Intergrain Magnetoresistance via Second-Order Tunneling in Perovskite Manganites

S. Lee,[1] H. Y. Hwang,[1] Boris I. Shraiman,[1] W. D. Ratcliff II,[1,2] and S-W. Cheong[1,2]
[1]*Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974*
[2]*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854*
(Received 1 December 1998)

The intergrain magnetoresistance (IMR) observed in polycrystalline half-metallic ferromagnets at temperatures below the Curie temperature T_C was investigated. The systematics of the IMR, as a function of field and temperature for ferromagnetic manganites with varying T_C, shows that the high field magnetoconductivity (MC), rather than the magnetoresistance, is linear with magnetic field and the slope monotonically decreases with increasing T_C. The low field MC value in the low temperature limit is universally close to $\frac{1}{3}$, irrespective of T_C or composition. These experimental findings are consistent with second-order tunneling through interfacial spin sites at the grain boundary. [S0031-9007(99)09282-0]

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

Recently, significant intergrain magnetoresistance (IMR) has been observed in a number of polycrystalline half-metallic ferromagnets at temperatures below the Curie temperature T_C [1–5]. This phenomenon is characterized by an initial, rapid drop of resistance with applied field, followed by a slow decrease at higher fields. These two regimes cross over at the field for which near magnetic saturation is achieved. It has been shown that the IMR occurs at the grain boundaries, and the large degree of spin-polarization characteristic of half-metallic ferromagnets enhances the scale of these effects. The abrupt low field MR can be qualitatively interpreted within the early models applied to ferromagnet/insulator/ferromagnet tunnel junctions [6,7]. Julliere considered the case for tunneling between magnetically aligned and antialigned electrode configurations. Assuming the same matrix element for the tunneling of majority and minority spin electrons, then the MR between these configurations arises from the polarization-dependent joint density of states. The degree of spin polarization of the carriers, in turn, would follow the magnetization M in its temperature dependence. Analogous considerations apply to the materials, where the hopping electron is strongly aligned with the local orientation of the magnetization (via intra-atomic Hund's rule interaction), such as double exchange ferromagnets [7,8].

Despite the apparent applicability of the direct tunneling model, there are a number of features that cannot be readily understood within this picture. Perhaps the most important feature is the rapid decrease in the magnitude of the IMR with increasing temperature, often far below T_C, and more rapidly than expected from the temperature dependence of the magnetization. Thus the utility of this effect at room temperature remains unclear. The second feature is the nontrivial high field IMR, which, in fact, can be even larger than the low field IMR. Below we present a systematic study of the low and high field IMR for ferromagnetic perovskite manganites with varying T_C. In all samples, the high field *conductivity* $\sigma(H)$ is found to be purely linear with applied field, and this slope monotonically decreases with increasing T_C. The low field magnetoconductivity $[\sigma(H) - \sigma_0]/\sigma_0$ is universally close to $\frac{1}{3}$ in the low temperature limit. These results are compared with the IMR observed in two other suspected half-metallic ferromagnets, $Tl_2Mn_2O_7$ and CrO_2. The experimental observations can be understood by assuming that the intergrain tunneling is not direct but proceeds in two steps involving an intermediate state at the grain boundary interface which makes it sensitive to the magnetization of the surface.

For this study, polycrystalline perovskite manganite samples were prepared through a conventional solid state reaction in air. The chemical compositions of our samples are listed in Table I. The divalent ion (Ca or Sr) concentration was chosen for the optimum T_C region (0.3–0.4) and T_C was monitored by the Pr^{+3} or Nd^{+3} doping level. Pyrochlore $Tl_2Mn_2O_7$ was prepared by using a piston-cylinder-type high pressure apparatus. Polycrystalline films of CrO_2 were prepared by the thermal decomposition of CrO_3 under high oxygen pressure. These samples are listed in Table I. The magnetoresistance was measured using the standard four-probe method in the longitudinal geometry (magnetic field **H** parallel to current **J**).

In the top panel of Fig. 1, $\sigma(H)$ at 5 K is shown for the series of perovskite manganites with varying T_C,

TABLE I. Polycrystalline half-metallic samples with their Curie temperatures (T_C) and low field magnetoconductance values (MC^*, defined in text) at $T = 5$ K.

No.	Samples	T_C	MC^*
1	$La_{0.08}Pr_{0.62}Ca_{0.3}MnO_3$	80 K	24%
2	$La_{0.3}Pr_{0.4}Ca_{0.3}MnO_3$	140 K	24%
3	$La_{0.35}Pr_{0.35}Ca_{0.3}MnO_3$	165 K	30%
4	$Nd_{0.7}Sr_{0.3}MnO_3$	205 K	28%
5	$La_{0.35}Pr_{0.35}Sr_{0.3}MnO_3$	310 K	28%
6	$La_{0.67}Sr_{0.33}MnO_3$	365 K	33%
7	$Tl_2Mn_2O_7$	120 K	40%
8	CrO_2	395 K	18%

 0031-9007/99/82(22)/4508(4)$15.00

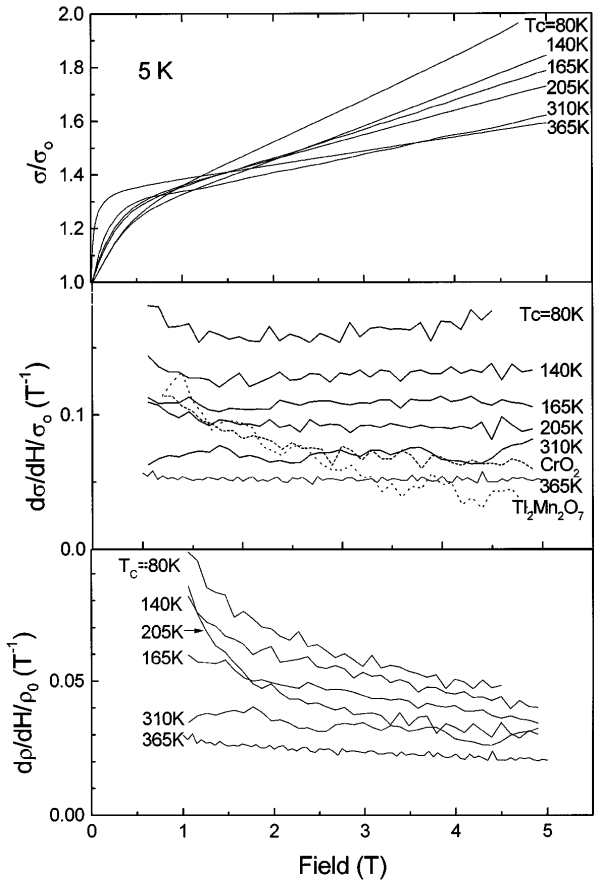

FIG. 1. The magnetic field dependence of the normalized conductivity at 5 K for perovskite manganite samples with varying T_C (top panel), and the corresponding normalized high field slopes of conductivity (middle panel), and resistivity (bottom panel) versus magnetic field. The middle panel also shows the data of $Tl_2Mn_2O_7$ and CrO_2.

normalized by the zero field value σ_0. Focusing first on the high field behavior ($H > 0.5$ T), two features are apparent. For all samples, $\sigma(H)$ is quite linear with the applied field, and the slope of the field dependence increases monotonically with decreasing T_C. To emphasize this point, the second and third panels of Fig. 1 compare the derivative of the conductivity with field $(d\sigma/dH)/\sigma_0$ and the derivative of the resistivity with field $(d\rho/dH)/\rho_0$ in the high field regime. Both $\sigma(H)$ and $\rho(H)$ can, of course, be described by a polynomial function of H, but as Fig. 1 demonstrates, $\sigma(H)$ is linear to a good approximation over the whole range of H. This feature appears to be a general characteristic of polycrystalline ferromagnetic manganites. By contrast, in the case of $Tl_2Mn_2O_7$ and CrO_2, the high field magnetoresistance is small and sublinear in field (see the middle panel of Fig. 1).

Having established the phenomenological behavior of $\sigma(H)$ in the high field regime, the data can be quantitatively analyzed by fitting the results to

$$\sigma/\sigma_0 = a(T) + b(T)H\,, \tag{1}$$

where constants a and b depend on temperature. The detailed field dependence in the low field region is a function of extrinsic quantities such as the geometric demagnetization factor. The important feature, however, is the low field magnetoconductance (denoted MC*), which can be described by $\mathrm{MC}^*(T) = a(T) - 1$. One of the interesting observations is that MC* (5 K) for all of the measured ferromagnetic manganites ranges between 24% and 33%, as shown in Table I. This low temperature value for MC* seems to be universal, irrespective of composition and T_C. By contrast, MC* of pyrochlore $Tl_2Mn_2O_7$ is 40%, and that of CrO_2 is 18%.

The behavior of $\sigma(H)$ described above may be attributed to the role of grain boundaries and the difference between the magnetization in the bulk and at the grain boundary surface. For the simplest model exhibiting such an effect, let us assume that the intergrain conductivity is dominated by a second-order tunneling process where the e_g electron first tunnels from the bulk of grain 1 to the state on the grain boundary interface then into the bulk of grain 2. In the double exchange magnets the spin of the hopping electron is aligned with the local t_{2g} moment so that the transfer integral between ions with normalized t_{2g} spins $\hat{\mathbf{s}}$ and $\hat{\mathbf{s}}'$ is proportional to $\sqrt{1 + \hat{\mathbf{s}} \cdot \hat{\mathbf{s}}'}$. Therefore, the conductivity via second-order tunneling across a grain boundary site is given by

$$\begin{aligned}\frac{\sigma}{\sigma_0} &\propto \langle (1 + \hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_b)(1 + \hat{\mathbf{s}}_b \cdot \hat{\mathbf{s}}_2)\rangle\,, \\ &\propto \langle 1 + \hat{\mathbf{s}}_b \cdot (\hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2) + (\hat{\mathbf{s}}_b \cdot \hat{\mathbf{s}}_1)(\hat{\mathbf{s}}_b \cdot \hat{\mathbf{s}}_2)\rangle\,,\end{aligned} \tag{2}$$

where $\hat{\mathbf{s}}_b$, $\hat{\mathbf{s}}_1$, and $\hat{\mathbf{s}}_2$ represent the spin orientations in the grain boundary and neighboring grains. The expression reduces to the zero field conductivity σ_0 in the absence of an external field provided that the spin directions of $\mathbf{S}_b$, $\mathbf{S}_1$, and $\mathbf{S}_2$ are uncorrelated in zero field, so that the average of all the spin product terms vanish. When the bulk magnetization is saturated at a low field, $\hat{\mathbf{s}}_1$ and $\hat{\mathbf{s}}_2$ become parallel, $\langle \hat{\mathbf{s}}_1 \rangle = \langle \hat{\mathbf{s}}_2 \rangle = \mathbf{M}$, with $\mathbf{M}$ being the normalized magnetization. The conductivity becomes

$$\frac{\sigma}{\sigma_0} \propto 1 + 2\mathbf{M} \cdot \langle \hat{\mathbf{s}}_b \rangle + \langle (\mathbf{M} \cdot \hat{\mathbf{s}}_b)^2 \rangle\,. \tag{3}$$

If the spins at the grain boundaries are disordered the second term vanishes, while the third term yields $M^2/3$ (since it can be written as $M^2\langle \cos^2\theta \rangle$, where θ is the angle between $\mathbf{S}_b$ and $\mathbf{M}$). Because of the normalization $M^2 < 1$, and the upper limit for conductivity rise just after saturation is 33.3%. This prediction is consistent with the experimental range of 24% to 33% in the initial conductivity rise at low temperatures. Any other resistivity neglected in our model, including bulk resistivity, would decrease the initial relative conductivity rise. The decrease of magnetization from full saturation is the source of temperature dependence. In the presence of a field, the thermal average of the boundary spin is proportional to $\chi_b H$.

Therefore, at high fields the conductivity is expressed by

$$\frac{\sigma - \sigma_0}{\sigma_0} \approx \frac{1}{3} M^2 + 2\chi_b HM , \qquad (4)$$

where χ_b is the spin susceptibility of the boundary states, predicting the linear increase of conductivity with H and in accord with the empirical form Eq. (1).

Let us now discuss the observed temperature dependence of MC* and the high field MC slope. The high field MC slope, defined as $b(T)$ in Eq. (1), changes with temperature and its temperature dependence depends on the T_C of the samples. In Fig. 2(b), the high field MC slope is plotted as a function of temperature for various manganites. If the slope is taken to be the measure of the boundary spin susceptibility χ_b according to Eq. (4), one interprets the lack of $1/T$ Curie divergence of the slope as evidence of surface spin interactions. The constant zero temperature limit of the susceptibility could be explained either by antiferromagnetic ordering of the boundary spins or by their freezing into a disordered state due to random exchange interactions or random anisotropies at the surface. It is entirely plausible that the Mn sites at the surface are quite different from the bulk, considering the reduced coordination of the surface sites, different distortions at the surface (so important for the bulk physical properties), etc. Furthermore, it is well known that depending on the orbital occupation and relative orientation of the orbitals, the neighboring Mn ions may have either ferro- or antiferromagnetic coupling. Figure 2(b) shows that there is a systematic trend of the temperature dependence with T_C. In perovskite manganites with $T_C \leq 205$ K (solid data points), the slope increases with temperature, while in those with $T_C \geq 310$ K (open data points), decreases. Curiously, the structure of the materials with $T_C \geq 310$ K happens to be rhombohedral while the other is orthorhombic [9]. In the perovskite manganites of orthorhombic structure, the strong colossal magnetoresistance effect, dominant near T_C, seems to be reflected in the increase of the high field MC slope as T_C is approached from below. The correlation of this effect with increasing orthorhombicity may suggest that the high field magnetoresistance is influenced by strains at the grain boundaries, especially near T_C.

In Fig. 2(a), the high field MC slope of ferromagnetic manganites obtained at $T = 5$ K is plotted for varying T_C along with those of $Tl_2Mn_2O_7$ and CrO_2. Since the MC slopes of $Tl_2Mn_2O_7$ and CrO_2 are not so well defined as explained above, the corresponding data points are somewhat qualitative. For ferromagnetic manganites the slope fits the functional form $A/(T_C + \Delta T)$ (solid line) with $A = 44 \pm 17$ and $\Delta T = 166 \pm 65$. The decrease of the MC slope with increasing transition temperature is consistent with the notion that it corresponds to a spin susceptibility which decreases as the characteristic energy scale of the exchange (and T_C) is increased.

The low field MC* also exhibits a strong temperature dependence which changes with T_C as shown in Fig. 3. The data have been normalized as $MC^*(T)/MC^*(T \to 0)$ and temperature as T/T_C. The graph shows that the higher T_C is, the more rapidly MC* diminishes with reduced temperature. Perovskite manganites share this tendency with $Tl_2Mn_2O_7$ and CrO_2. Although the T_C dependence of MC* may in part arise from that of the zero field resistivity of each sample [10], it is not the only factor responsible for

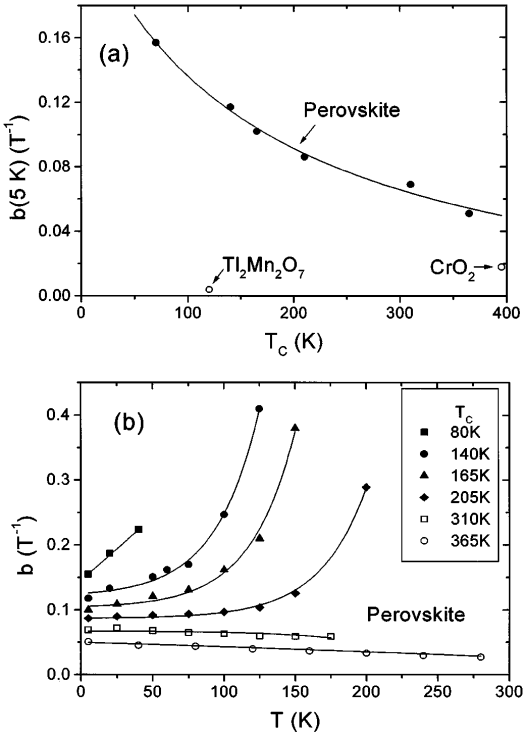

FIG. 2. (a) The high field MC slopes of perovskite manganites (solid circles), $Tl_2Mn_2O_7$, and CrO_2 (open circles) versus T_C at 5 K. The solid line represents the fit of manganite data to $A/(T_C + \Delta T)$. (b) The high field MC slope of perovskite manganites versus temperature for varying T_C. The solid lines are a guide to the eye.

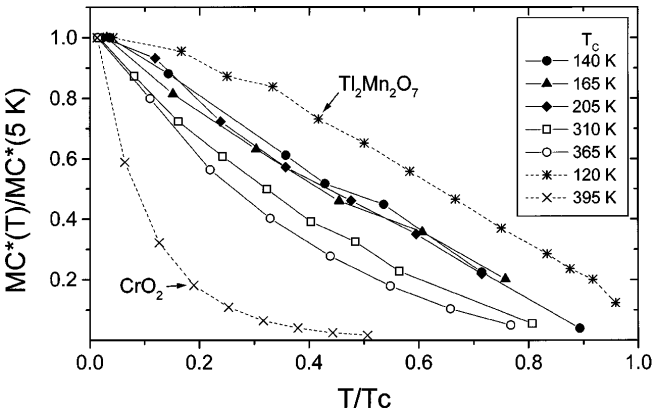

FIG. 3. The normalized MC* vs normalized temperature. The solid lines represent perovskite manganites, and the dashed lines represent $Tl_2Mn_2O_7$ and CrO_2.

the systematic trend of more rapidly decreasing MC^* with increasing T_C. The tunneling models of interfacial magnetoresistance, especially Eq. (4), predict $MC^* \propto M^2$. The MC^* data of low T_C materials roughly follow this relationship with bulk magnetization. However for the high T_C materials MC^* decays much faster than M^2 as $T/T_C \rightarrow 1$. This could be explained if the relevant magnetization controlling the tunneling were that of the surface and not the bulk (possibly because the carrier coherence length may be quite short compared to magnetic correlation length). The surface magnetization may be quite different from the bulk; even in the simplest case when magnetic interactions on the surface are the same as in the bulk, mean field theory predicts the surface magnetization to approach T_C as $M_S \sim T_C - T$ [11]. The approximately linear dependence of the surface magnetization on $T_C - T$ has been seen in a recent photoemission study on $La_{0.7}Sr_{0.3}MnO_3$ films with a $T_C = 350$ K [12]. When squared, this magnetic moment will induce the temperature dependence of MC^* similar to those of high T_C materials in Fig. 3. Yet, as we have already noted, the nature of magnetic interactions at the surface is not known, but may well be different from the bulk. Spin-polarized photoemission studies on low-T_C materials would help elucidate the T_C dependence of $M_S(T)$.

The discrepancy between the MC^* and high field slope of $Tl_2Mn_2O_7$ and those of perovskite manganites can be understood on the basis of our model provided the assumption that the magnetic phase of the insulating grain boundaries of polycrystalline $Tl_2Mn_2O_7$ is ferromagnetic. This is supported by the observation that $In_2Mn_2O_7$, isostructural with $Tl_2Mn_2O_7$, is a ferromagnetic insulator with a similar T_C [13]. The ferromagnetism in these materials appears to originate from superexchange due to a small Mn-O-Mn bond angle ($\sim$135°). Therefore, it is expected that the surface spin fluctuations are suppressed (relative to the perovskite case) and the magnetization is almost saturated at low field in grain boundaries. This results in an initial conductivity rise greater than $\frac{1}{3}$ and very low slope at high field as shown in Table I and Fig. 2(a).

In summary, we have investigated the systematics of the low field and high field IMR in polycrystalline half-metallic ferromagnets with varying T_C: perovskite manganites, $Tl_2Mn_2O_7$, and CrO_2. Analysis of the magnetoconductance indicates the dominant role of second-order tunneling through the interfacial spins at the grain boundary. Thus the interface magnetism and spin fluctuations are reflected in the magnetotransport properties, and controlling the interfacial magnetism would enhance the IMR effects, especially at room temperature.

W. D. R. and S. W. C. are partially supported by the NSF under Grant No. NSF-DMR-9802513.

[1] M. K. Gubkin, T. M. Perekalina, A. V. Bykov, and V. A. Chubarenko, Phys. Solid State **35**, 728 (1993).
[2] For a recent survey, see H. Y. Hwang and S-W. Cheong, in "Colossal Magnetoresistance Oxides," edited by Y. Tokura, Monographs in Condensed Matter Science (Gordon and Breach, New York, to be published).
[3] H. L. Ju, J. Gopalakrishnan, J. L. Peng, Q. Li, G. C. Xiong, T. Venkatesan, and R. L. Green, Phys. Rev. B **51**, 6143 (1995).
[4] R. D. Sanchez, J. Rivas, C. Vazquez-Vazquez, A. Lopez-Quintela, M. T. Causa, M. Tovar, and S. Oseroff, Appl. Phys. Lett. **68**, 134 (1996).
[5] R. Mahesh, R. Mahendiran, A. K. Raychaudhuri, and C. N. R. Rao, Appl. Phys. Lett. **68**, 2291 (1996).
[6] M. Julliere, Phys. Lett. **54A**, 225 (1977).
[7] S. Zhang, P. M. Levy, A. C. Marley, and S. S. P. Parkin, Phys. Rev. Lett. **79**, 3744 (1997).
[8] C. Zener, Phys. Rev. **82**, 403 (1951).
[9] P. G. Radaelli, M. Marezio, H. Y. Hwang, and S-W. Cheong, J. Solid State Chem. **122**, 444 (1996).
[10] G. J. Snyder, R. Hiskes, S. DiCarolis, M. R. Beasley, and T. H. Geballe, Phys. Rev. B **53**, 14 434 (1996).
[11] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, England, 1988).
[12] J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Phys. Rev. Lett. **81**, 1953 (1998).
[13] S-W. Cheong, H. Y. Hwang, B. Batlogg, and L. W. Rupp, Jr., Solid State Commun. **98**, 163 (1996).