Temperature dependence of magnetoresistance and nonlinear conductance of the bicrystal grain boundary in epitaxial $La_{0.67}Ba_{0.33}MnO_3$ thin films

Neeraj Khare,[a] U. P. Moharil, and A. K. Gupta
National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi-110012, India

A. K. Raychaudhuri
Department of Physics, Indian Institute of Science, Bangalore, India

S. P. Pai and R. Pinto
Tata Institute of Fundamental Research, Colaba, Mumbai-400005, India

We investigated conduction through an artificial grain-boundary junction made in $La_{0.67}Ba_{0.33}MnO_3$ thin films, deposited on a 36.7° $SrTiO_3$ bicrystal substrate using a laser ablation technique. The grain boundary exhibits substantial magnetoresistance at low temperatures and also shows nonlinear $I-V$ characteristics. Analysis of temperature dependence of the dynamic conductance allows us to identify three carrier transport mechanisms across the grain boundary. These mechanisms exist in parallel, and at a given temperature one mechanism may dominate. Particularly, at higher temperatures ($T > 175$ K) the transport across the grain boundary involves spin–flip scattering, which we establish leads to decrease of the bicrystal grain-boundary contribution in magnetoresistance. At lower temperature (4.2–45 K), tunneling through a disordered oxide at the grain boundary dominates, whereas in the temperature range from 100 to 175 K, carrier transport is dominated by inelastic tunneling via pairs of manganese atoms.

Observation of colossal magnetoresistance (CMR) in perovskite manganese oxides has generated a lot of scientific interest.[1–3] Epitaxial thin films of hole-doped $LaMnO_3$ show large magnetoresistance at a large field ($\sim$ few tesla) and in a narrow temperature range at the ferromagnetic transition temperature.[4] Unlike epitaxial thin films, bulk samples and polycrystalline films of doped $LaMnO_3$ show large magnetoresistance effects in the low-field region and even at a temperature much lower than the ferromagnetic transition temperature.[4–6] Recently, artificially created grain boundaries in epitaxial CMR films such as the bicrystal junction in $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) or $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films,[7,8] edge junction in LCMO film[9] have been found to exhibit substantial low-field magnetoresistance at a low temperature. In polycrystalline film or in bulk samples electrical transport across the grain boundaries is proposed to be due to spin-polarized tunneling[5] or due to spin-dependent scattering of polarized electrons at the grain boundaries.[3,4] A mesoscopic magnetoresistance model based on a grain-boundary region with strongly suppressed T_c has also been proposed.[10] Realization of a single artificial grain boundary in CMR epitaxial film provides a good opportunity for studying the role of the grain boundary in CMR materials. Todd *et al.*[11] studied the current–voltage characteristics of a bicrystal grain boundary in $La_{1-x}(Sr/Ca)_xMnO_3$ film and found that the results cannot be fully explained by direct tunneling across an insulating barrier.[12] Particularly, they found that the magnetoresistance might be uncorrelated to grain-boundary transport. Ziese *et al.*[9] proposed a model of spin-polarized tunneling in a ferromagnet/spin-glass/ferromagnet geometry to account for the observed nonlinear current–voltage characteristic across a step-edge junction in LCMO films. This letter reports the temperature dependence of magnetoresistance and dynamic conductance of a bicrystal grain boundary in $La_{0.67}Ba_{0.33}MnO_3$ (LBMO) thin film. Our study indicates that the mechanism of grain-boundary transport strongly depends on the temperature. At low temperatures carrier transport across a bicrystal grain boundary in LBMO thin film is dominated by inelastic tunneling, whereas at higher temperatures spin–flip scattering dominates. In the past, the temperature dependence of nonlinear transport through the grain boundary led to contradictory results.[9,11] This letter attempts to resolve the issue through an independent measurement.

A thin film of LBMO was prepared on a 36.7° bicrystal substrate of $SrTiO_3$ from a stoichiometric LBMO target using a pulsed-laser deposition technique in 400 mTorr oxygen partial pressure with the substrate at 750 °C. For studying the effect of the grain boundary on the transport characteristics, two microbridges (width$\sim$700 μm) have been fabricated. One microbridge was created across the bicrystal grain boundary and the other one away from the bicrystal grain boundary. The resistance–temperature ($R-T$) and current–voltage ($I-V$) characteristics of these microbridges were studied using a four-probe technique. For magnetoresistance (MR) measurements, a magnetic field was applied in the plane of the film, parallel to the grain boundary.

Figure 1(a) shows the $R-T$ curves for both microbridges. The microbridge across the bicrystal grain boundary (referred to as bridge A) showed a larger resistance and a smaller value of peak temperature ($T_p \sim 236$ K) in the $R-T$ curve. For the microbridge away from the grain boundary (referred to as bridge B), R was distinctly lower and T_p was

---

[a] Electronic mail: nkhare@csnpl.ren.nic.in

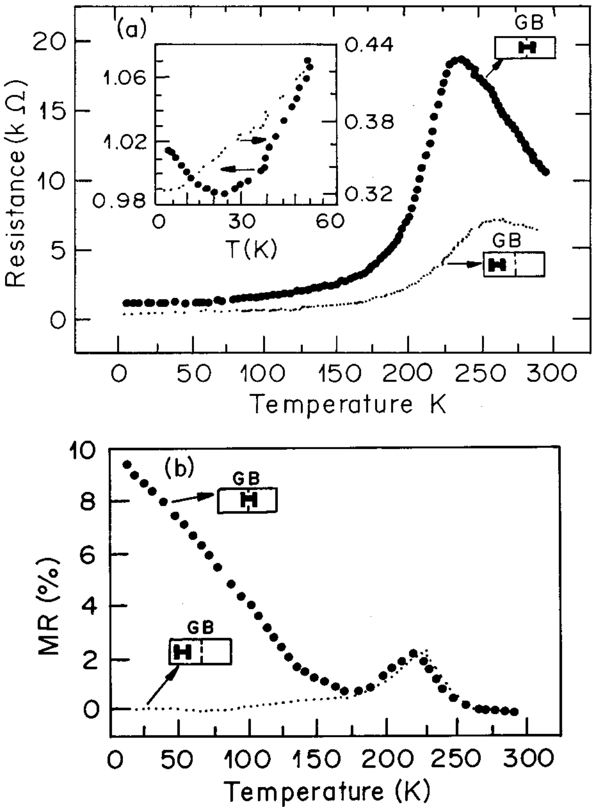

FIG. 1. (a) R–T curves for the LBMO thin-film microbridges. Inset shows a close up for $T<60$ K. (b) Temperature dependence of the magnetoresistance (MR) of the LBMO thin film microbridges across the bicrystal grain boundary and away from the grain boundary. $\mathrm{MR}=[R(0)-R(H)]/R(0)\times 100\%$; where $R(H)$ and $R(0)$ are the resistance of the microbridge in presence and in the absence of the magnetic field, respectively.

higher (~250 K). The observed smaller value of T_p of bridge A is most likely due to an oxygen-deficient layer at the grain boundary. Figure 1(b) shows the temperature dependence of the magnetoresistance for both microbridges at a 1 kOe magnetic field. Microbridge A shows a peak in MR–T curves at $T=215$ K, whereas microbridge B shows a peak at 225 K. At lower temperatures in microbridge B the value of the MR decreases with the decrease in temperature, and for $T<100$ K MR→0, as one expects for an epitaxial thin film. In sharp contrast, the value of the MR for bridge A shows a large rise as the temperature is lowered to 175 K. At 77 K, the value of the MR for bridge B is 0.02%, which is much smaller than the MR of 6% for bridge A. The grain-boundary contribution in total MR is found to decrease with the increase in temperature and it becomes negligibly small above 175 K.

Figure 2(a) shows the $I-V$ curves for both bridges at 4.2 K. Bridge A exhibits a nonlinear $I-V$ characteristic, whereas bridge B shows a linear $I-V$ characteristic. It is evident that this nonlinearity is due to the presence of the grain boundary. Figure 2(b) shows the normalized dynamic conductance (G/G_0; $G=dI/dV$) versus voltage curves for the bicrystal junction at different temperatures. Here, G_0 is the conductance of the junction at zero-bias voltage. It is clear that the nonlinearity in $I-V$ curves is a strong function of temperature, and above 175 K the nonlinearity becomes very small. We fitted the normalized conductance to the phenomenological relation, which quantifies the contribution of the nonlinear part:

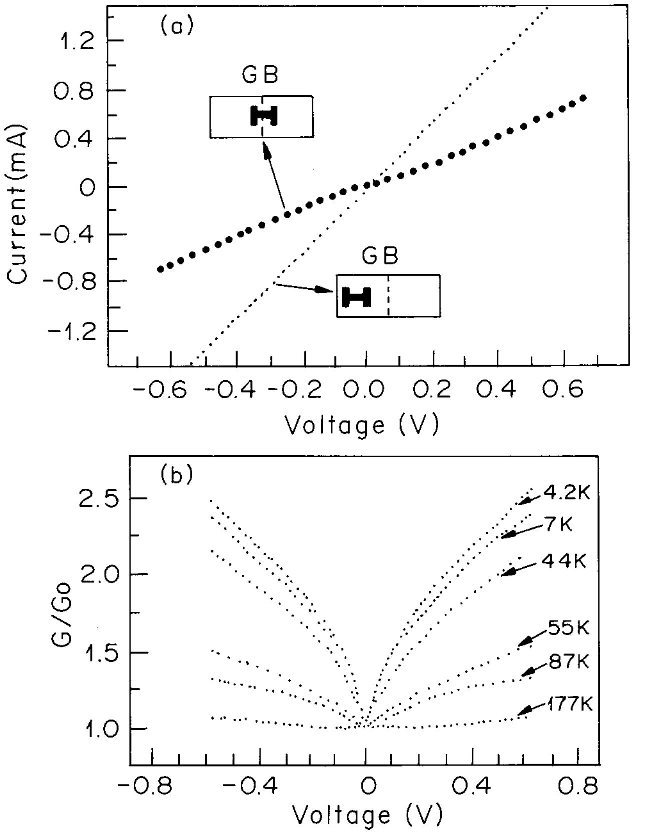

FIG. 2. (a) $I-V$ curves for the LBMO thin-film microbridge across the bicrystal grain boundary and for the microbridge away from the grain boundary. (b) Variation of normalized dynamic conductance (G/G_0) with voltage drop across the bicrystal junction at different temperatures.

$$G/G_0=1+k|V|^{\alpha}, \tag{1}$$

where k and α are constants. Figure 3 shows α as a function of temperature from 4.2 to 300 K. In the same graph we also show the temperature dependence of k, which measures the relative components of the nonlinearity. The value of k becomes very small as T approaches 300 K. The value of α is 0.6 at 4.2 K, and it has a weak temperature dependence until $T=50$ K. As the temperature is further increased, α increases sharply and approaches 1.0 at $T\approx 80$ K. For $100\ \mathrm{K}<T<175$ K, α reaches a distinct plateau ≈1.3 and then increases again for $T>175$ K. At higher temperatures, α approaches a plateau ≈1.8. Our result on the temperature variation of α is similar to that of Zeise *et al.*[9] for a step-edge junction in $\mathrm{La_{0.7}Ca_{0.3}MnO_3}$ film. These results, however, are in sharp contrast to that observed by Todd *et al.*[11] on the bicrystal junction in a $\mathrm{La_{1-x}(Sr/Ca)_xMnO_3}$ film, where the value of α was ≈2.0 and it was independent of temperature.

In order to explain our results, we propose that a layer of oxygen-deficient LBMO with lower T_c (or with canted spin structure) is present at the grain boundary. The observed behavior suggests that there are essentially three types of current transport through the grain boundary, which may occur in parallel, but one of the mechanisms may dominate over the other in a given temperature range. In temperature range I (4.2–45 K), $\alpha\approx 0.6$. Such behavior has been observed in the past in tunneling experiments on a number of disorder

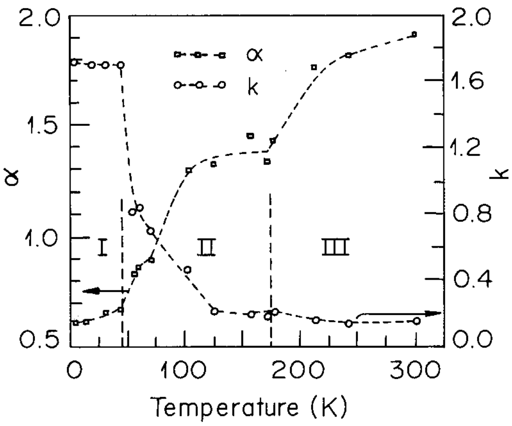

FIG. 3. Variation of α and k with temperature. The values of α and k at different temperatures are obtained by fitting the equation $G/G_0=1+k|V|^{\alpha}$ to the experimental curves of (G/G_0) vs V shown in Fig. 2(b).

oxides, which has been explained as due to an electron–electron interaction in disorder systems.[13] It is likely that the region immediately close to the grain boundary or the grain boundary itself acts like a disordered metallic oxide. This also is clearly visible in the temperature variation of the resistance of the grain boundary for $T<20\,\mathrm{K}$ [inset in Fig. 1(a)]. This is a very common occurrence in a number of disordered metallic oxides.[14] In region II $(45\,\mathrm{K}<T<175\,\mathrm{K})$, the dominant contribution comes from quasiparticle tunneling via the localized state where one expects $\alpha\approx 4/3$.[15] In region III $(T>175\,\mathrm{K})$, spin–flip scattering in the grain boundary becomes dominant.[16] It is suggested that the relative contribution of the three processes will depend on the temperature as well as on the nature of the grain boundary itself. The junction region in the microbridge of Ref. 11 may be different from ours so that at low temperatures direct tunneling occurs and at higher temperature spin–flip scattering dominates. In such a situation one gets $\alpha\approx 2$ for all temperatures.

The MR from the bicrystal grain boundary increases below 175 K. A comparison of Figs. 1 and 3 shows that this occurs in a temperature region where the dominant grain-boundary transport mechanism is via single, or multiple-step tunneling and also tunneling through a disordered layer. The spin-polarized tunneling mechanism can give rise to MR, which will increase on cooling because of the following reasons:

The tunneling MR is a strong function of the spin polarization of the ferromagnetic layers on the two sides of the grain boundary. The spin polarization increases on cooling, leading to an increase of MR from the grain boundary.[17,18] Dependence of α on T indicates that the spin–flip scattering process becomes dominant at higher temperatures. The MR in a junction is suppressed by the spin–flip scattering in the grain-boundary region. On cooling, the spin–flip scattering rate is reduced, leading to an increase of the MR. The transition probability at the grain-boundary junction also depends on the difference of the work function $(\Delta\varphi)$ between the grain-boundary material (which is paramagnetic or a low-T_c material) and the material (which is ferromagnetic) on the two sides. This difference is a function of the difference of the magnetization (ΔM) of the two materials. On cooling, ΔM increases leading to an increase in $\Delta\varphi$ and an increase in MR.[19]

To summarize, it has been found that the presence of a bicrystal grain boundary in the LBMO epitaxial film enhances low-field magnetoresistance and introduces nonlinearity in $I-V$ characteristics. We could identify three mechanisms of grain-boundary transport that may operate in parallel. The mechanism of the transport across the grain boundary is found to be temperature dependent. At low temperatures (4.2–45 K) the dominant carrier transport across the grain boundary is due to tunneling through a disordered oxide at the grain boundary and for temperatures 100–175 K the dominant mechanism for transport is inelastic tunneling via Mn pairs of atoms. At temperatures above 175 K, spin–flip scattering becomes dominant. The increase of grain-boundary MR with the decrease in temperature $(T<175\,\mathrm{K})$ is due to an increase in spin polarization and suppression of spin–flip scattering on cooling.

The work was supported by the Department of Science and Technology, Government of India. One of the authors wants to thank BRNS (DAE), Government of India for a sponsored research scheme.

[1] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
[2] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).
[3] P. Schiffer, A. P. Ramirez, W. Bao, and S. W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).
[4] X. W. Li, A. Gupta, G. Xiao, and G. Q. Gong, Appl. Phys. Lett. **71**, 1124 (1997).
[5] H. Y. Hwang, S. W. Cheong, N. P. Ong, and B. Batlogg, Phys. Rev. Lett. **77**, 2041 (1996).
[6] X. L. Wang, S. X. Dou, H. K. Liu, M. Ionescu, and B. Zeimetz, Appl. Phys. Lett. **73**, 396 (1998).
[7] N. D. Mathur, G. Burnell, S. P. Issac, T. J. Jackson, B. S. Teo, J. L. MacManus-Driscoll, L. F. Cohen, J. E. Evetts, and M. G. Blamire, Nature (London) **387**, 266 (1997).
[8] K. Steenbeck, T. Eick, K. Kirsch, K. O'Donell, and E. Steinbeiß, Appl. Phys. Lett. **71**, 968 (1997).
[9] M. Ziese, G. Heydon, R. Honne, and P. Equinazi, Appl. Phys. Lett. **74**, 1481 (1999).
[10] J. E. Evetts, M. G. Blsmitr, N. D. Mathur, S. P. Issac, B. S. Teo, L. F. Cohen, and J. L. MacMaunus–Driscoll, Philos. Trans. R. Soc. London, Ser. A **356**, 1593 (1998).
[11] N. K. Todd, N. D. Mathur, J. E. Evettes, and M. G. Blamire, J. Appl. Phys. **85**, 7263 (1999).
[12] J. G. Simmons, J. Appl. Phys. **34**, 1793 (1963).
[13] A. K. Raychaudhri, K. P. Rajeev, H. Srikanth, and N. Gayathri, Phys. Rev. B **51**, 7421 (1995).
[14] A. K. Raychaudhri, Adv. Phys. **44**, 21 (1995).
[15] L. I. Glazman and K. A. Matveev, Zh. Eksp. Teor. Fiz. **94**, 332 (1988); [Sov. Phys. JETP **67**, 1276 (1988)].
[16] F. Guinea, Phys. Rev. B **58**, 9212 (1998).
[17] A. M. Bratkovsky, Phys. Rev. B **56**, 2344 (1997).
[18] J. H. Park, E. Vescovo, H. J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Phys. Rev. Lett. **81**, 1953 (1998).
[19] J. Klein, C. Hofener, S. Uhlenbruck, L. Alef, B. Buchner, and L. Cross, Europhys. Lett. **47**, 371 (1999).