

## Extrinsic giant magnetoresistance in chromium (IV) oxide, CrO<sub>2</sub>

S. Sundar Manoharan<sup>a)</sup>

Max-Planck Institut für Mikrostrukturphysik, Halle (Saale), D-06120, Germany

D. Elefant and G. Reiss

Institute for Solid State and Materials Research Helmholtzstrasse 20, D-01069, Dresden, Germany

J. B. Goodenough

Center for Materials Science & Engineering, ETC 9, 102, University of Texas at Austin, Austin, Texas 78712-1063

(Received 22 October 1997; accepted for publication 9 December 1997)

Polycrystalline CrO<sub>2</sub> is shown to exhibit a giant magnetoresistance (GMR) at low temperatures. A rapid decrease in the GMR with increasing temperature is correlated with a decrease in the intergranular resistance. Single-crystal CrO<sub>2</sub> is a half-metallic ferromagnet, as the data are interpreted to reflect two types of charge carriers, crossing a grain boundary: those that tunnel between conduction bands of adjacent grains and those that hop after residing at a localized state for a time long compared to a spin relaxation time. © 1998 American Institute of Physics. [S0003-6951(98)03106-4]

The electron carries in spin as well as a charge. Traditionally, the electronics industry has exploited its ability to control the transport of mobile electronic charges and the orientation of stationary electron spins. Recently, interest in the transport properties of electron spins has been stimulated by attempts to obtain a giant negative magnetoresistance (GMR) at room temperature in modest applied fields. Two mechanisms for achieving a GMR have been investigated: (i) Changing from *antiferromagnetic* to *ferromagnetic* in a modest magnetic field where the coupling across a paramagnetic layer  $P$  between alternate ferromagnetic layers in a multilayer  $F/P/F$  stack supporting preferential spin transport perpendicular to the layers. Control of the thickness of the  $P$  layers in a “magnetic superlattice” consisting of many alternating layers has been needed to obtain an adequate signal. Prototype magnetic readout heads for magnetic storage are already under active development.<sup>1</sup> (ii) Changing the spin transport across a  $F|F$  interface by sweeping an applied field through the coercivity of the ferromagnetic layers; the interfacial layer which is parallel may be a grain boundary or a thin dielectric layer across which an electron spin tunnels with conservation of its spin angular momentum. This process has been demonstrated in the manganese-oxide perovskite La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>, which is a half-metallic ferromagnet, but the signal is rapidly suppressed on raising the temperature above 77 K.<sup>2</sup> In either approach, the signal would be optimized where the ferromagnetic layers are half-metallic ferromagnets, i.e., where the itinerant electrons all have the same spin. In this case, parallel alignment of the half-metallic ferromagnets allows transfer of electrons that retain their spin on crossing the  $P$  or interfacial layer whereas antiparallel alignment blocks these electrons.

Chromium (IV) oxide, CrO<sub>2</sub>, is a room-temperature ferromagnet and, at  $T=0$  K, it is a half-metallic ferromagnet.<sup>3</sup> In an ionic model, CrO<sub>2</sub> contains Cr<sup>4+</sup>: $3d^2$  configurations in

octahedral sites of a tetragonal rutile structure having the space group  $P4_2/mmm$  of the three non- $\sigma$ -bonding  $3d$  orbitals per Cr atom symmetry which distinguishes a single localized orbital directed along the  $c$  axis from the other two, which form a narrow, orbital quasidegenerate band as a result of stronger Cr-O:2 $p$ -Cr interactions. With one electron in the localized orbital, a strong Hund's intraatomic exchange field removes the spin degeneracy of the bands; but with one electron per Cr atom in these bands, the majority-spin band remains only half filled, so ferromagnetic coupling remains compatible with occupancy of only bonding states. The ferromagnetic coupling via the itinerant electrons dominates the antiferromagnetic superexchange interactions between next-near-neighbor Cr atoms along the  $c$  axis via the localized electrons.

In this letter we report the observation of a GMR below 77 K in polycrystalline CrO<sub>2</sub>. In a saturation applied field the spins on either side of a grain boundary are oriented parallel, and the resistance is lowest; at the coercive field, misalignment of spins on crossing a grain boundary is maximized, and the resistance is highest. The origin of the sharp decrease in signal at higher temperatures is qualitatively modeled.

CrO<sub>2</sub> powders were prepared hydrothermally as described elsewhere.<sup>4</sup> The particles were fine-grained needles of acicular shape. Uniaxially cold-pressed samples of 10 mm diameter were prepared with thicknesses ranging from 1.5 to 3.0 mm; the magnetoresistance ratio varied little with pressure from 300 to 400 MPa. Decomposition of CrO<sub>2</sub> above 250 °C sets an upper limit to the sintering temperature. Therefore, we have also prepared hot-pressed CrO<sub>2</sub> samples in a polymer matrix; the GMR of these samples will be published elsewhere.<sup>5</sup> A scanning electron micrograph of the cold-pressed samples indicates a porosity of less than 30%; the pellet had a density 70% of theoretical (4.899) g/cm<sup>3</sup>. The electrical resistance was obtained with a standard four-probe technique; Ohmic contacts were made with Ag. The room-temperature specific resistivity of the cold-pressed samples was 0.05  $\Omega$  cm, that of the hot-pressed samples was

<sup>a)</sup>For correspondence: Dept. of Chemistry, Indian Institute of Technology Kanpur, 208 016, India. Electronic mail: ssundar@iitk.ernet.in

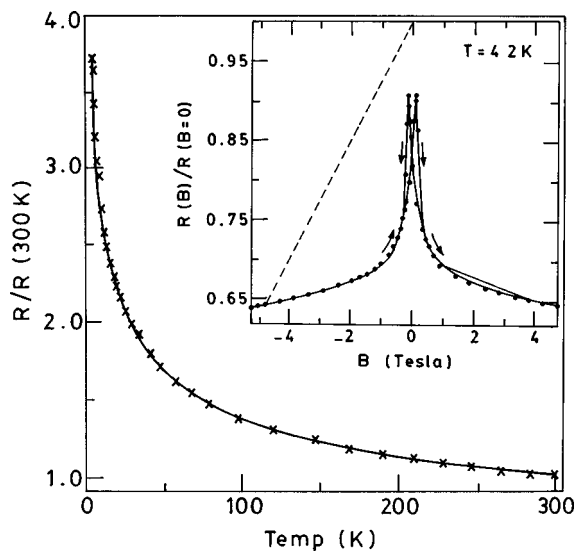


FIG. 1. The temperature dependence of resistance of a cold-pressed  $\text{CrO}_2$  sample. Inset shows the dependence of the resistance at 4.2 K on magnetic field applied parallel to the current direction.

10  $\Omega$  cm. The oxygen content,  $38 \pm 0.05$  wt %, of the cold-pressed samples was obtained by thermogravimetric analysis of the weight loss on oxidizing the sample to  $\text{Cr}_2\text{O}_3$ ; it corresponds to a molecular formula  $\text{CrO}_{2.01 \pm 0.02}$ .

Figure 1 shows the temperature dependence of the resistance  $R(T)$  normalized to the room-temperature resistance  $R(300 \text{ K})$  for a virgin (demagnetized) sample, 2.60 mm thick that was cold pressed at 400 MPa. Although the single-crystal samples are metallic,<sup>6</sup> the cold-pressed samples have a negative slope of  $R$  vs  $T$  in the range  $150 < T < 300 \text{ K}$  that increases dramatically with decreasing temperature below 150 K. The hot-pressed samples, on the other hand, exhibit a positive slope of  $R$  vs  $T$  in the range of  $150 < T < 300 \text{ K}$ ; the resistance then increases sharply with decreasing temperatures below 150 K. The negative slope of the  $R$  vs  $T$  curve of Fig. 1 is clearly an extrinsic property associated with the intergranular resistance.

The inset of Fig. 1 shows, for the cold-pressed sample, the dependence of the resistance at 4.2 K in a magnetic field  $B$  applied parallel to the current direction normalised to the resistance of the virgin sample in zero applied field. Little difference was found if  $B$  was applied perpendicular to the current direction. On the initial magnetization to  $B = -5 \text{ T}$  (straight line in inset), the resistance  $R(B)$  at 4.2 K was higher than the  $R(B)$  curves taken on subsequent cycling of  $B$  between  $-5 \text{ T}$ . This behavior reflects the removal of mis-oriented magnetic domains and the reorientation of the atomic spins in the magnetic field; the magnetic domain configuration after the initial magnetization is different from that of the virgin sample, and the  $180^\circ$  domain walls that are nucleated and/or move in the sample with changing  $B$  are different after magnetization than in the virgin samples. The sharp maxima in the  $R_{(B)}/R_{(B=0)}$  curves in subsequent cycles of  $B$  between  $\pm 5 \text{ T}$  are found at the coercive field  $\pm B_c$ , where the domain wall density is a maximum. These data clearly demonstrate that the resistance increases with the density of misaligned domains facing each other across a grain boundary. Such a thermal hysteresis effect is also characteristic of the hot-pressed  $\text{CrO}_2$  samples<sup>5</sup> and of thin-film

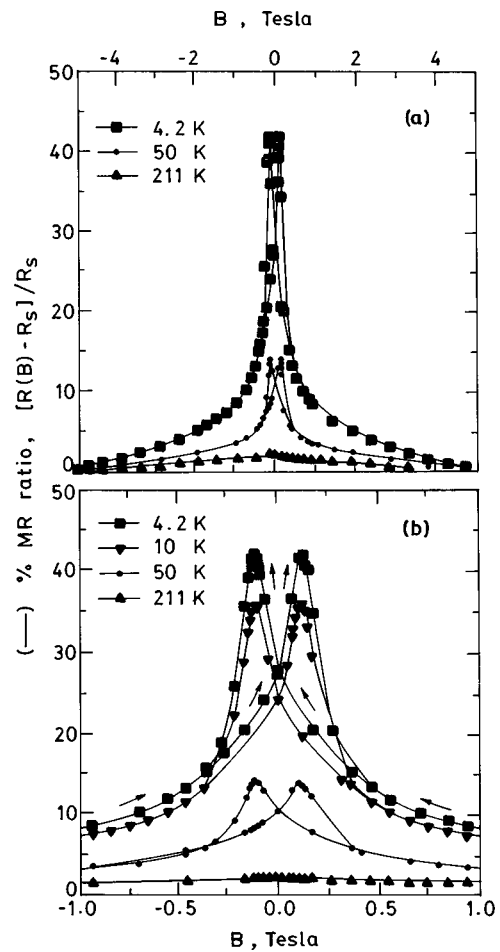


FIG. 2. The field dependence of the magnetoresistance (MR) ratio at different temperatures for (a)  $B < 5 \text{ T}$  and (b)  $B < 1.1 \text{ T}$ . The separation of the peak resistances on the forward and backward sweep of  $B$  correspond to the coercivities  $\pm B_c$ .

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  samples.<sup>2</sup> In the latter case, it has been shown<sup>7</sup> to be related to the grain-boundary resistance rather than to a resistance associated with traversing a domain wall. Given the dominant grain-boundary contribution to the resistance of our  $\text{CrO}_2$  samples, the same conclusion would appear to apply to the  $\text{CrO}_2$  samples also.

Figure 2(a) compares the magnetoresistance at 4.2 K with that at 50 K and 211 K. Saturation was not reached at  $\pm 5 \text{ T}$  at any temperature;  $\text{CrO}_2$  is a hard ferromagnet. At room temperature, there is little change in the resistance with magnetic field for  $B < 5 \text{ T}$ . This observation is consistent with an earlier report by Rodbell *et al.*<sup>6</sup> that the drop in room-temperature resistance of a hot-pressed  $\text{CrO}_2$  sample was less than 1.5% in an applied field  $B = 2.7 \text{ T}$ . However, below 150 K the magnetoresistance increases significantly with decreasing temperature down to 4.2 K the lowest temperature at which measurements were made. The magnetoresistance ratio  $[R_{(5 \text{ T})} = R_{(B=0)}]/R(5 \text{ T})$  increases sharply with decreasing temperature see Fig. 3, from 3% at 210 K to 42% at 4.2 K. Figure 2(b) shows similar curves for  $B < 1.1 \text{ T}$  taken at 4.2, 10, 50, and 211 K. The coercivity obtained from the separation of the peak resistances on the forward and backward sweep of  $B$  is  $B_c = \pm 0.11 \text{ T}$  for a  $B < 1.1 \text{ T}$ . On lowering the maximum applied field to  $B < 0.02 \text{ T}$  (200 g), an appreciable magnetoresistance was re-

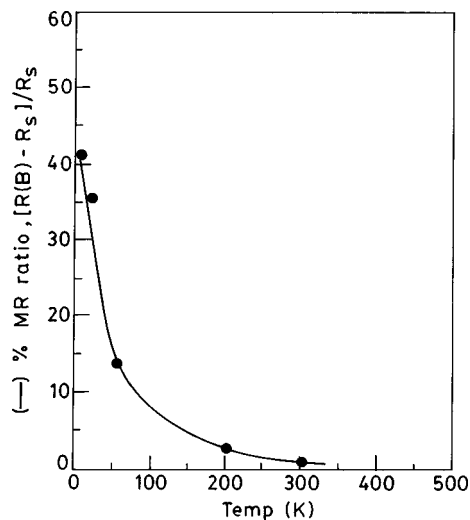


FIG. 3. Temperature dependence of the MR ratio for the cold-pressed  $\text{CrO}_2$  sample; solid line is a guide to the eye.

tained; 20%, 11%, 5% at 4.2, 10, and 50 K, respectively. No appreciable difference in the magnetoresistance was found on varying the sample thickness from 1.5 to 3.0 mm.

Comparison of Fig. 1 and Fig. 3 shows that the magnetoresistance ratio increases with the resistance in the virgin sample, which indicates that the intergranular resistance depends sensitively not only on the alignment of the magnetization on either side of a grain boundary, but also on the concentration of charge carriers traversing a grain boundary. The dramatic increase in intergranular resistance with decreasing temperature suggests a simple qualitative model in which two types of electrons traverse a grain boundary: those that hop in a succession of steps and a smaller number that tunnel across in one step between the conduction bands of the two grains. The latter would continue to conduct at lowest temperatures and would conserve their spin angular momentum in a single jump; these are the primary contributions to the GMR. The electrons that traverse a grain boundary in two or more steps have time to relax their spin orientation between jumps, in which case they make no contribution to the GMR. At low temperatures, the electrons that move in successive steps become increasingly trapped out on lowering the temperature, and the single-step electrons contribute an increasing fraction to the conductivity. Therefore, the GMR increases at low temperatures where the electrons that tunnel in a single step are the dominant mobile charge carriers

crossing a grain boundary. At higher temperatures, the multistep hopping electrons dominate the conductivity and the GMR effect of the single-step electrons becomes overwhelmed by the conduction of electrons that lose their initial spin orientation.

In summary a giant negative magnetoresistance (GMR) has been found below 77 K in cold-pressed, polycrystalline  $\text{CrO}_2$  samples. It does not occur at the Curie temperature ( $T_c = 125^\circ\text{C}$ ) as does the intrinsic colossal magnetoresistance (CMR) found in certain manganese oxides with the perovskite structure. It is to be compared with the extrinsic GMR found at low temperatures in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ . In principle, the extrinsic GMR should be optimized at the coercive field  $B$  of a polycrystalline half-metallic ferromagnet with a relative square  $B$ - $H$  hysteresis loop. However, realization of the effect requires that the conduction electrons tunnel in a single step from the conduction band of one grain to that of the other across the grain boundary. If the electrons are trapped for a time long compared to the spin relaxation time (either at surface states or at intermediate trapping centers) during traversal of a grain boundary, they lose their spin information and cannot contribute to the GMR effect. At lowest temperatures, filling the trap states with immobilized charge carriers makes dominant the carriers that tunnel from conduction band to conduction band across a grain boundary in one step; these electrons must dominate at higher temperatures if a grain-boundary GMR mechanism is to be realized at room temperature.

One of the authors (S.S.M.) thanks the Max-Planck Gesellschaft for a visiting fellowship, and Professor Kirschner for his encouragement and interest in this work. Initiation grant from IIT Kanpur is greatly acknowledged. One of the authors (J.B.G.) thanks NSF for the financial support.

<sup>1</sup>A. Hellemano, *Nature (London)* **273**, 881 (1996).

<sup>2</sup>J. Z. Sun, W. J. Gallagher, P. R. Duncombe, L. Krusin Elbaum, R. A. Altman, A. Gupta, Yu Lu, G. Q. Gong, and Gang Xiao, *Appl. Phys. Lett.* **69**, 3266 (1996).

<sup>3</sup>J. B. Goodenough, *Prog. Solid State Chem.* **5**, 141 (1972).

<sup>4</sup>T. S. Kannan and A. Jaleel, Indian Patent No. 627/Del/87.

<sup>5</sup>S. Sundar Manoharan, A. Daniel, D. Elefant, and G. Reiss (submitted for Patent).

<sup>6</sup>D. S. Rodbell, *J. Phys. Soc. Jpn.* **21**, 1224 (1966), D. S. Rodbell, J. M. Lommel, and R. C. De Vries, *ibid.* **21**, 2430 (1966).

<sup>7</sup>N. D. Mathur, G. Burnell, S. P. Isac, T. J. Jackson, B. S. Teo, J. L. Mac Manus-Driscoll, L. F. Cohen, J. E. Evetts, and M. G. Blamire, *Nature (London)* **387**, 266 (1997).