Spin-Polarized Intergrain Tunneling in $La_{2/3}Sr_{1/3}MnO_3$

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(Received 27 March 1996)

The magnetoresistance (MR) and the field dependent magnetization have been systematically examined in the low temperature ferromagnetic metallic state of single crystal and polycrystalline $La_{2/3}Sr_{1/3}MnO_3$. We find that the intrinsic negative MR in single crystal is due to the suppression of spin fluctuations, and magnetic domain boundaries do not dominate the scattering process. In contrast, we demonstrate that the MR in the polycrystalline samples exhibits two distinct regions: large MR at low fields dominated by *spin-polarized tunneling* between grains and high field MR which is remarkably temperature independent from 5 to 280 K. [S0031-9007(96)01016-2]

PACS numbers: 72.15.Gd, 75.30.Kz, 75.50.Cc

The recent renaissance of interest in perovskite manganites has focused on the large magnetoresistance (MR) observed near the ferromagnetic ordering of Mn spins [1–6]. The Curie temperature T_C marks a transition from a high temperature paramagnetic insulator to a low temperature ferromagnetic metal. The basis for the theoretical understanding of these materials is the notion of "double exchange," which considers the magnetic coupling between Mn^{+3} and Mn^{+4} that results from the motion of an electron between the two partially filled *d* shells with strong on-site Hund's coupling [7–9]. At temperatures below T_C, the MR should be simply related to the reduction of spin fluctuations by an applied magnetic field. Despite this expectation, there is a wide range of reported behavior for the MR far below T_C, ranging from a linear field dependence of the magnetoconductivity, an exponential field dependence of the MR, and even more complicated field dependences have been observed [10–12]. Thus far it has been difficult to interpret the MR in this supposedly simple low temperature regime.

In order to address these discrepancies and to gain an understanding of the MR in the ferromagetic phase, we have carefully studied and compared the MR and the field dependent magnetization in single crystal and polycrystalline $La_{2/3}Sr_{1/3}MnO_3$. We find that the negative MR of the single crystal is due to the suppression of spin fluctuations, and magnetic domain boundaries do not dominate the scattering process. In contrast, we show that the negative MR of the polycrystalline samples is dominated by spin-polarized tunneling between grains, and the key feature observed is a large negative MR at very low fields associated with magnetic domain rotation at the grain boundaries. Above $\sim$0.5 T, we have discovered that the MR is independent of temperature over a wide range from 5 to 280 K. These phenomena are greatly enhanced by the high degree of spin polarization in the low temperature ferromagnetic regime.

For this study, single crystal $La_{2/3}Sr_{1/3}MnO_3$ was grown using the floating zone method, and polycrystalline $La_{2/3}Sr_{1/3}MnO_3$ was prepared through conventional solid-state reaction processing in air. Two polycrystalline samples were studied, with final sintering temperatures of 1300 and 1700 °C. Two samples were prepared to compare the effects of grain size and intergrain connectedness in the polycrystalline samples. Powder x-ray diffraction showed clean single-phase patterns. Resistivity ρ was measured using the standard four probe technique, and magnetization was measured using a commercial magnetometer (Quantum Design).

$\rho(T)$ for single crystal and polycrystalline $La_{2/3}Sr_{1/3}MnO_3$ are shown in the top panel of Fig. 1 [13]. All three samples show a sharp drop in ρ at 365 K, which also marks the ferromagnetic transition. At low temperatures, ρ for the 1700 °C polycrystalline sample is an order of magnitude larger than that of the single crystal, a typical consequence of the scattering introduced by grain boundaries. The 1300 °C sample is almost an order of magnitude larger than the 1700 °C sample, due to the smaller grain size formed at the lower sintering temperature. We note that the low temperature ρ of 35 $\mu\Omega$ cm for the single crystal is by far the lowest reported value for perovskite manganites.

Despite these differences in ρ, the temperature dependence of the magnetization at 0.5 T is very similar in these three samples, as shown in the lower panel of Fig. 1. The inset shows the field dependent magnetization at 5 and 280 K for the three samples. The magnetization response is typical for a soft ferromagnet—a quick rise in magnetization due to magnetic domain rotation at low applied fields, and then near saturation at higher applied fields. The small differences between the samples at low fields are due to the different demagnetization factors. Although the three samples were cut to the same geometry and thus have the same bulk geometric demagnetization factor, the polycrystalline samples have an additional factor due to their slight porosity. The magnetization was taken at 0.5 T to avoid the variation due to magetic domain rotation at lower fields.

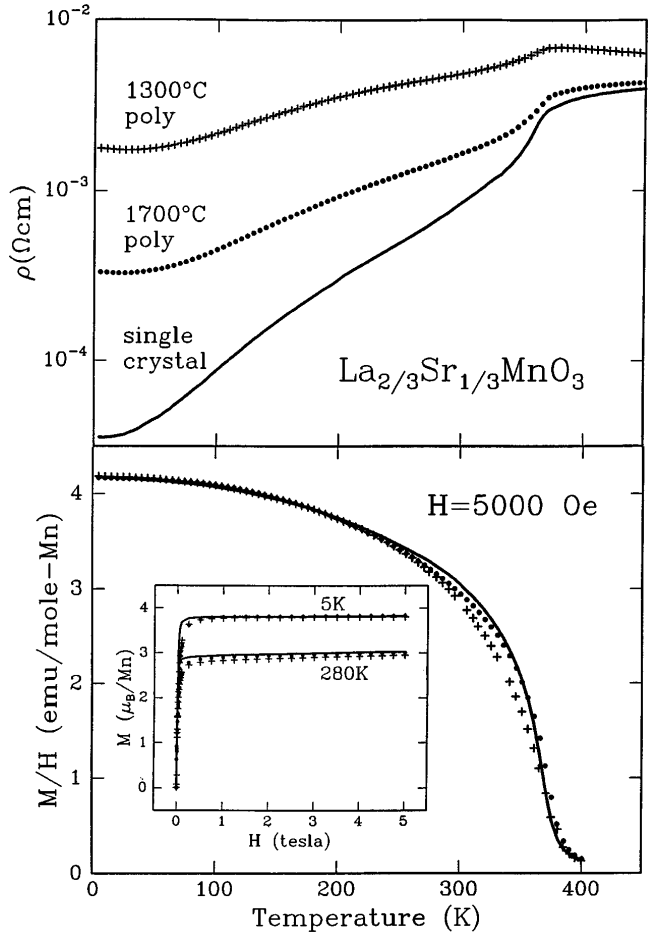

FIG. 1. Top panel: $\rho(T)$ of $La_{2/3}Sr_{1/3}MnO_3$ for a single crystal sample and two polycrystalline samples with final sintering temperatures of 1300 and 1700 °C. Bottom panel: The temperature dependence of the magnetization for these three samples at 0.5 T. Inset: The field dependent magnetization of these samples at 5 and 280 K.

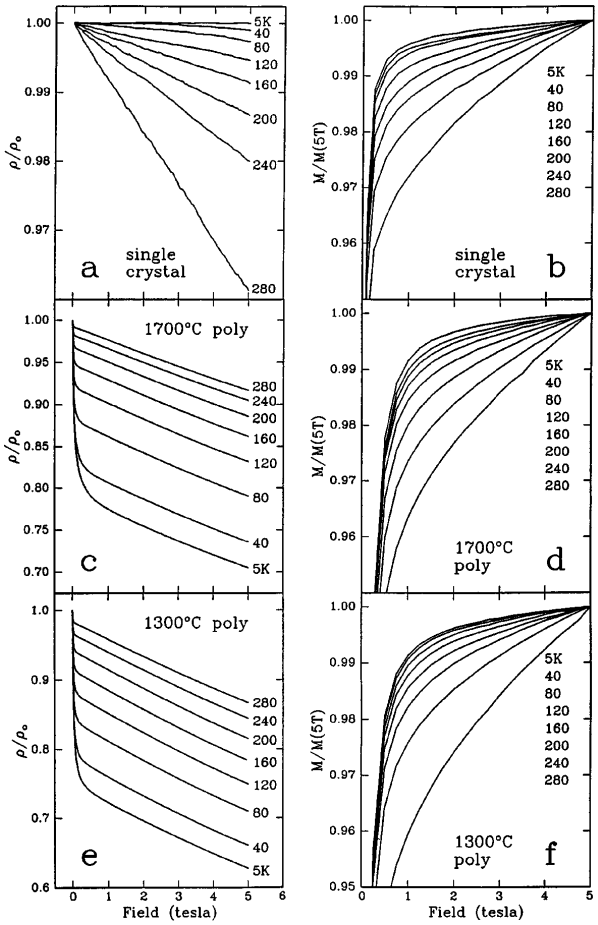

FIG. 2. Panels a, c, and e: The magnetic field dependence of the normalized resistance at various temperatures from 5 to 280 K. Panels b, d, and f: The magnetic field dependence of the magnetization (normalized to the 5 T value) at various temperatures from 5 to 280 K.

In Fig. 2 we present a detailed comparison of the field dependence of ρ in the longitudinal geometry (magnetic field **H** parallel to current **J**) and the magnetization of the single crystal and the two polycrystalline samples for a range of temperatures 5–300 K. Figure 2(a) shows the variation in the resistance (normalized by the zero field value) of the single crystal. At low temperatures there is negligible MR, and with increasing temperature there is increasing negative MR. Note that ρ smoothly varies through the region of magnetic domain rotation (inset to Fig. 1), indicating that electron scattering at magnetic domain boundaries does not dominate transport. In Fig. 2(b), the field dependent magnetization (normalized by the 5 T value) is shown for the same sample measured in Fig. 2(a). Although the magnetization has reached $\geq$95% of its value by 0.5 T (due to magnetic domain rotation), clearly there is still significant increase in the magnetization above 0.5 T. The striking feature of this comparison is that the variation in the magnetization at various temperatures tracks the MR. At 5 K, when there is no detectable MR, the magnetization is nearly saturated. At 280 K, there is a 4% variation in the resistance and a 4% variation in the magnetization once magnetic domain rotation is completed. Thus it appears that the suppression of magnetic fluctuations is the origin of the negative MR in this sample.

The MR and magnetization of the polycrystalline sample sintered at 1700 °C are displayed in Figs. 2(c) and 2(d). The magnetization data look identical to that of the single crystal to very high accuracy (excluding small variations at low fields due to the demagnetization factor), indicating that the intragrain properties reflect bulk intrinsic properties. The MR, however, looks radically different. The predominant feature is a sharp drop in the resistance at low fields, and then a slower background negative MR. This sharp drop is greatest at lowest temperatures, and decreases with increasing temperature.

The MR and magnetization of the polycrystalline sample sintered at 1300 °C are displayed in Figs. 2(e) and 2(f). The magnetization data again are identical to that of Figs. 2(b) and 2(d), and the MR is very similar to that

of the other polycrystalline sample. This is quite remarkable, given that $\rho(T)$ of this 1300 °C sample is so different from the 1700 °C sample (see top panel of Fig. 1). It appears that a fundamentally different process is dominating the MR of the polycrystalline samples.

The unusual MR data of Figs. 2(c) and 2(e) can be understood by considering the following points: (1) The MR in the polycrystalline samples is dominated by intergrain effects. Even at 5 T, ρ values of the polycrystalline samples are far above that for the single crystal (see top panel of Fig. 1). (2) Volume fraction sensitive measurements (magnetization, x-ray diffraction) show no detectable difference between the single crystal and polycrystalline samples. (3) The magnetic field associated with the sharp drop in resistance is identical to that associated with magnetic domain rotation. This was established by comparing samples with different geometric demagnetization factors—both features (in MR and magnetization) are shifted to different applied magnetic fields together.

These points lead to the conclusion that the MR in the polycrystalline sample is dominated by transport across grain boundaries that is extremely sensitive to an applied magnetic field. We propose that our results are most consistent with spin-polarized intergrain tunneling.

Spin-polarized transport in granular ferromagnetic systems has received a resurgence of interest in recent years [14–16]. The early pioneering study of the MR in granular nickel films was followed by a derivation of the tunneling of spin-polarized electrons between magnetic metallic particles [17,18]. When the electron spin is conserved in the tunneling process, there is an additional magnetic coupling energy when the magnetic moments of the neighboring grains are not parallel. By considering the magnetic field dependence of this intergrain coupling energy, the first term in the high temperature expansion of the MR is given by

$$\Delta\rho/\rho_0 = -\frac{JP}{4k_BT}\left[m^2(H,T) - m^2(0,T)\right], \qquad (1)$$

where J is intergrain exchange constant, P is the electron polarization, and m is the magnetization normalized to the saturation value.

One reason that spin-polarized transport effects should be significant in the perovskite manganites is the high degree of spin polarization in these materials. In a typical itinerant ferromagnet such as nickel, a very wide conduction band (~4.5 eV) is split into minority and majority carrier bands offset by a small exchange energy (~0.6 eV), leading to a partial polarization of the electrons (~11%) [19,20]. In manganites, however, a relatively narrow majority carrier conduction band (~1.5 eV) is completely separated from the minority band by a large Hund's energy, as well as an exchange energy (~2.5 eV), leading to a nearly complete polarization of the electrons [21,22]. This is shown diagrammatically in Fig. 3.

We turn now to examine the MR in polycrystalline $La_{2/3}Sr_{1/3}MnO_3$ in this framework. Consistent with the

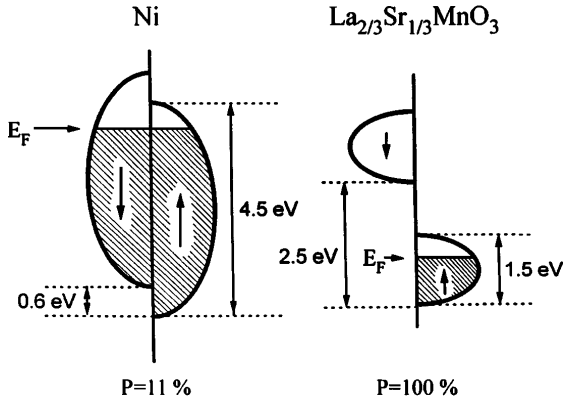

FIG. 3. Energy level diagram comparing the conduction band of Ni with $La_{2/3}Sr_{1/3}MnO_3$. Numerical values are taken from Refs. [19–22].

m^2 dependence of the MR, the sharp drop in resistance is associated with the sharp increase in magnetization. Because the MR is negative, J is positive, indicating an antiferromagnetic intergrain interaction. Thus the ferromagnetic alignment of the grains by an applied field gives rise to increased electron tunneling. The fact that both polycrystalline samples show quite similar MR, despite their radically different ρ values, is also consistent with the above considerations as there is no dependence on the absolute value of the ρ of the sample.

In order to analyze the temperature dependence of the part of the MR most clearly identified with spin-polarized tunneling, the sharp drop at low fields, we have back-extrapolated the high field $\rho(H)/\rho_0$ to find the zero field intercept. The magnitude of one minus this quantity, denoted MR*, quantifies the magnitude of the MR associ-

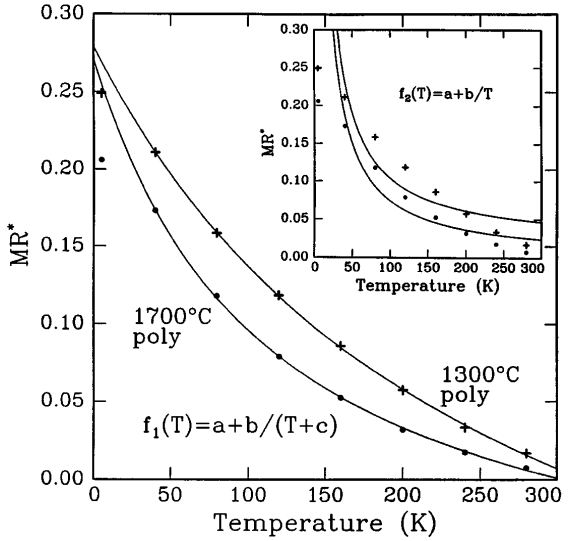

FIG. 4. The temperature dependence of MR* (defined in text). The lines are fits of the form $a + b/(T + c)$ for $T \geq 40$ K. For the 1300 °C sample, $a = -0.10$, $b = 41.6$ K, and $c = 112$ K. For the 1700 °C sample, $a = -0.22$, $b = 129$ K, and $c = 255$ K. Inset: Best fits to the same data of the form $a + b/T$ for $T \geq 40$ K.

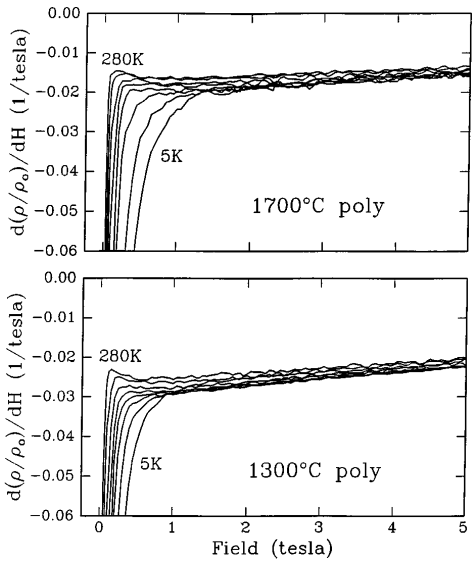

FIG. 5. $d(\rho/\rho_0)/dH$ from the data of Figs. 2(c) and 2(e) for the 1300 and 1700 °C polycrystalline samples.

ated with magnetic domain rotation. Figure 4 shows the temperature dependence of MR^* for both polycrystalline samples. There is good qualitative agreement with the prediction of an increasing MR with decreasing temperature. We find, however, a quantitative discrepancy in the temperature dependence which is unsurprising for a comparison to a simplified model. The inset to Fig. 4 shows the best $a + b/T$ fits to the data for $T \geq 40$ K, and it can be seen that this does not accurately describe the temperature dependence of MR^*. The main panel of Fig. 4 shows that the function $a + b/(T + c)$ describes the data quite well for $T \geq 40$ K, although the significance of this functional form is not understood at this time.

A striking feature of the polycrystalline samples is that above ~0.5 T, the MR appears to have the exact same field dependence for the entire temperature range 5–280 K. In Fig. 5 this is demonstrated for both samples by examining $d(\rho/\rho_0)/dH$. In both cases all of the data at different temperatures collapse to the same line. It apears that the MR in this region has a weak H^2 dependence in addition to the visually obvious dominant H linear term.

The low field MR of the polycrystalline samples is quite interesting from a technological perspective. Some of the early criticisms about the technological relevance of the manganites was the fact that the large MR associated with T_C was restricted to a narrow temperature range, and the large ρ near T_C (and the simultaneous metal-insulator transition) would give rise to unacceptably high levels of electrical noise in any real field sensing device. In the case of our polycrystalline samples, however, the temperature range appears to be all temperatures up to near T_C, throughout which the material is metallic and thus highly conductive. So although our first results are far from optimal, they seem to suggest that further work may lead to technologically important advances. Perhaps the most obvious and most promising route is the manifestation of these results in magnetic multilayers in analogy with those developed for giant magnetoesistance (GMR) systems. In the near future, the already somewhat artificial distinctions between GMR, so-called "colossal" magnetoresistance, and spin-polarized tunneling may be increasingly irrelevant.

In summary, we have examined the MR and magnetization of $La_{2/3}Sr_{1/3}MnO_3$ in the ferromagnetic metallic regime. The negative MR of the single crystal is due to the suppression of spin fluctuations, as expected of a double exchange ferromagnet. The dominant feature of the MR in the polycrystalline sample is a sharp low field MR due to spin-polarized electron tunneling between grains. This study has clarified the relative effects of bulk properties and interface properties. The unique nature of double exchange mediated ferromagnetism results in very high spin polarization of the conduction electrons in the ferromagnetic state, which makes this material an ideal candidate for maximizing spin-polarization dependent phenomena, including low field spin-valve MR.

We thank G. Aeppli, R. N. Bhatt, Y. B. Kim, and B. I. Shraiman for helpful discussions.

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