Large two-level magnetoresistance effect in doped manganite grain boundary junctions

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We performed a systematic analysis of the tunnel magnetoresistance (TMR) effect in single grain boundary junctions formed in epitaxial La₂/₃Ca₁/₃MnO₃ films deposited on SrTiO₃ bicrystals. For magnetic fields \( H \) applied parallel to the grain boundary barrier, an ideal two-level resistance switching behavior with sharp transitions is observed with a TMR effect of up to 300% at 4.2 K and still above 100% at 77 K. Varying the angle between \( H \) and the grain boundary results in differently shaped resistance vs \( H \) curves. The observed behavior is explained within a model of magnetic domain pinning at the grain boundary interface.

Ferromagnetic tunneling junctions have been studied intensively over the last years due to possible applications in magnetoelectronics devices. The tunneling magnetoresistance (TMR) between two ferromagnetic layers \( i = 1, 2 \) separated by a thin insulating barrier depends on the relative orientation of the magnetization and the spin polarization \( P_i = 2\alpha_i - 1 \), where \( \alpha_i \) is the fraction of majority spin electrons in the density of states of layer \( i \). Within the Jullière model the TMR is estimated to

\[
\frac{\Delta R}{R} = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\uparrow}} = \frac{2P_1P_2}{1 - P_1P_2},
\]

where \( R_{\uparrow\downarrow} \) and \( R_{\uparrow\uparrow} \) is the tunneling resistance for parallel and anti-parallel magnetization orientation. Depending on the spin polarization, for parallel magnetization the tunneling resistance is significantly reduced, since the large density of occupied and empty states for the majority spin electrons in both junction electrodes allow for a large tunneling current. We note that in the Jullière model only elastic tunneling without any spin-flip processes is assumed and the junction electrodes are assumed to be single domain.

So far, most of the investigated TMR devices are based on transition metals and compounds such as Ni, Co, Fe, or Co₅₀Fe₅₀ with \( P \lesssim 50\% \) (for recent overviews see Moodera et al. and Parkin et al.). It is evident that \( P \) close to unity is desired to achieve a high TMR-effect. There are several candidates for materials with large \( P \) close to 100% such as the Mn-based Heusler alloys \( \text{Fe}_2\text{O}_4 \) or \( \text{Cr}_2\text{O}_3 \), and the doped manganites of composition \( \text{La}_{2}D_{1-x}\text{MnO}_3 \) with \( D = \text{Ca}, \text{Sr}, \text{and Ba} \). While for the former materials the high spin polarization is still under question, recently photoemission spectroscopy has provided direct evidence for the half-metallic nature of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) with \( P \) close to unity. Indeed, using doped manganite high TMR values have been achieved, including trilayer spin valve devices with a TMR value above 450% at 4.2 K corresponding to a spin polarization above 80% and even above 1000% at 2 K corresponding to a spin polarization above 90%. We emphasize that the TMR-effect in manganite tunnel junctions is observed at low applied magnetic field of less than 100 mT and has to be distinguished from the intrinsic, high-field colossal magnetoresistance (CMR) of the doped manganites. While most tunnel junctions rely on multilayer technology, one can also form ferromagnetic tunnel junctions by using well-defined individual grain boundaries (GBs) separating two ferromagnetic grains. This is achieved by growing epitaxial manganite films on a SrTiO₃ bicrystal substrate. In this configuration the barrier is formed by a straight, few nm wide distorted GB interface as shown by transmission electron microscopy. After annealing in oxygen atmosphere, single GB junctions (GBJs) with large TMR effects have been achieved.

For many applications not only a large TMR effect but also a sharp switching between two distinct resistance values at a well-defined magnetic field is required. Such ideal, almost rectangular shaped \( R(H) \) curves with a maximum resistance change below 50% have been observed for some devices based on transition metals. However, for tunnel junctions based on doped manganite junctions (and also for many devices based on transition metals), usually strongly rounded and noisy \( R(H) \) curves are sharply peaked structures or multiple resistance level switching is reported. This behavior most likely originates from an uncontrolled domain switching. Here, we present a detailed study of the shape of the \( R(H) \) curves of GBJs based on doped manganites. We show that an almost perfect two-level resistance switching behavior with a sharp transition between the resistance values can be obtained. We further show that such ideal behavior is achieved with the magnetic field applied within the film plane parallel to the GB barrier. We also demonstrate that it is possible to vary the magnitude of the switching field \( H_s \) by changing the angle between the GB and the applied field. Our results provide evidence that domain wall pinning structures, intergran coupling, and the direction of the applied field can be combined to tailor the \( R(H) \)-curves of magnetic tunnel junctions.

GBJs were fabricated by pulsed laser deposition of epitaxial, 80 nm thick \( \text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 \) films on symmetrical, [001] tilt SrTiO₃ bicrystals with a misorien-
tation angle of 24°. After film deposition the samples were annealed ex-situ at 950°C in oxygen atmosphere for one hour. X-ray analysis of the films shows only (00ℓ) reflexes and the FWHM of the (002) rocking curve was 0.04°. Microbridges of 30 μm width straddling the GB were patterned using optical lithography and Ar ion beam etching. In this way, well-defined individual GBJs were obtained. The La_{2/3}Ca_{1/3}MnO_{3} films typically had a Curie-temperature T_{C} of about 225 K. Further details on the transport properties and the microstructure of the GBJs have been reported recently.

In Fig. 1, typical R(H) curves of a La_{2/3}Ca_{1/3}MnO_{3} GBJ are shown for different angles θ between H and the GB barrier measured at 4.2 K and a bias voltage of 5 mV. For clarity, the R(H) curve is shown only for one direction of the field sweep. The inset shows a sketch of the GBJ geometry.

![FIG. 1: R(H) curves of a La_{2/3}Ca_{1/3}MnO_{3} GBJ for different angles θ between H and the GB barrier measured at 4.2 K and a bias voltage of 5 mV. For clarity, the R(H) curve is shown only for one direction of the field sweep. The inset shows a sketch of the GBJ geometry.](image1)

The switching field H_{s} is set by the coercivity field H_{c} close to the GB. Unfortunately, little is known on the detailed interface and surface properties of doped manganites. Nonetheless, the fact that the measured TMR values are below the Julli`ere model for a tun-

FIG. 2: R(H)-curves for θ = 0° at 4.2 K (upper panel) and 77 K (lower panel). The direction of the field sweep is indicated by the arrows.

![FIG. 2: R(H)-curves for θ = 0° at 4.2 K (upper panel) and 77 K (lower panel). The direction of the field sweep is indicated by the arrows.](image2)
has already been observed indicates that a further improvement of junction and interface quality will allow for a further increase of the TMR effect both in GBJs and planar tunnel junctions based on doped manganites.

![Diagram](image)

FIG. 3: Sketch of the domain structures in a manganite thin film sample containing a single GB for applied magnetic fields of different magnitude and direction. The shaded parts represent regions consisting of domains with perpendicular and non-collinear magnetization with respect to the applied field. In the left hand panel the width of the shaded parts is overemphasized.

We now discuss the dependence of the shape of the $R(H)$-curve on the direction of the applied field using a simple domain model taking into account the magnetic domain pinning at the GB interface. A sketch of the expected domain structure is shown in Fig. 3 for $H \perp GB$ and $H \parallel GB$. We first note that at the GB interface the easy axis of magnetization is parallel to the GB. This is well known from surface studies of magnetic materials. Furthermore, for $|H| > H_c$ the magnetization is parallel to $H$ in both junction electrodes, that is, $R(H)$ is low. However, on decreasing the field from $|H| > H_c$ a different domain structure is expected for different field directions. We first discuss the case $\theta = 0^\circ$, where $H \parallel GB$, i.e. parallel to the easy axis at the GB. In this case, $R(H)$ can be low or high depending on whether the magnetization direction in the electrodes is parallel or anti-parallel. Furthermore, on varying the field in the high-resistance state, a small resistance change below 1% is observed due to the formation of small domains with different magnetization direction at the edges of the sample (shaded regions in Fig. 3). Since these domains are small, they do not contribute considerably to the transport behavior and magnetoresistance of the GBJ. In a first approximation, both junction electrodes can be considered single domain as assumed in the Julli`ere model. We note that for $H \parallel GB$ the single domains are strongly pinned by the GB interface. Thus, on decreasing the field amplitude from $|H| < H_c$ a parallel magnetization orientation and hence low $R(H)$ is preserved until the coercivity field of opposite direction is reached. Then, at $|H| \approx H_c$ the magnetization direction in one electrode switches resulting in an anti-parallel magnetization configuration and, thus, high resistance state. This anti-parallel magnetization configuration is stabilized in a finite field range around $H_c$ due to a reduction of the magnetic energy by reducing stray fields. On further increasing the field also the second electrode switches resulting again in a parallel magnetization configuration and low resistance state.

For $\theta = 90^\circ$, we have $H \perp GB$, i.e. $H$ perpendicular to the easy axis at the GB. When the field is decreased, domains form at the GB with magnetization parallel to the GB. Since these perpendicular and non-collinear (with respect to the applied field) oriented domains are located at the GB, they will strongly affect the transport properties and magnetoresistance. In this case, the electrode regions adjoining the GB can no longer be considered as single domain. The measured triangular shaped $R(H)$ curves can be attributed to a continuous change of the size of the non-collinear domains. Note that for $|H| < H_c$ the magnetization configuration at the GB is similar for $\theta = 0^\circ$ and $\theta = 90^\circ$ resulting in similar $R(H)$ values in agreement with our experiments. We further note that for $\theta = 90^\circ$ the anti-parallel domain configuration is present along the whole GB, because the applied field has no component parallel to the GB. Such a component destabilizes the anti-parallel configuration and, in turn, causes a switching of the magnetization. This explains why the $R(H)$ curves for $\theta = 90^\circ$ form is the envelope of the $R(H)$ curves measured for $\theta < 90^\circ$.

For intermediate $0^\circ < \theta < 90^\circ$ the behavior can be understood qualitatively within the same picture. An increase of $\theta$ is found to increasing $H_c$. This is caused by the fact that the field component parallel to the GB which drives the switching transition decreases with increasing $\theta$. At the same time the plateau width of the high-resistance state becomes wider since the reduced parallel field component also drives the second switching transition into the low-resistance state by overcoming the energy gain in the anti-parallel configuration due to reduction of stray fields. Fig. 3 clearly shows that only for $\theta > 45^\circ$ a significant angle dependence is observed. This is caused by the strong tendency of the domains to align parallel to the easy axis along the GB. Certainly, the direct imaging of the domain structure in the vicinity of the GB would be helpful to verify our model. In particular, the formation of multiple stable resistance states for large $\theta$ that may be related to the microstructure of individual GBs and their interface roughness has to be clarified. Similar effects have also been observed in planar sandwich junctions employing Co and MnFe electrodes with different aspect ratios. So far, we have not studied in detail the influence of different GB misorientation angles. However, we suppose that the effect of different misorientation angles is small compared to the effect of the relative orientation between $H$ and the GB discussed here.

In summary, we have shown that an almost ideal, two-level resistance switching behavior can be obtained for GBJs based on doped manganites. The switching field, the magnitude of the TMR effect, and the shape of the $R(H)$ curves can be varied systematically by varying the orientation of the applied field relative to the GB bar-
rier. The measured $R(H)$ characteristics have been interpreted in terms of a simple domain model demonstrating the key role of a strong domain wall pinning at the grain boundary. Our results outline possible roads for the tailoring of the properties of magnetic tunnel junctions based on doped manganites for applications in magneto-electronic devices.

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1. M. Julli`ere, Phys. Lett. A 54, 225 (1975).
2. J. S. Moodera and G. Mathon, J. Magn. Magn. Mater. 200, 248 (1999).
3. S. S. P. Parkin, K. P. Roche, M. G. Samant, P. M. Rice, R. B. Byers, R. E. Scheuerelein, E. J. O’Sullivan, S. L. Brown, J. Bucchigano, D. W. Abraham, Yu Lu, M. Rooks, P. L. Trouiloud, R. A. Wanner, and W. J. Gallagher, J. Appl. Phys. 85, 5828 (1999).
4. R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. 50, 2024 (1983).
5. K. P. Kämper, W. Schmitt, G. Güntherodt, R. J. Gambin, and R. Ruf, Phys. Rev. Lett. 59, 2788 (1988).
6. J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Nature 392, 794 (1998).
7. Yu Lu, X. W. Li, G. Q. Gong, Gang Xiao, A. Gupta, P. Lecoeur, J. Z. Sun, Y. Y. Wang, and V. P. Dravid, Phys. Rev. B 54, R8357 (1996).
8. J. Z. Sun, W. J. Gallagher, P. R. Duncombe, L. Kruisin-Elbaum, R. A. Altman, A. Gupta, Yu Lu, G. Q. Gong, and Gang Xiao, Appl. Phys. Lett. 69, 3266 (1996).
9. M. Viret, M. Drouet, J. Nassar, J. P. Contour, C. Fermon, and A. Fert, Europhys. Lett. 39, 545 (1997).
10. Moon-Ho Jo, N. D. Mathur, N. K. Todd, M. G. Blamire, Phys. Rev B 61, R14905 (2000).
11. Yafeng Lu, J. Klein, C. Höfener, B. Wiedenhorst, F. Herbstritt, L. Alff, and R. Gross, to be published.
12. R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. 71, 2331 (1993).
13. S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science 264, 413 (1994).
14. N. D. Mathur, G. Burnell, S. P. Isaac, T. J. Jackson, B.-S. Teo, J. L. MacManus-Driscoll, L. F. Cohen, J. E. Evetts, and M. G. Blamire, Nature 387, 266 (1997).
15. K. Steenbeck, T. Eick, K. Kirch, K. O’Donnell, and E. Steinbeiß, Appl. Phys. Lett. 71, 968 (1997).
16. J. Klein, C. Höfener, S. Uhlenbruck, L. Alff, B. Büchner, and R. Gross, Europhys. Lett. 47, 371 (1999).
17. R. Gross, L. Alff, B. Büchner, B. H. Freitag, C. Höfener, J. Klein, Yafeng Lu, W. Mader, J. B. Philipp, M. S. R. Rao, P. Reutler, S. Ritter, S. Thienhaus, S. Uhlenbruck, B. Wiedenhorst, J. Magn. Magn. Mater. 211, 150 (2000).
18. C. Höfener, J. B. Philipp, J. Klein, L. Alff, A. Marx, B. Büchner, and R. Gross, Europhys. Lett. 50, 681 (2000).
19. B. Wiedenhorst, L. Alff, C. Recher, J. Klein, R. Gross, T. Walther, and W. Mader, subm. for publ. (2000).
20. R. Gross, J. Klein, B. Wiedenhorst, C. Höfener, U. Schoop, J. B. Philipp, M. Schonecke, F. Herbstritt, L. Alff, Yafeng Lu, A. Marx, S. Schymon, S. Thienhaus, and W. Mader, SPIE Conf. Proc. Vol. 4058 (2000).
21. B. Wiedenhorst, C. Höfener, Y. Lu, J. Klein, L. Alff, R. Gross, B. H. Freitag, and W. Mader, Appl. Phys. Lett. 74, 3636 (1999).
22. S. Zhang, P. M. Levy, A. C. Marley, and S. S. P. Parkin, Phys. Rev. Lett. 79, 3744 (1997).
23. A. Hubert and R. Schäfer, Magnetic Domains, Springer Verlag, Berlin, Heidelberg, New York (1998).
24. V. K. Vlasko-Vlasov, Y. K. Lin, D. J. Miller, U. Welp, G. W. Crabtree, V. I. Nikitenko, Phys. Rev. Lett. 84, 2239 (2000).
25. W. J. Gallagher, S. S. P. Parkin, Yu Lu, X. P. Bian, A. Marley, K. P. Roche, R. A. Altman, S. A. Rishton, C. Jahnes, T. M. Shaw, and Gang Xiao, J. Appl. Phys. 81, 3741 (1997).