Magnetoresistance at artificial interfaces in the itinerant $SrRuO_3$ ferromagnet

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The magnetoresistance across interfaces in the itinerant ferromagnetic oxide $SrRuO_3$ have been studied. To define appropriately the interfaces, epitaxial thin films have been grown on bicrystalline and laser-patterned $SrTiO_3$ substrates. Comparison is made with results obtained on similar experiments using the double-exchange ferromagnetic oxide $La_{2/3}Sr_{1/3}MnO_3$. It is found that in $SrRuO_3$, interfaces induce a substantial negative magnetoresistance, although no traces of the low-field spin tunneling magnetoresistance are found. We discuss these results on the basis of the distinct degree of spin polarization in ruthenates and manganites and the different nature of the surface magnetic layer formed at interfaces. [S0163-1829(99)05134-6]

Half-metallic ferromagnetic oxides such as chromium dioxide or the celebrated manganese perovskites are predicted to be almost fully spin-polarized systems. This is a requisite of ideal electrodes for the newcoming generation of magnetoelectronic devices. These materials also share the notable characteristic of being double-exchange (DE) ferromagnets, i.e., systems with localized atomic moments coexisting with itinerant ones and where the ferromagnetic coupling is transmitted via the mobile charge carriers.

Owing to their 100% polarization, spin-polarized tunnel experiments in sandwiched FM/I/FM heterostructures (FM is a ferromagnet and I an insulating tunnel barrier) have indeed revealed a very large resistivity change upon reversing the relative magnetization of the FM electrodes. Resistivity changes of about 85% at 5 K have been reported for $La_{2/3}Sr_{1/3}MnO_3/SrTiO_3/La_{2/3}Sr_{1/3}MnO_3$ junctions.[1] Large magnetoresistance ratios have also been reported for artificial grain boundaries either in bicrystals[2] or even in granular materials.[3–6] However, a serious drawback has appeared: there is a sharp decay of the magnetoresistance (MR) of the junction when rising the temperature, and it becomes vanishingly small well below the Curie temperature T_C when the magnetization M_b of the sample is still almost saturated. This appears to be a common trend, observed in all DE materials either manganites[2–4] or CrO_2.[5]

In contrast, the tunnel magnetoresistance observed in ceramic superexchange ferromagnets, such as $Tl_2Mn_2O_7$, displays a weaker temperature dependence and the MR follows basically the magnetization.[7] It thus appears that the mechanism of magnetic interaction has profound effects on the temperature dependence of the magnetoresistance.

It has been suggested that DE materials are prone to display carrier depolarization at interfaces, which reduces the observed magnetoresistance at low fields below its ideal 100% value and promotes the sharp decay with temperature. Experiments and theoretical models indicate that this may arise from the existence of a nonferromagnetic surface layer at interfaces.[4,8–10] In superexchange ferromagnets the strength of the magnetic interaction is independent of any charge transfer, and thus ferromagnetism at interfaces is expected to be more robust.

Itinerant metallic ferromagnetic oxides, such as $SrRuO_3$,[11] appear to be an intermediate class of materials, where the role of interfaces on the magnetoresistance has not been explored yet. The purpose of this paper is to study the magnetoresistance through artificial interfaces created in epitaxial $SrRuO_3$ (SRO) thin films. We will show that in this itinerant ferromagnet, magnetoresistance develops at magnetically disordered interfaces. However, no traces of the low-field tunnel magnetoresistance are observed. From the comparison between data obtained in SRO and from equivalent experiments using $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) thin films, we will conclude that whereas interfaces in manganites introduce a magnetic decoupling, this is not the case in SRO. We will argue that this difference arises mainly from the distinct nature of the magnetic interface layer in DE and itinerant ferromagnets, while the distinct degree of spin polarization of both metals appears to have only a secondary role.

$SrRuO_3$ and $La_{2/3}Sr_{1/3}MnO_3$ epitaxial thin films of about 20 nm have been grown using a pulsed-laser ablation deposition system, on $SrTiO_3$ (001) single crystals or 23° bicrystalline $SrTiO_3$ (001) substrates.

Prior to film deposition the $SrTiO_3$ single-crystalline substrates were patterned by using a 248-nm (KrF) laser beam. By appropriate focusing and motion the beam spot can be used to produce an artificial and well-defined scratch of the $SrTiO_3$ substrate. Electron microscopy images have revealed that the track formed is about 25 μm in width and 1–2 μm deep. Details of the substrate-patterning process can be found elsewhere.[12] Extensive structural characterization will be reported separately.[13] Here we only mention that the SRO film covers the track and large portions of the patterned region is undisturbed SRO film. In fact, within the track, the roughness of the SRO film is of about 1.2 nm, similar to that observed in regions far away from the track. The defective area is restricted to the microcracks existing at the track bot-

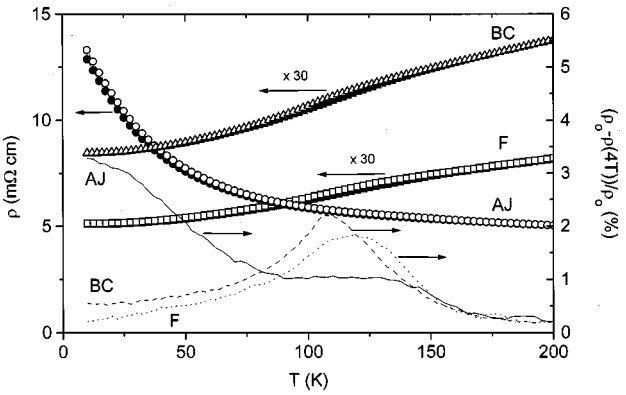

FIG. 1. Temperature dependence of the resistance across the laser-patterned artificial junction (AJ, ○), parallel to it (F, □), and across the bicrystal grain boundary (BC, △). $\mu_0 H=0$: open symbols. $\mu_0 H=4$ T: solid symbols. Temperature dependence of the magnetoresistance $\mathrm{MR}=[\rho(4T)-\rho_0]/\rho_0$ across the laser-patterned artificial junction (AJ, solid line), parallel to it (F, dashed line) and across the bicrystal grain boundary (BC, dotted line).

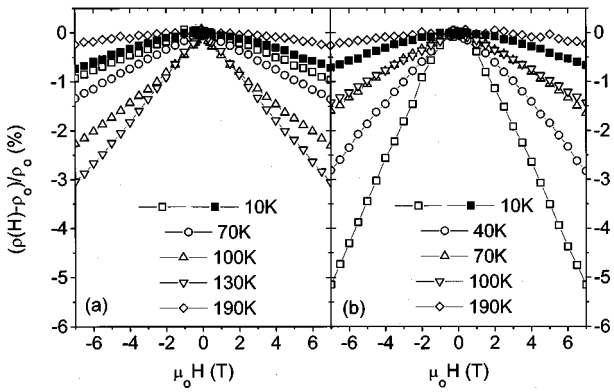

FIG. 2. Field dependence of the resistivity at various temperatures: (a) parallel to the laser-patterned artificial junction (open symbols) and parallel to the bicrystal grain boundary (solid symbols) and (b) across the laser-patterned artificial junction (open symbols) and across the bicrystal grain boundary (solid symbols).

tom, the rim, and the debris regions.[13] It is plausible that magnetoresistance develops mainly at these disturbed regions.

Magnetotransport measurements up to 9 T have been performed by using a four-probe technique. Gold pads for current and voltage contacts have been defined on the films by using the appropriate masks. They are placed in such a way that simultaneous measurement of the resistance across the junctions (either the artificial ρ_{AJ} or the bicrystalline ρ_{BC}) or parallel to it (ρ_f) can be performed. In all experiments reported here the magnetic field is perpendicular to the film plane. Magnetization has been determined by using a superconducting quantum interference device (SQUID) system.

As shown in Fig. 1, the film resistivity ρ_f (squares) displays a metallic behavior through the entire temperature range (200–5 K) with a kink at about $T_C \approx 125$ K, which signals the Curie temperature. The room-temperature resistivity ρ(300 K), of about 346 $\mu\Omega$ cm, is in good agreement with the reported values for epitaxial thin films and single crystals. The magnetization data, included in the inset of Fig. 4, indeed reveal the onset of spontaneous magnetization at $T \approx 130$ K. Although the measured T_C is somewhat lower than that observed in single crystals,[14] this can be explained by substrate induced stress.[15] The resistivity across the artificial junction (AJ) ρ_{AJ}, which is also shown in Fig. 1 (circles), is about a factor of 30 larger than ρ_f. It displays an insulating like temperature dependence, thus meaning that the AJ has generated a highly resistive interface in the SRO film. In Fig. 1 we have also included the resistivity ρ_{BC} measured across the bicrystal interface (triangles). In this latter case ρ_{BC} and the corresponding ρ_f (not shown) are metalliclike through the entire temperature range, thus meaning that the bicrystal interface has not created a substantial insulating barrier in the SRO film. In fact, ρ_{BC} is only about a factor of 2 larger than ρ_f.

In Fig. 1 we have also included ρ_f, ρ_{AJ}, and ρ_{BC} data recorded under a field of $\mu_0 H=4$ T (solid symbols). A negative magnetoresistance can be appreciated in ρ_f, particularly noticeable at $T \approx T_C$. The field dependence of these resistivities can be better observed through the magnetoresistance ratio $\mathrm{MR}=[\rho_0-\rho(H)]/\rho_0$, where ρ_0 is the resistivity at the coercive field. In Fig. 1 (right axis) we show the MR for ρ_f (MR_B), ρ_{BC} ($\mathrm{MR}_{\mathrm{BC}}$), and ρ_{AJ} ($\mathrm{MR}_{\mathrm{AJ}}$) at $\mu_0 H=4$ T. As expected, a pronounced bump appears in MR_f at $T \approx T_C$. At lower temperature MR_f is substantially reduced.

A very similar behavior is displayed by the bicrystalline junction: $\mathrm{MR}_{\mathrm{BC}}$ has its maximum at $T \approx T_C$ and progressively reduces when lowering temperature. It is important to notice that no significant difference is observed between the magnetoresistance across the bicrystalline junction $\mathrm{MR}_{\mathrm{BC}}$ and the film MR_f. In contrast, $\mathrm{MR}_{\mathrm{AJ}}$ displays some enhancement at T_C, but progressively increases when lowering the temperature below T_C. It becomes larger than MR_f, thus clearly indicating an enhanced magnetoresistance across the artificial junction. This behavior is reminiscent of that observed in $La_{2/3}Sr_{1/3}MnO_3$ films grown on top of bicrystalline substrates[2] or ceramic samples.[3,4]

The field dependence of the resistivity, at various temperatures, for the films and across the junctions (laser patterned and bicrystal), is shown in Fig. 2. We first note that all of them vary almost linearly with the field. Of the highest significance is that in $\mathrm{MR}_{\mathrm{AJ}}$ and $\mathrm{MR}_{\mathrm{BC}}$ [Fig. 2(b)], there are no traces of the low-field resistance drop as observed in artificial junctions in manganite films.[2] On the other hand, it can be observed in Fig. 2(a) that the bulk magnetoresistance MR_f, at any field, increases with rising temperature and displays a maximum close to T_C. This is the expected behavior when the magnetoresistance is only related to spin-spin correlations setting in at the Curie temperature. As shown in Fig. 2(b), $\mathrm{MR}_{\mathrm{BC}}$ (solid symbols) does not reveal any modification with respect to the bulk MR_f magnetoresistance. In contrast, $\mathrm{MR}_{\mathrm{AJ}}$ (open symbols) only has a modest enhancement at T_C, but remarkably, it gradually increases when lowering the temperature. Clearly, at 10 K, $\mathrm{MR}_{\mathrm{AJ}}$ is much larger than $\mathrm{MR}_{\mathrm{BC}}$. Therefore, the data of Figs. 1 and 2 conclusively show that a bicrystal or laser-patterning-induced interfaces do not promote the low-field spin-tunneling magnetoresistance as observed in LSMO. However, a significant negative magnetoresistance is induced in the laser-patterned interface.

In order to compare the magnetoresistance of ruthenates

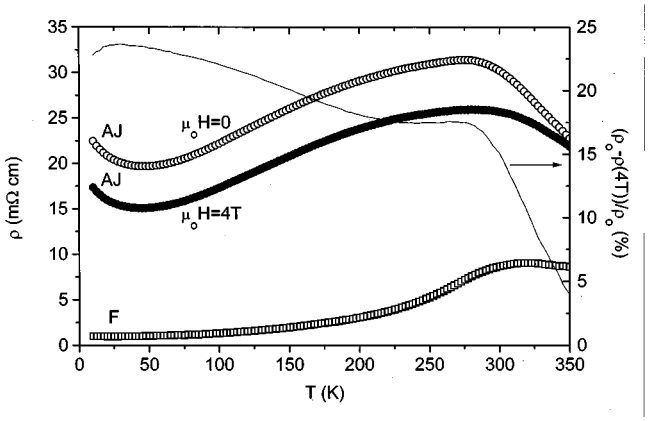

FIG. 3. Temperature dependence of the resistivity of LSMO film across the laser-patterned artificial junction (AJ, ○), and parallel to it (F, □). $\mu_0 H=0$: open symbols. $\mu_0 H=4$ T: solid symbols.

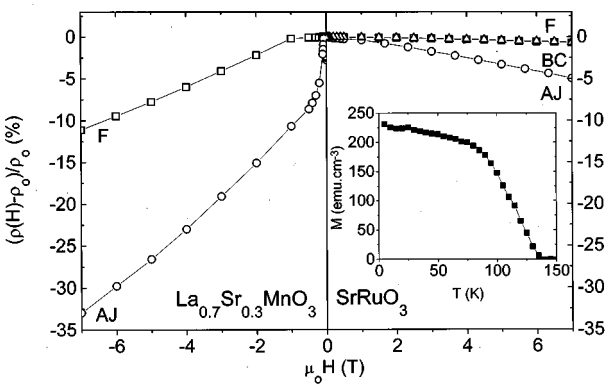

FIG. 4. Comparison of the field dependence of the magnetoresistance of the LSMO (left) and SRO (right) films at 10 K. Inset: temperature dependence of the magnetization of the SRO film ($\mu_0 H=1$ T).

and manganites, we have measured the magnetoresistance of a $La_{2/3}Sr_{1/3}MnO_3$ epitaxial film grown on top of a similarly patterned $SrTiO_3$ substrate. In Fig. 3 we show the temperature and field dependence of the corresponding ρ_{AJ} and ρ_f. We first note that, as expected, ρ_{AJ} is larger than ρ_f and, what is more important, whereas MR_f has the characteristic maximum at T_C (not shown), MR_{AJ} (right axis) is much larger than MR_f and it increases when reducing the temperature below T_C. This behavior simply reveals an enhanced magnetoresistance at the interface induced by the scratched substrate and mimics the results obtained in bicrystalline junctions.[2]

Of relevance is the comparison of the field dependence of the low-temperature MR_{AJ} and MR_f values of the LSMO and SRO films. This is shown in Fig. 4. It is clear that at 10 K, MR_{AJ}(LSMO) displays the low-field drop typical of tunneling magnetoresistance and a high-field (>0.5 T) response which is believed to be due to field-induced spin reorientation at interfaces.[4,10] In contrast, as mentioned above, the low-field response is absent in SRO either in MR_{AJ} or in MR_{BC} (right panel). In addition, one should notice that the high-field slope $d\mathrm{MR}/dH$ is much larger in LSMO (-3.23% T^{-1}) than in SRO (-0.71% T^{-1}), thus producing a magnetoresistance across the junction MR_{AJ} much larger for the LSMO films than for the SRO film. In fact, at 7 T, for instance, $MR_{AJ}(\mathrm{LSMO})/MR_{AJ}(\mathrm{SRO})\approx 6$.

The differences among the magnetoresistance of SRO and LSMO junctions can be summarized as follows: (a) the absence in SRO of the low-field tunnel magnetoresistance; (b) the bicrystalline junction in SRO does not produce significant changes of resistivity and magnetoresistance, whereas it does in LSMO; (c) laser-patterned junctions produce substantial high-field magnetoresistance in both SRO and LSMO; and (d) the high-field slope $d\mathrm{MR}/dH$, through similar interfaces, is much larger in LSMO than in SRO. We shall discuss now the origin of such distinct behavior.

(a) The absence of low-field spin tunnel magnetoresistance at the bicrystal and artificial junctions in SRO strongly suggests that the created interfaces do not produce a magnetic decoupling of adjacent sides: i.e., ferromagnetic coupling extends all the way thorough the interface region. Even for the wider structurally and magnetically disrupted regions obtained in the AJ's, the low-field spin tunnel response is absent. These results suggest that the magnetic coupling through the AJ and BC interface in SRO is strong enough to avoid any switch from parallel to antiparallel magnetization. Of course, this is not the case in LSMO where this magnetic switching produces the low-field magnetic response.

(b) The observation that in SRO ρ_{BC} is similar to ρ_f indicates that the bicrystalline interface does not have a large resistivity. In addition, the fact that the MR_{BC} is practically identical to MR_f even at high field implies that no significant magnetic disorder is induced at the bicrystal interface. These results are clearly in contrast to those observed in LSMO, where ρ_{BC} is found to be much larger than the corresponding ρ_f and where a significant high-field magnetoresistance across the junction is also found.[16] Therefore, from (a) and (b) we should conclude that highly resistive tunnel barriers are formed at interfaces in LSMO, but not in SRO. We will discuss this important issue in connection with point (d) (see below).

(c) However, the wider spatial extent of the structurally disturbed material in the laser-induced artificial junctions leads to a significant resistivity enhancement both in LSMO and SRO. The observance of a high-field magnetoresistance in both materials reflects the existence of some degree of spin disorder at the AJ interfaces.

(d) In order to account for the observed larger $d\mathrm{MR}/dH$ in LSMO than in SRO, we note that the high-field magnetoresistance can be simply written as $d\mathrm{MR}/dH\approx F(P)\chi$, where χ is the interface magnetic susceptibility[4,16,17] and $F(P)$ is a function of the polarization P of the current flowing across. Naturally, LSMO and SRO differ in both aspects.

We consider, first, the distinct degree of spin polarization and the nature of the ferromagnetic interaction in SRO and LSMO. The reported saturation magnetization of SRO is of about $(1.4-1.1)\mu_B$,[11,14,18] which is well below the expected value for a low-spin $4d^4$ configuration ($S=1$). The reduced ferromagnetic moment has been attributed to band ferromagnetism.[11] Recent band structure calculations have indeed predicted such behavior and a partial polarization of the conduction band.[19] From the ratio between measured magnetic moment to that expected for a $S=1$ configuration one can estimate a band polarization $P_{SRO}\approx 50\%$. Therefore, the magnetoresistance and $d\mathrm{MR}/dH$ in SRO should be

smaller than in LSMO where $P_{\mathrm{LSMO}} \approx 100\%$. This is indeed our experimental observation.

We should consider now the nature of the interface layer in LSMO and SRO. In LSMO, interfaces are thought to be formed by a strongly frustrated magnetic array due to the competition of existing antiferromagnetic (superexchange) and ferromagnetic (double-exchange) interactions. It has been proved that DE materials have a poor magnetic surface layer. Indeed Park *et al.*[9] have shown that the surface magnetization at $T/T_C > 0.10$ is well below the bulk one. Theoretical calculations have shown that a highly resistive and magnetically disrupted surface layer results from the strong competition among existing ferromagnetic and antiferromagnetic interactions.[10] Therefore, insulating barriers can be easily formed increasing ρ_{BC} and ρ_{AJ} well above ρ_f and leading to the spin tunnel low-field $\mathrm{MR_{AJ}}$ and $\mathrm{MR_{BC}}$. Of course, the magnetic susceptibility of this interface contributes to the measured $d\mathrm{MR}/dH$.

In SRO our experimental finding is that modifications of the structure at the interfaces, as in artificial junctions, have a significant role on its magnetic and transport properties. In fact, Allen *et al.*[19] have shown that for an ideal undistorted cubic structure, the Stoner factor is only about 1.04, whereas for the actual structure the Stoner factor increases as much a 40% (1.39). The observation that $SrRuO_3$ is a ferromagnetic oxide whereas $CaRuO_3$ does not order magnetically down to 1 K (Ref. 19) illustrates that tiny structural distortions of the oxygen octahedra may change the $4d(\mathrm{Ru})$-$2p(\mathrm{O})$ orbital hybridization, suppressing the itinerant ferromagnetism. Therefore, a substantial interface susceptibility should be expected and consequently the appearance of a negative magnetoresistance. We note, however, that although ferromagnetism is suppressed in the more distorted $CaRuO_3$ perovskite, it remains metallic. Similarly, it can be also expected that structurally distorted interfaces in SRO will remain mainly metallic, and thus there will be no chances for the observation of tunnel magnetoresistance. This is agreement with our experimental findings.

In summary, we have demonstrated that artificial interfaces created in SRO epitaxial thin films lead to an enhanced magnetoresistance. This magnetoresistance appears to be mainly determined by the existence of weakly ferromagnetic or paramagnetic (Pauli) disordered regions at interfaces. The smaller degree of spin polarization in the SRO oxides accounts for the observed weaker magnetoresistance. This result reflects that also in this itinerant ferromagnet, the ferromagnetic coupling is sensitive to structural modifications. The absence of any substantial low-field tunnel magnetoresistance in bicrystal or laser-patterned interfaces in SRO, whereas it is apparent in LSMO, indicates that ferromagnetic exchange coupling across interfaces remains and that the magnetic switching phenomenon is not operative. In LSMO the situation is just the opposite, and insulating, antiferromagnetic, or spin-glass-like interface barriers allow magnetic decoupling across interfaces and thus they are susceptible for a large tunnel magnetoresistance. This appears to be the key difference between interfaces in DE and itinerant ferromagnets.

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