Nature of the giant magnetoresistance in ferromagnetic lanthanum manganites

M. K. Gubkin and T. M. Perekalina
Institute of Crystallography, Russian Academy of Sciences, 117333 Moscow, Russia

(Submitted 24 October 1994)
Pis'ma Zh. Eksp. Teor. Fiz. **60**, No. 10, 727–730 (25 November 1994)

A qualitative explanation is offered for the unusually high value (by a factor of nearly 1300) of the magnetoresistance which was recently discovered in epitaxial La–Ca–Mn–O films. The effect is attributed to the existence of a spatially nonuniform magnetic order in the samples, which leads to a percolation metal–semiconductor transition. This interpretation is supported by results found previously by the present authors in electrical, magnetic, and NMR measurements on lanthanum manganites with similar properties. It is argued that equally high values of the magneotresistance should be observed in a wide range of compositions, in particular, in $La_{0.9}Na_{0.1}Mn_{1-x}Me_xO_3$ (Me=Re,Cu,Co), if these materials are prepared as single crystals or epitaxial films. The magnetoresistance of these ceramics in weak fields (<1 kOe) is higher than that of La–Ca–Mn–O films. © *1994 American Institute of Physics.*

McCormack *et al.*[1] recently caused a sensation with their report of the observation of a giant, isotropic, negative magnetoresistance in epitaxial La–Ca–Mn–O films. When an external magnetic field $H = 60$ kOe is applied, the resistivity ρ changes by three orders of magnitude $\rho(H=0)\equiv\rho_0=1270\rho(H)\equiv 1270\rho_H$ (the value $\Delta\rho\equiv\rho_0-\rho_H$, which is typical of this class, is a few tenths of ρ_0). There are good prospects for applications of this effect in microelectronics. McCormack *et al.*[1] wrote that the mechanism responsible for this high magnetoresistance was unclear. In the present letter we offer a qualitative explanation for the effect, based on experimental data from Ref. 1 and also some of our own results from Refs. 2–5, which were studies of manganites of various compositions.

We begin by listing the basic features of the experimental curves reported in Ref. 1:

(1) The temperature T_ρ (~77 K) at which the anomalies were seen in ρ_0 and ρ_0/ρ_H was well below the Curie point T_C: $T_C-T_\rho\sim 200$ K. In contrast, according to double-exchange theory, which explains the ferromagnetism and electrical conductivity of lanthanum manganites (Refs. 6–8, for example), the temperatures T_C and T_ρ should be the same: The ferromagnetic phase has a metallic conductivity, and the paramagnetic phase a semiconducting conductivity.
(2) The temperature T_ρ depended on the heat treatment. After a sample was annealed in oxygen at 900 °C, T_ρ decreased from 110 K to 77 K.
(3) The height of the ρ_0/ρ_H peak also depended on the heat treatment. After this annealing, the ratio ρ_0/ρ_H increased from 110 to 1270.
(4) The temperature dependence of the magnetization M was very different from the

$M(T)$ curves characteristic of ferromagnets, particularly in the interval $T_\rho < T < T_C$.

All these features (aside from the high values of ρ_0/ρ_H, which will be discussed below) have also been seen in our own experiments[2,4,5] on $La_{0.9}Na_{0.1}Mn_{1-x}Me_xO_3$ (Me =Re,Cu,Co) ceramics. In an effort to explain them, NMR apparatus was used to study local fields set up at ^{139}La nuclei by spin-polarized charge carriers executing a double exchange.[3] It was concluded from the results of Ref. 3 that the separation of magnetic phases predicted theoretically by Nagaev (Ref. 9, for example) occurs in the lanthanum manganite compositions which were studied. In other words, in addition to the ferromagnetic regions with a metallic conductivity, there are nonferromagnetic regions[1)] in the samples which have an activation-law conductivity. According to the data of Ref. 3, the volume fraction of the latter regions increases with increasing T. At a certain temperature, the highly conducting ferromagnetic regions may then disconnect from each other, and at even higher temperatures the conductivity will be governed to a progressively greater extent by the nonferromagnetic matrix. In terms of percolation theory (Ref. 10, for example), the temperature T_ρ corresponds to a percolation threshold. The application of an external magnetic field H increases (if only slightly) the volume fraction of the ferromagnetic phase, so an anomaly in ρ_0/ρ_H is also observed near the percolation threshold. These comments explain item 1 in the list above.

It is also a simple matter to explain item 2 in terms of a separation of magnetic phases. According to Ref. 9, this separation results from fluctuations of the acceptor concentration. It is widely known (Ref. 11, for example) that the oxygen content in lanthanum manganites varies with the heat treatment. Superstoichiometric oxygen is an acceptor impurity, which gives rise to additional Mn^{4+} holes. A change in the spatial distribution of acceptors during annealing obviously also affects the spatial nonuniformity of the magnetic order and thus the temperature T_ρ. The relationship between T_ρ and the heat-treatment conditions for lanthanum manganites was noted and studied in Ref. 12, among other places.

The increase in ρ_0/ρ_H with decreasing T_ρ mentioned in item 3 can be explained in the following way. The temperature dependence of ρ in the paramagnetic phase is described well by an activation law $\exp(\Delta E/kT)$, where ΔE is the activation energy, and k the Boltzmann constant. At $T \sim T_C \sim 300$ K, the resistivity of the paramagnetic phase is $\sim 10^{-2}\ \Omega\cdot$cm (Ref. 8, for example). The resistivity of the ferromagnetic metallic phase is on the same order of magnitude. It is for this reason that the transition to a metallic conductivity at $T_\rho \sim T_C$ is not accompanied by a sharp increase[2)] in ρ. We have exactly the opposite situation at $T_\rho \ll T_C$, because of (see the discussion above) the separation of magnetic phases. The resistivity of the nonferromagnetic regions with an activation-law conductivity increases exponentially upon cooling from T_C to T_ρ, and the percolation transition to a metallic conductivity should be accompanied by a change of several orders of magnitude in ρ. The magnetoresistance should evidently increase by about the same amount near T_ρ. This conclusion finds qualitative support in the experimental data in Ref. 1. We can also offer a (rather crude) quantitative estimate. According to Ref. 1, at $T_\rho = 110$ K we have $\rho_0/\rho_H = 110$, while at $T_\rho = 77$ K (after heat treatment) we have $\rho_0/\rho_H = 1270$. From the $\rho(T)$ curve in Ref. 1 we find $\Delta E \approx 0.07$ eV. Assuming that ρ_H corresponds roughly to the resistivity of the metallic phase and has a weak tempera-

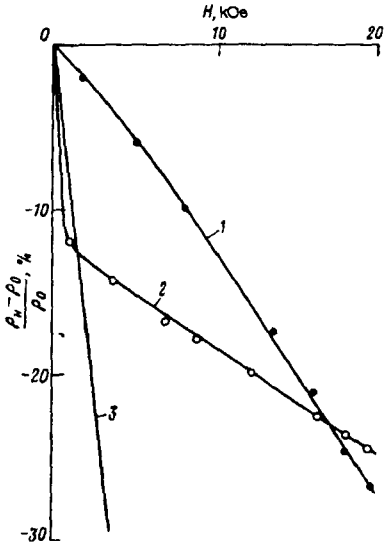

FIG. 1. Magnetoresistance isotherms near T_ρ. 1—$La_{0.9}Na_{0.1}MnO_3$ single crystal (290 K); 2—$La_{0.9}Na_{0.1}Mn_{0.9}Cu_{0.1}O_3$ (77 K); 3— La–Ca–Mn–O epitaxial film (77 K).

ture dependence, and also assuming that ρ_0 is determined primarily by the nonferromagnetic phase, we find that the ratio of magnetoresistances at $T_1=77$ K and $T_2=110$ K $[\rho_0(T_1)/\rho_H(T_1)]/[\rho_0(T_2)/\rho_H(T_2)]$ should be on the order of $\rho_0(T_1)/\rho_0(T_2) \approx \exp[\Delta E(1/kT_1 - 1/kT_2)] \approx 25$. In the experiments of Ref. 1, this ratio was on the same order of magnitude: ≈ 12.

The occurrence of a spatially nonuniform order in the samples also explains the unusual $M(T)$ dependence mentioned in item 4. At $T<T_\rho$, the relative size of the ferromagnetic regions which contribute to the magnetization decreases, leading to a characteristic bending of the $M(T)$ curve. The measurements of Ref. 1 were carried out in a fairly strong field ($H=10$ kOe)—apparently strong enough to orient most of the ferromagnetic clusters. At $T<T_\rho$, the value of $M(T)$ thus remained high $[\sim 0.5M(0)]$.

The probable reason why the ceramic $La_{0.9}Na_{0.1}Mn_{1-x}Me_xO_3$ samples which we studied do not have high magnetoresistances in strong fields, although they do exhibit features 1–4, is a large contribution of grain boundaries to ρ. This contribution does not depend on the magnetic field. When ρ decreases markedly as a field H is applied, the value of ρ_0/ρ_H remains bounded. McCormack *et al.*[1] themselves suggested that grain boundaries play a governing role in the value of the magnetoresistance. They made the case that size effects do not play any significant role in the observed giant magnetoresistance. The contribution of grain boundaries to the resistance can explain the difference between the magnetoresistance isotherms near T_ρ which we found for ceramic samples with $T_\rho \ll T_C$ and for single crystals with $T_\rho \approx T_C$ (some typical curves are shown in Fig. 1). We see that, while the $\Delta\rho(H)$ dependence for the single crystals is approximately linear, the isotherm for the ceramics at $H>1$ kOe has a slope change and exhibits a tendency toward "saturation." The magnetoresistance is observed to be much more sensitive to a magnetic field at small values of H in the case of the ceramic. For convenience in comparison, we also show in Fig. 1 part of a magnetoresistance isotherm for a

La–Ca–Mn–O film plotted from the data of Ref. 1. We see that the value of the magnetoresistance in weak fields (the case of primary interest for applications) for these ceramics is in fact slightly higher than the "record" values reported in Ref. 1.

In summary, we can assert quite confidently that the magnetoresistance anomaly near $T_\rho \ll T_C$ is associated with a percolation threshold for ferromagnetic regions, whose volume fraction falls off with increasing T. In this case the magnetoresistance peak should be higher, the greater the difference between T_C and T_ρ. There is every reason to believe that high values of the magnetoresistance will be observed in strong fields (~60 kOe) in a wide class of substances with $T_\rho \ll T_C$, in particular, in $La_{0.9}Na_{0.1}Mn_{1-x}Me_xO_3$ (Me=Re,Cu,Co), if these substances are prepared in the form of single crystals or epitaxial films. Measurements of the magnetoresistance in weak fields (<1 kOe) which we have already carried out yield values greater than those reported in Ref. 1.

This study had financial support from the Russian Fund for Fundamental Research (Grant 94-02-04713-a).

[1)]Probably paramagnetic in this case.
[2)]At $T_\rho \sim T_C$, the magnetoresistance is apparently dominated by carrier scattering by critical fluctuations of the magnetization.

[1]M. McCormack *et al.*, Appl. Phys. Lett. **64**, 3045 (1994).
[2]M. K. Gubkin *et al.*, Fiz. Tverd. Tela (Leningrad) **35**, 1443 (1993) [Phys. Solid State **35**, 728 (1993)].
[3]M. K. Gubkin *et al.*, JETP Lett. **60**, 56 (1994).
[4]M. K. Gubkin and T. M. Perekalina, Kristallografiya (in press).
[5]M. K. Gubkin and T. M. Perekalina, Kristallografiya (in press).
[6]C. Zener, Phys. Rev. **82**, 403 (1951).
[7]K. Kubo and Ohata, J. Phys. Soc. Jpn. **33**, 21 (1972).
[8]S. Krupicčka, *Physik der Ferrite und der Verwandten Magnetischen Oxide* (Academia, Prague, 1973).
[9]É. L. Nagaev, *Magnetic Materials with Complex Exchange Interactions* [in Russian] (Nauka, Moscow, 1988).
[10]J. M. Ziman, *Models of Disorder* (Cambridge Univ. Press, London, 1979).
[11]G. H. Jonker and G. Van Santen, Physica **16**, 337 (1950).
[12]T. M. Perekalina *et al.*, Fiz. Tverd. Tela (Leningrad) **31**, 681 (1991) [Sov. Phys. Solid State **31**, 388 (1991)].

Translated by D. Parsons