed thousand percent.[6]

Although experimental TMR ratios for Fe/MgO/Fe have increased over the years,[7,8] there still appears disagreement with regard to theoretical and experimental values: Experimental TMR ratios are at least one order of magnitude smaller than their theoretical counterparts. One explanation to come into question is that transport calculations mainly rely on ordered samples, hence considering *specular* transport processes in the commonly applied Landauer-Büttiker theory. Instead, *diffusive* transport could play a significant role, as is supported by x-ray surface diffraction experiments, which evidence a disordered (substoichiometric) FeO layer at the Fe/MgO interface.[9,10] Theory substantiates a significant effect of FeO interface layers on the TMR ratio as compared to MTJs without FeO layer.[11] However, these calculations were performed for ordered (stoichiometric) FeO layers. Further, photoelectron spectroscopy experiments establish that off stoichiometry in MgO films on Fe(001) affects the electronic structure at the Fe/MgO interface.[12] Please note that interface properties essentially determine the transport properties.[13,14]

In this Brief Report we report on first-principles transport calculations which provide evidence for an explanation of the aforementioned disagreement of theoretical and experimental TMR ratios by means of a *substoichiometric* FeO interface layer. Both specular and diffusive transport processes are taken into account within a supercell approach. A striking result is that even small O concentrations (less than 5%) reduce the TMR ratio sizably and consequently improve the agreement with experiment significantly.

The effect of disorder in Fe/MgO/Fe MTJs has already been investigated theoretically by superposing incoherently conductances for different MTJs (Ref. 15) and by the coherent-potential approximation without vertex corrections.[16] These approaches lack either coherency or current conservation,[17] both of which are treated properly in a supercell approach. A reduction of the TMR was also found for MTJs with intermixing of Fe and MgO (Ref. 18) as well as with O vacancies in the MgO spacer.[19,20]

First-principles electronic-structure calculations, within the framework of multiple-scattering theory [spin-polarized-Korringa-Kohn-Rostoker (KKR) and layer-KKR methods[21]], provided self-consistent potentials of Fe/MgO/Fe(001) MTJs. The charge density was normalized by Lloyd's formula[22] using a maximum angular momentum of $l_{max}=3$. For the junctions with FeO layers, stoichiometry is assumed (oxygen concentration $c=100\%$), thus allowing the use of a two-dimensional 1×1 unit cell (UC). The atomic positions, in particular those of interstitial oxygen at the interface, were taken from experiment.[23] The self-consistent potentials serve as input for the transport calculations, an approach which proved to be successful.[23]

For treating the substoichiometric junctions properly, ballistic electronic transport was calculated for large supercells (SCs). It turned out that 5×5 SCs, containing 50 sites/layer, provide a reasonable description of the disordered systems within acceptable computer requirements. Instead of computing the SC potentials self-consistently (a very demanding task) these were constructed from the UC potentials. The O potentials in the FeO_c layer were taken from the completely oxidized UC system, whereas the other potentials were computed within the virtual-crystal approximation (concentration-weighted superposition of the potentials of the nonoxidized UC system with those of the completely oxidized UC system).

TABLE I. Optimistic TMR ratios for selected O concentrations c in $Fe/FeO_c/(MgO)_4/Fe$ junctions.

O concentration	Theory	Experiment
0%	520%,[a] 400%,[b] 330%[c]	50%[d]
100%	−50%,[b] −23%,[e] −10% [c]	

[a]References 6 and 29.
[b]Reference 11.
[c]This work.
[d]Reference 8 for 6 ML MgO.
[e]Reference 23.

Considering here zero-bias voltage, the conductance

$$G^{SC}(E_F) = \frac{e^2}{h}\int_{2BZ^{SC}} \sum_{\alpha\beta} T_{\alpha\to\beta}(E_F;\boldsymbol{k}^{SC})(d\boldsymbol{k}^{SC})^2 \qquad (2)$$

at the Fermi energy E_F is calculated according to Landauer-Büttiker theory[24] using an S-matrix scheme within layer KKR.[25] The probability $T_{\alpha\to\beta}$ for the incoming Bloch state α at $(E_F;\boldsymbol{k}^{SC})$ being transmitted into the outgoing Bloch state β is integrated over the two-dimensional Brillouin zone (2BZ) of the SC system. An equidistant mesh of 225 wave vectors reproduced TMR ratios of the ordered UC systems (O concentration $c=0\%$ and 100%) with sufficient accuracy. The latter was computed with an adaptive integration scheme.[26] Results were conveniently analyzed by means of transmittance maps which display $\Sigma_{\alpha\beta}T_{\alpha\to\beta}(E_F;\boldsymbol{k}^{SC})$ versus $\boldsymbol{k}^{SC}$.

Due to the two-dimensional translational invariance in the leads, w.r.t. the UC, each Bloch state is characterized by a wave vector $\boldsymbol{k}^{UC}=\boldsymbol{k}^{SC}+\boldsymbol{g}^{SC}$, i.e., related to $\boldsymbol{k}^{SC}$ by an *umklapp* with a reciprocal-lattice vector $\boldsymbol{g}^{SC}$ of the SC system. Hence, all tunneling processes $\alpha\to\beta$ can be distinguished as specular or diffusive with respect to the conservation of $\boldsymbol{k}^{UC}$,

$$\boldsymbol{k}^{UC}-\boldsymbol{g}^{SC}=\boldsymbol{k}^{SC}\to\boldsymbol{k}^{SC}=\begin{cases}\boldsymbol{k}^{UC}-\boldsymbol{g}^{SC} & \text{specular}\\ \boldsymbol{k}^{UC'}-\boldsymbol{g}^{SC'} & \text{diffusive}\end{cases} \qquad (3)$$

($\boldsymbol{k}^{SC}$ is conserved). Accordingly, the conductance G^{SC} is decomposed into a specular and a diffusive contribution,

$$G^{SC}=G^{UC}_{spec}+G^{UC}_{diff}. \qquad (4)$$

This partitioning requires computation of the Bloch states at all $\boldsymbol{k}^{UC}=\boldsymbol{k}^{SC}+\boldsymbol{g}^{SC}$ in the UC system and their transformation into the SC basis with bookkeeping of $\boldsymbol{g}^{SC}$.

Because the computation time increases drastically with system size, we focus here on $Fe/FeO_c/(MgO)_4/Fe$ junctions with MgO spacers of four-monolayer (ML) thickness. For each selected O concentration c, a single random configuration was set up in the 5×5 SCs, although one has to average over all topologically inequivalent configurations. This restriction is justified by the rather large supercell and by the small conductance variations with configuration (about 1%) reported earlier.[27,28]

Our SC approach captures the essential features of the ordered sample, as is evident from the agreement with theoretical TMR ratios reported elsewhere (Table I). Differences may be attributed to details in the self-consistent electronic-structure calculations, to the Brillouin-zone integration, and to the geometry of the interfaces. Attention should be paid to the experimental TMR ratio for $c=0\%$ (Ref. 8), which is about one order of magnitude smaller than the theoretical values.

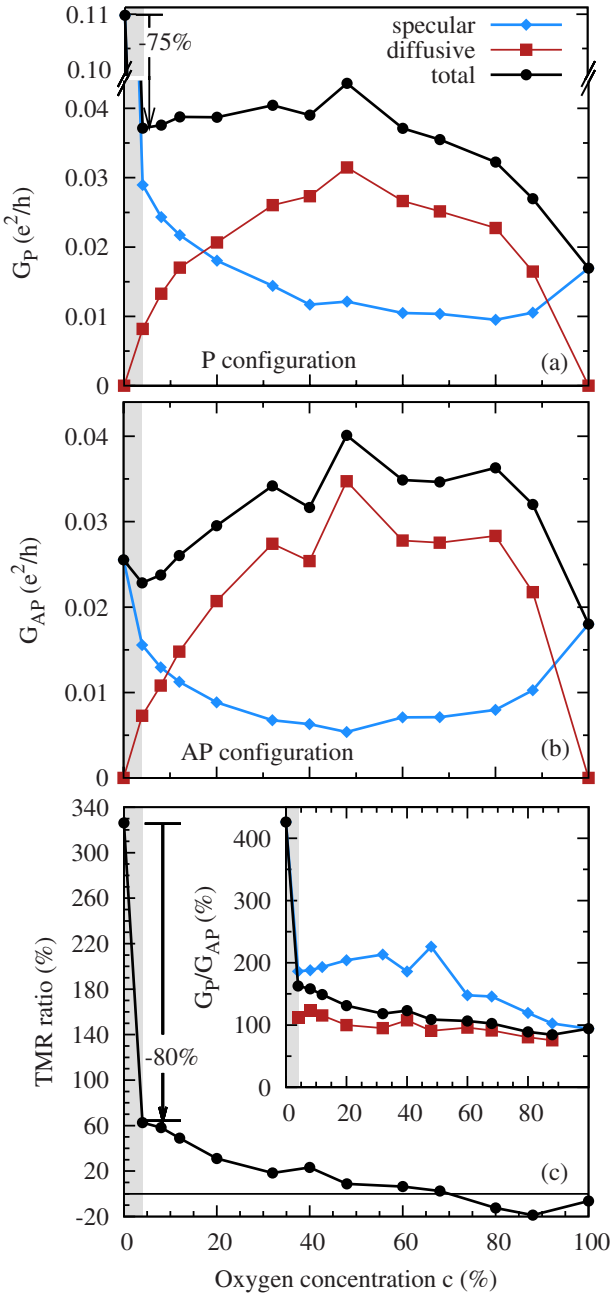

FIG. 1. (Color online) Transport properties of $Fe/FeO_c/(MgO)_4/Fe$ junctions at zero-bias voltage versus oxygen concentration c in the FeO layer. (a) and (b) Conductances G for the (a) parallel P and (b) antiparallel AP configuration. The conductances (black; filled circles) are decomposed into specular (blue; diamonds) and diffusive (red; squares) contributions. (c) Optimistic tunnel magnetoresistance and conductance ratios (inset). The gray areas at low concentrations highlight the region of the sizable drop in G_P and in the TMR ratio [indicated by the vertical arrows in (a) and (c); note the broken ordinate in (a)].

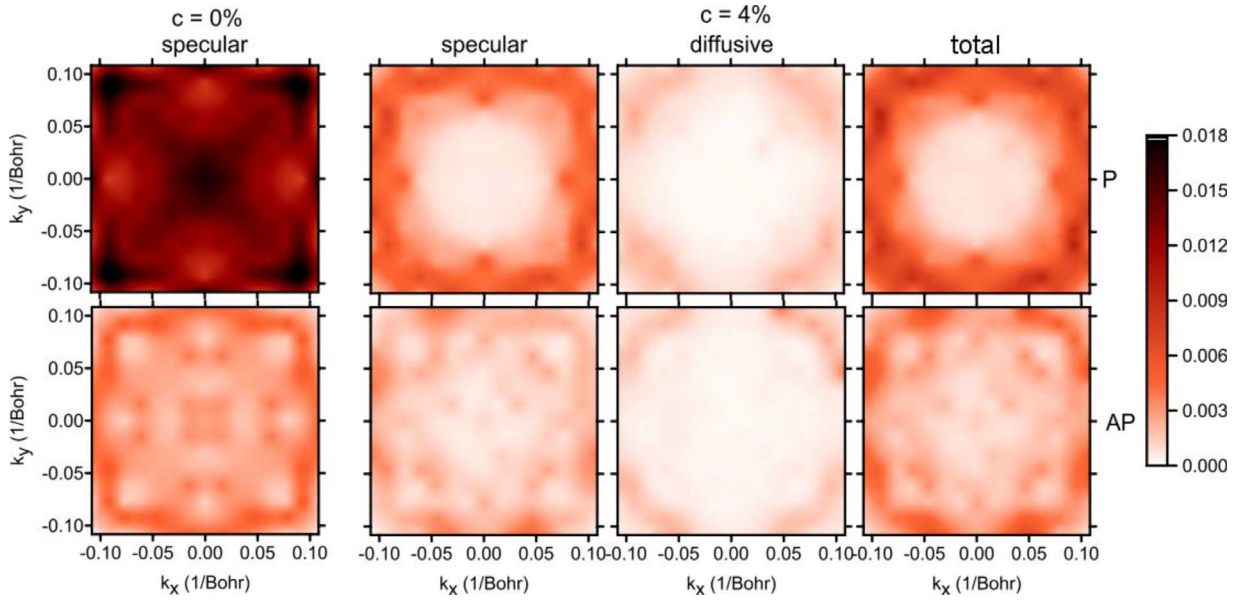

FIG. 2. (Color online) Transmittances $T(E_F;\boldsymbol{k}^{SC})$ versus $\boldsymbol{k}^{SC}=(k_x,k_y)$ for oxygen concentrations $c=0\%$ (left) and 4% (right) in $Fe/FeO_c/(MgO)_4/Fe$ junctions depicted as color (gray) scale in the 2BZ of the 5×5 SC systems. The total transmittances for $c=4\%$ are decomposed into a specular and a diffusive contribution. For $c=0\%$ there are only specular tunnel processes. The data are interpolated to achieve a smooth color gradient.

concentration c. Indeed, G_P and G_{AP} [circles in Fig. 1(a) and 1(b)] show broad maxima around $c=50\%$ which can be attributed to the diffusive contribution (squares). The specular contributions (diamonds) display broad minima at about $c=80\%$ (P) and 50% (AP), respectively. Similar dependences were found for Fe-Cr[100] and Co-Cu[100] systems.[27]

An eye-catching feature is the drop of G_P at small c (gray area). The total conductance decreases by 75% upon increasing c from 0% to 4%, which is mediated by the specular contribution. Note that a concentration of 4% is equivalent to a single O atom in the 5×5 SC. This finding suggests that even small degrees of disorder at the Fe/MgO interfaces reduce G_P sizably. G_{AP} also drops for small c but moderately. Here, the decrease in G_{spec} is almost canceled by the increase in G_{diff}.

The similar shapes of G_P and G_{AP} result in an almost linear c dependence of the TMR ratio in a large range of concentrations [Fig. 1(c)]. Likewise the conductance ratios G_P/G_{AP} depend smoothly on c (inset). The drop of G_P at small concentrations leads to a reduction of the TMR ratio from about 330% for $c=0\%$ to about 60% for $c=4\%$ (gray area) which is attributed to the decrease in the specular contribution to G_P [diamonds in the inset of Fig. 1(c)]. Hence, we are confronted with a large TMR reduction by small degrees of disorder, a finding that considerably improves the agreement of theoretical with experimental TMR ratios (Table I).

The spin-dependent ballistic transport in Fe/MgO/Fe junctions is governed by symmetry selection and proceeds notably by resonant tunneling.[30–32] Thus, large TMR ratios are obtained if interface resonances at identical $(E,\boldsymbol{k})$ at either interfaces of the junction are present, e.g., in symmetric MTJs (here $c=0\%$). Wave vector conservation is less likely in junctions with disorder at one interface. Hence, the diffusive (specular) conductance increases (decreases) with c up to a maximum (minimum). An analogous argument holds for $c=100\%$ and decreasing concentration.

The above explanation is corroborated by inspection of transmittance maps. The P transmittance for $c=0\%$ shows maxima in the center and in the corners $[\boldsymbol{k}\approx(\pm0.09,\pm0.09)\ \text{Bohr}^{-1}]$ of the 2BZ (left in Fig. 2). The AP transmittance is comparably small in the entire 2BZ, with an exception of the corners. This effect can be understood by means of the orbital composition of the electronic states. Δ_1-like states (sp orbitals) are located at the 2BZ center and decay least across the MgO spacer in comparison to Δ_2- or Δ_5-like states (d orbitals).[29,33,34]

As compared to $c=0\%$, the specular P-transmittance map for $c=4\%$ shows a broad minimum at the 2BZ center (right in Fig. 2). This feature, in conjunction with the much less pronounced contributions at the corners, results in the sizable conductance drop of 75%. On the contrary, the specular AP-transmittance maps for $c=0\%$ and 4% compare well. The maps of the diffusive P and AP contributions look very similar too. These findings corroborate that resonant tunneling is less likely for $c>0\%$.

As a "rule of thumb," the relative contribution of the 2BZ center to the conductance increases with MgO spacer thickness.[29,33] Hence, we expect that small oxygen concentrations strongly reduce theoretically predicted TMR ratios also for thicker MgO spacers, thereby improving the agreement with experiment in general (cf. Table I).

In summary, the present transport calculations reveal that oxygen concentrations at the interface of a few percent reduce the tunnel magnetoresistance of Fe/MgO/Fe junctions sizably. Our findings suggest that the disagreement between theoretical and experimental TMR ratios is due to substoichiometric FeO layers with small oxygen concentrations or,

reworded, large TMR ratios require perfectly ordered interfaces. Because small degrees of imperfections at the interfaces of real samples can hardly by excluded, systematic studies of the disorder in MTJs (Ref. 12) are encouraged.

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[1] G. A. Prinz, Science **282**, 1660 (1998).
[2] S. A. Wolf, A. Y. Chtchelkanova, and D. M. Treger, IBM J. Res. Dev. **50**, 101 (2006).
[3] T. Miyazaki and N. Tezuka, J. Magn. Magn. Mater. **139**, L231 (1995).
[4] J. S. Moodera, L. R. Kinder, T. M. Wong, and R. Meservey, Phys. Rev. Lett. **74**, 3273 (1995).
[5] D. Wang, C. Nordman, J. M. Daughton, Z. Qian, and J. Fink, IEEE Trans. Magn. **40**, 2269 (2004).
[6] J. Mathon and A. Umerski, Phys. Rev. B **63**, 220403(R) (2001).
[7] S. S. P. Parkin, C. Kaiser, A. Panchula, P. M. Rice, B. Hughes, M. Samant, and S.-H. Yang, Nat. Mater. **3**, 862 (2004).
[8] S. Yuasa, T. Nagahama, A. Fukushima, Y. Suzuki, and K. Ando, Nat. Mater. **3**, 868 (2004).
[9] H. L. Meyerheim, R. Popescu, J. Kirschner, N. Jedrecy, M. Sauvage-Simkin, B. Heinrich, and R. Pinchaux, Phys. Rev. Lett. **87**, 076102 (2001).
[10] H. L. Meyerheim, R. Popescu, N. Jedrecy, M. Vedpathak, M. Sauvage-Simkin, R. Pinchaux, B. Heinrich, and J. Kirschner, Phys. Rev. B **65**, 144433 (2002).
[11] C. Heiliger, P. Zahn, B. Y. Yavorsky, and I. Mertig, Phys. Rev. B **72**, 180406(R) (2005).
[12] M. Müller, F. Matthes, and C. M. Schneider, Europhys. Lett. **80**, 17007 (2007).
[13] P. X. Xu, V. M. Karpan, K. Xia, M. Zwierzycki, I. Marushchenko, and P. J. Kelly, Phys. Rev. B **73**, 180402(R) (2006).
[14] E. Y. Tsymbal, K. D. Belashchenko, J. P. Velev, S. S. Jaswal, M. van Schilfgaarde, I. I. Oleynik, and D. A. Stewart, Prog. Mater. Sci. **52**, 401 (2006).
[15] C. Heiliger, P. Zahn, and I. Mertig, J. Magn. Magn. Mater. **316**, 478 (2007).
[16] X.-G. Zhang, W. H. Butler, and A. Bandyopadhyay, Phys. Rev. B **68**, 092402 (2003).
[17] K. Carva, I. Turek, J. Kudrnovský, and O. Bengone, Phys. Rev. B **73**, 144421 (2006).
[18] J. Mathon and A. Umerski, Phys. Rev. B **74**, 140404(R) (2006).
[19] J. P. Velev, K. D. Belashchenko, S. S. Jaswal, and E. Y. Tsymbal, Appl. Phys. Lett. **90**, 072502 (2007).
[20] H. Itoh, J. Ozeki, and J. Inoue, J. Magn. Magn. Mater. **303**, e205 (2006).
[21] *Electron Scattering in Solid Matter*, edited by J. Zabloudil, R. Hammerling, L. Szunyogh, and P. Weinberger (Springer, Berlin, 2005).
[22] R. Zeller, J. Phys.: Condens. Matter **20**, 035220 (2008).
[23] C. Tusche, H. L. Meyerheim, N. Jedrecy, G. Renaud, A. Ernst, J. Henk, P. Bruno, and J. Kirschner, Phys. Rev. Lett. **95**, 176101 (2005).
[24] Y. Imry and R. Landauer, Rev. Mod. Phys. **71**, S306 (1999).
[25] J. M. MacLaren, X.-G. Zhang, W. H. Butler, and X. Wang, Phys. Rev. B **59**, 5470 (1999).
[26] J. Henk, Phys. Rev. B **64**, 035412 (2001).
[27] J. Velev and W. H. Butler, Phys. Rev. B **69**, 024404 (2004).
[28] J. Velev and W. H. Butler, J. Appl. Phys. **97**, 10C517 (2005).
[29] W. H. Butler, X.-G. Zhang, T. C. Schulthess, and J. M. MacLaren, Phys. Rev. B **63**, 054416 (2001).
[30] O. Wunnicke, N. Papanikolaou, R. Zeller, P. H. Dederichs, V. Drchal, and J. Kudrnovský, Phys. Rev. B **65**, 064425 (2002).
[31] K. D. Belashchenko, J. Velev, and E. Y. Tsymbal, Phys. Rev. B **72**, 140404(R) (2005).
[32] J. P. Velev, K. D. Belashchenko, and E. Y. Tsymbal, Phys. Rev. Lett. **96**, 119601 (2006).
[33] C. Heiliger, P. Zahn, and I. Mertig, Mater. Today **9**, 46 (2006).
[34] S. Yuasa and D. D. Djayaprawira, J. Phys. D **40**, R337 (2007).