Giant Negative Magnetoresistance in Perovskitelike $La_{2/3}Ba_{1/3}MnO_x$ Ferromagnetic Films

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At room temperature a large magnetoresistance, $\Delta R/R(H=0)$, of 60% has been observed in thin magnetic films of perovskitelike La-Ba-Mn-O. The films were grown epitaxially on $SrTiO_3$ substrates by off-axis laser deposition. In the as-deposited state, the Curie temperature and the saturation magnetization were considerably lower compared to bulk samples, but were increased by a subsequent heat treatment. The samples show a drop in the resistivity at the magnetic transition, and the existence of magnetic polarons seems to dominate the electric transport in this region.

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Giant magnetoresistance (GMR) due to spin-dependent scattering at the interface between ferromagnetic and nonmagnetic regions has been the subject of intense research in the last years [1–4]. At room temperature, resistance changes $\Delta R/R(H=0)$ as high as 40% have been observed in Cu/Co multilayers [2] and up to 11% in heterogeneous Cu/Co alloys [3,4], compared to only 2%–3% for "conventional" materials such as permalloy. A much higher magnetoresistance was found near a metal/insulator and simultaneous magnetic phase transition, e.g., in $Eu_{1-x}Gd_xSe$ [5], but in this material the effect is restricted to temperatures below 50 K. The anomalous transport phenomena in these Eu-chalcogenide alloys have been explained by the appearance of giant spin molecules [6] and spin polarons [7]. Similar observations have been made in the mixed valence perovskitelike $Nd_{0.5}Pb_{0.5}MnO_3$ in the region around the ferromagnetic phase transition at 184 K [8]. A large drop in resistivity and a high magnetoresistance $\Delta R/R(0) > 50\%$ was found, which is also believed to be caused by the existence of magnetic polarons. $La_{2/3}Ba_{1/3}MnO_3$ is also well known as a mixed valence metallic ferromagnet, but with a considerably higher Curie temperature of $T_C = 343$ K [9,10]. At the Curie temperature a cusp in the resistivity was found and therefore gives rise to the assumption of a high magnetoresistance effect at room temperature.

Targets of stoichiometric composition were prepared by standard ceramic techniques from the metallic oxides and carbonates of 99.9% purity by repeated grinding and annealing in air. The x-ray diffraction patterns showed no other reflections than those of the rhombohedral unit cell found in Ref. [10] ($a = 0.3910$ nm, $\gamma = 90.12°$). Thin films of 150 ± 10 nm thickness were grown on $SrTiO_3$ 10×10 mm^2 substrates in (100) and (110) orientation. A laser deposition technique in off-axis geometry was used, which had previously turned out to be a powerful tool in preparing high-T_c superconducting thin films with a smooth surface [11]. Different substrate temperatures between 600 and 900 °C were used, at a deposition pressure of 0.4 mbar oxygen. Epitaxial films were obtained for a substrate temperature of $T_S = 600$ °C as confirmed by x-ray diffraction and reflection high-energy electron diffraction (RHEED), while a higher substrate temperature resulted in polycrystalline films.

Magnetization measurements were performed at room temperature in a vibrating sample magnetometer in a magnetic field of up to 2 T. Paramagnetic behavior was found in the sample deposited at $T_S = 600$ °C, but after a subsequent heat treatment at 900 °C in air, a ferromagnetic magnetization curve was measured (Fig. 1). No saturation could be achieved up to $\mu_0 H = 2$ T, and the magnetization is still significantly lower than that observed in bulk samples (280 A/m) [10], so one can still assume paramagnetic or superparamagnetic regions due to sample inhomogeneities.

The dc resistivity was measured between 30 and 320 K in an applied field of up to 7 T. Since no saturation of the magnetoresistive effect (MR) was achieved in this field range, the values were related to the resistance at zero field, i.e., $R_{MR} = \Delta R/R(0)$. Figure 2 shows the temperature dependence of the resistance (a) before and (b) after the heat treatment, measured in standard four probe geometry. In the ferromagnetic region, all samples show metallic behavior, i.e., a positive temperature coefficient of the resistivity. Near the ferromagnetic transition, spin

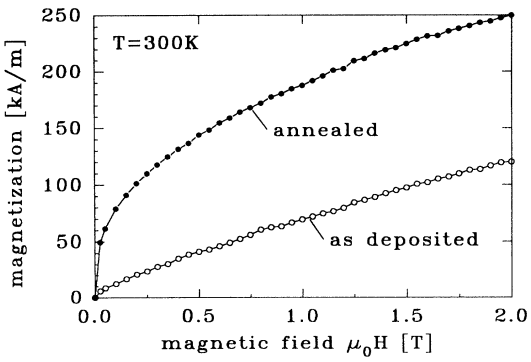

FIG. 1. Room temperature magnetization curve for the as-deposited sample ($T_S = 600$ °C) showing paramagnetic behavior. The ferromagnetic curve is measured at the same sample after annealing in air for 12 h at $T_A = 900$ °C.

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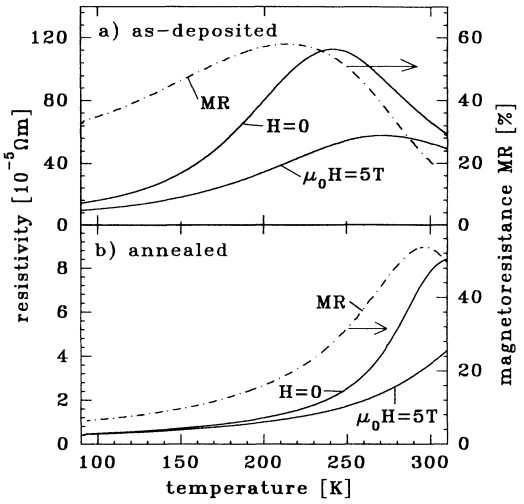

FIG. 2. Temperature dependence of the resistivity at zero field and under an applied field of $\mu_0 H = 5$ T for the film (a) as-deposited at $T_S = 600\,^\circ$C and (b) after a subsequent annealing at $T_A = 900\,^\circ$C for 12 h. The dashed curves represent the relative MR effect $R_{MR} = [R(0\text{ T}) - R(5\text{ T})]/R(0\text{ T})$.

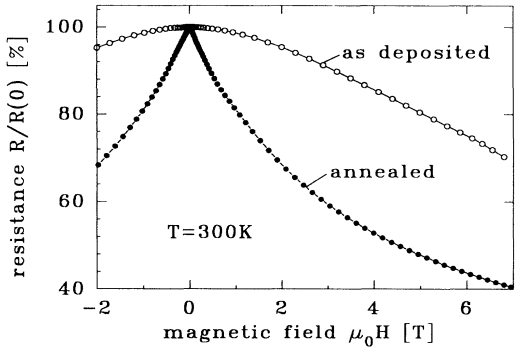

FIG. 3. Resistivity versus field curves for the as-deposited sample ($T_S = 600\,^\circ$C) and after annealing at $T_A = 900\,^\circ$C for 12 h, measured at $T = 300$ K.

disorder leads to a sharp increase of the resistivity, as has already been observed in several metallic ferromagnets with a narrow conduction band [7,8,10]. The application of an external magnetic field leads to a decrease in the resistivity, with the largest difference and hence the largest negative magnetoresistance occurring close to the magnetic transition, which is indicated by the peak in the zero-field resistivity. The peak in the resistivity becomes smaller and shifts to higher temperatures as the field is increased.

The magnetoresistance measurements (Fig. 3) show a large MR effect of more than 60% at room temperature, which is significantly higher than that observed in Cu/Co multilayers where $R_{MR} \leq 40\%$. Normalizing the resistivity to the high field value, as is usually done for magnetic multilayers, the respective values are 150% compared to 65%. Like the magnetization, the resistance cannot be saturated in a magnetic field of up to $\mu_0 H = 7$ T. The curves are almost independent from the relative orientation of magnetic field, electric current, and crystal axes, if one takes into account the different demagnetization factors for various orientations. Also, polycrystalline samples did not differ from the epitaxial ones. Compared to single phase sintered bulk samples [10], where a sharp cusp in the resistivity is observed, the as-deposited thin films show a broadening of the magnetic transition [Fig. 2(a)] and simultaneously a weak temperature dependence of the MR effect below 250 K. An annealing in air results in an increased transition temperature and a sharper transition [see Fig. 2(b)], so we assume that the sample becomes more homogeneous during the annealing treatment. In this case the difference from the bulk material values presumably results from chemical disorder and oxygen deficiency. A deviation of the film from the target composition possibly occurs during the deposition because of the high vapor pressure of MnO and may explain why there is still a slight difference in the magnetic and electric properties compared to the bulk samples.

Since $LaMnO_3$ is an insulating antiferromagnet with a superexchange coupling between the Mn^{3+} ions by the interaction of the d shells of manganese and oxygen, the mixed Mn^{3+}/Mn^{4+} valence in $La_{1-x}Ba_xMnO_3$ is believed to give rise to both ferromagnetism and metallic behavior [12]. Below the Curie temperature the antiferromagnetic superexchange is overcome by ferromagnetic double exchange, transferred by the conduction electrons in the narrow d band. These competing interactions give rise to a strongly perturbed spin lattice in the region of the ferromagnetic transition, which in combination with the narrow conduction band can lead to a partial localization at these magnetic impurities and to the constitution of magnetic polarons, as originally suggested by Mott [13]. At temperatures well below the ferromagnetic onset, the formation of magnetic polarons will become impossible since the magnetic ions are ferromagnetically ordered; i.e., at zero field the resistivity significantly decreases with decreasing temperature. On the other side, at a constant temperature near the transition temperature an external magnetic field also increases the ferromagnetic order leading to the prominent MR observed in this region. Since conduction by magnetic polarons proceeds via thermal hopping, one observes activated behavior and therefore a negative temperature coefficient of the resistivity above the Curie temperature. This conception is supported by the observation of Mott's law, $\ln(\rho) \sim T^{-1/4}$, in the activated region of Cu-doped samples [10], which is consistent with variable range hopping because of frozen-in spin disorder in this case. Furthermore, for $Nd_{0.5}Pd_{0.5}MnO_3$ spin polarized neutron scattering showed dynamic fluctuations in the magnetic structure above the Curie temperature [8] which are believed

to be produced by hopping of magnetic polarons.

In summary, an intrinsic MR effect has been observed in epitaxial ceramic films at room temperature which is considerably higher than that of artificial ferromagnetic/nonmagnetic multilayers and of heterogeneous materials. It is also isotropic, but based on a completely different physical effect. Magnetic polaron hopping provides a plausible model to describe the transport mechanism. Since magnetic impurities are introduced by thermal disorder, the homogeneous single phase material the high MR effect is restricted to a temperature region around the ferromagnetic transition, while in the case of chemical disorder a broad transition results in a much smaller temperature dependence of the MR effect.

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[1] M. N. Baibich, J. M. Broto, A. Fert, F. N. V. Dau, F. Petroff, P. Etienne, G. Creutzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).

[2] S. S. P. Parkin, Z. G. Li, and D. J. Smith, Appl. Phys. Lett. **58**, 2710 (1991); P. M. Levy, Science **156**, 972 (1992).

[3] A. E. Berkowitz, J. R. Mitchell, M. J. Carey, A. P. Young, S. Zhang, F. E. Spada, F. T. Parker, A. Hutten, and G. Thomas, Phys. Rev. Lett. **68**, 3745 (1992); J. Q. Xiao, J. S. Jiang, and C. L. Chien, Phys. Rev. B **43**, 8089 (1991).

[4] J. Wecker, R. von Helmolt, L. Schultz, and K. Samwer, Appl. Phys. Lett. **62**, 1985 (1993).

[5] S. von Molnar and S. Methfessel, J. Appl. Phys. **38**, 959 (1967).

[6] T. Kasuya and A. Yanase, Rev. Mod. Phys. **40**, 648 (1968).

[7] S. von Molnar, J. Appl. Phys. **39**, 899 (1968).

[8] R. M. Kusters, J. Singleton, D. A. Keen, R. McGreevy, and W. Hayes, Physica (Amsterdam) **155B**, 362 (1989).

[9] G. H. Jonker and J. H. van Santen, Physica (Amsterdam) **16**, 337 (1950); G. H. Jonker, Physica (Amsterdam) **22**, 707 (1956).

[10] R. von Helmolt, L. Haupt, K. Bärner, and U. Sondermann, Solid State Commun. **82**, 641 (1992).

[11] B. Holzapfel, B. Roas, L. Schultz, P. Bauer, and G. Saemann-Ischenko, Appl. Phys. Lett. **61**, 3178 (1992).

[12] C. Zener, Phys. Rev. **82**, 403 (1951); P. G. de Gennes, Phys. Rev. **118**, 141 (1960).

[13] N. F. Mott and E. A. Davies, *Electronic Processes in Noncrystalline Materials* (Clarendon, Oxford, 1979); N. F. Mott, Adv. Phys. **21**, 785 (1972).