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# Magnetic surface effects and low-temperature magnetoresistance in manganese perovskites

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**Abstract.** The low-field magnetoresistance and the magnetization of ceramic $La_{2/3}Sr_{1/3}MnO_3$ oxides have been studied as a function of the grain size. It is shown that these ceramics become magnetically harder when reducing the particle size, exhibiting large magnetic anisotropy ($K_1 \approx 10^7$ erg cm$^{-3}$) that also increases when reducing the grain size. In concomitance with this enhancement of the magnetic hardness a gradual increase of the low-field magnetoresistance is also detected. We suggest that both phenomena are closely related and associated with the existence of some degree of spin disorder at the grain boundaries. Implications of these findings for improvements of the field response sensitivity of these materials are discussed.

## 1. Introduction

Since the first results of the huge magnetoresistive effect in manganites came out it was clear that extensive use of the extraordinary magnetoresistance (MR) of these materials (up to $10^7$% in fields of about 5 T, [1]) could only be achieved if the low-field response was appropriately controlled. In this sense, the experimental finding of two well separated MR contributions in ceramic $La_{2/3}Sr_{1/3}MnO_3$ samples, one attributed to an intrinsic intragranular component and the other to a non-intrinsic intergranular effect, is very significant and could be of a major importance in technological applications [2].

However, up to now, a clear understanding of this low-field regime, although it is clear that it should be related to grain boundary effects, is still missing. Spin polarized tunnelling of charge carriers from grain to grain has been proposed as one of the possible origins [2] of this low-field response, but spin-dependent scattering at the grain boundaries may also account for the observed behaviour [3]. The relevance of the magnetic disorder at the interfaces for the low-field magnetoresistance is therefore evident. In the case of the spin tunnelling mechanism in metallic/insulating systems, the MR is proportional to the intergrain exchange coupling [4], that can be tuned by appropriate tailoring of both bulk and surface magnetic interactions [5, 6]. On the other hand, it has also been shown that a magnetically disordered surface layer does exist in magnetic nanoparticles [7, 8]. Therefore, it is evident that, whatever the mechanism, reducing the particle size of the ceramics would imply an increase of the low-field MR.

In this paper, we explore some of these issues in ceramic samples of $La_{2/3}Sr_{1/3}MnO_3$, showing that a reduction of the grain size implies an increase of the magnetic hardness as well as the low-field magnetoresistance of the samples.

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## 2. Experiment

Ceramic powders of $La_{2/3}Sr_{1/3}MnO_3$ were prepared by conventional solid-state techniques in oxygen atmosphere: details can be found elsewhere [5, 6]. The samples were sintered about $t_s = 4$ h at 1400 °C. X-ray powder diffraction analysis showed pure single-phase samples. Four samples, having significantly different grain size, were prepared from powders from the same batch according to the following procedures.

Using a mechanical attrition system the ceramics were ground for 72 h. To perform transport and magnetic measurements, a pellet was prepared and sintered for a short time ($t_s = 0.1$ h) at 1200 °C (sample A). Two samples, prepared by the standard procedure, were sintered at different conditions: 1400 °C and $t_s = 48$ h (sample B) and 1500 °C and $t_s = 96$ h (sample C). Finally, sample D was prepared by melting a preformed pellet, using the solar furnace facilities of the IMP—CNRS (France). Very high temperatures may be reached by using this system, allowing to melt the sample followed by a fast cooling leading to a polycrystalline sample having large grains.

Scanning electron microscopy (SEM) and optical pictures were taken to explore the microstructure, grain connectivity and porosity of the samples. It turns out that the major and more relevant difference among these four samples is the particle size and density. The observed sizes are as follow: A $\approx$ 0.5–1 $\mu$m, B $\approx$ 2–5 $\mu$m, C $\approx$ 10–20 $\mu$m and D $\approx$ 50–100 $\mu$m.

Magnetization measurements were made using a QD SQUID system up to 5 T. Transport measurements were performed, using the standard four-probe method, on samples of about $0.5 \times 1 \times 5$ mm$^3$ with the current applied perpendicular to the magnetic field.

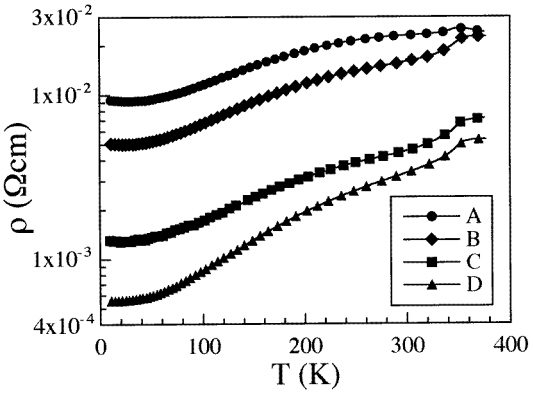


**Figure 1.** Thermal dependence of the electrical resistivity of the four samples, having different particle size, used in this work. A $\approx$ 0.5– 1 $\mu$m, B $\approx$ 2–5 $\mu$m, C $\approx$ 10–20 $\mu$m, D $\approx$ 50–100 $\mu$m.

In figure 1 we show the $\rho(T)$ curves for the four samples. It is worth emphasizing some features of this figure. (a) The electrical resistivity has essentially the very same form and steadily increases, in all the temperature range, from sample D to A reflecting the progressive reduction of the grain size and the degradation of the grain connectivity, as observed in the SEM pictures. (b) A sort of maximum of the resistivity exists at $T \approx 365$ K for all the samples, thus showing that the oxygen stoichiometry is essentially identical for all samples. Therefore, it can be concluded that the possible differences in the magnetoresistivity of these samples should be related to the microstructure associated to the grain boundaries.

## 3. Results and discussion

The isothermal $R(H)/R(H = 0)$ and $M(H)$ curves measured for sample B (2–5 $\mu$m) at several temperatures between 10 and 300 K are shown in figure 2. As expected, $R(H)/R(H = 0)$ curves, that is the magnetoresistance, display two well defined regions (figure 2(a)). In the low-field region extending only a few kOe, it is found that $R(H)$ decreases sharply, with variations of $R(H)/R(H = 0)$ up to 30% at low temperatures, but decreasing when $T$ increases. In the high field regime the variation of $R(H)$ is almost linear with a slope $S = \mathrm{d}R(H)/\mathrm{d}H$ much smaller than for low fields.

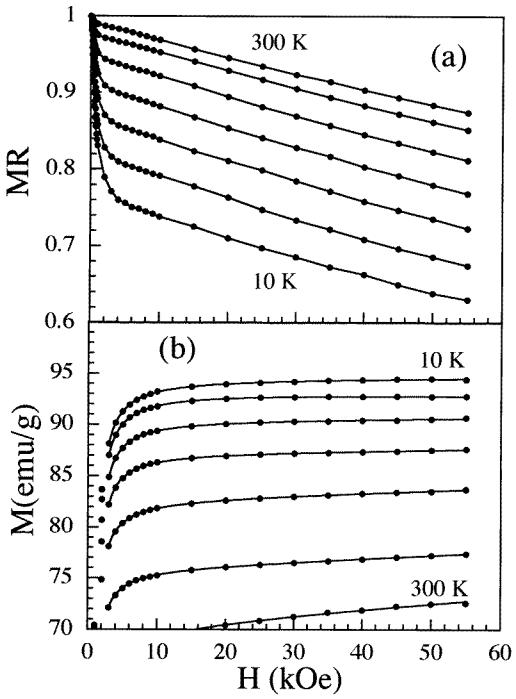


**Figure 2.** Field dependence of the magnetoresistance, defined as MR $= R(H)/R(H = 0)$ (a) and magnetization (b) for sample B (particle size $\approx$2–5 $\mu$m) measured at several temperatures from 10 K to 300 K. The solid lines through the $M(H)$ data correspond to the fits using (1) in the text.

Using a similar procedure to that reported in [2] we have evaluated the low-field magnetoresistance by extrapolating back to $H = 0$ the almost linear behaviour of $R(H)/R(0)$ observed above 5 kOe. Subtracting the intercept with the $Y$-axis from unity we have the variation of the magnetoresistance in the low-field regime, the so-called low-field magnetoresistance (LFMR) depicted in figure 3(a) for the four samples as a function of temperature. As mentioned before LFMR decreases when increasing temperature. The key point in this figure is that LFMR not only decreases with $T$ but also depends on the particle size, becoming smaller as the particle size increases.

Even though the actual meaning is not known yet, it is found that the temperature dependence of the LFMR displays a Curie–Weiss law-like behaviour, i.e. LFMR($T$) =

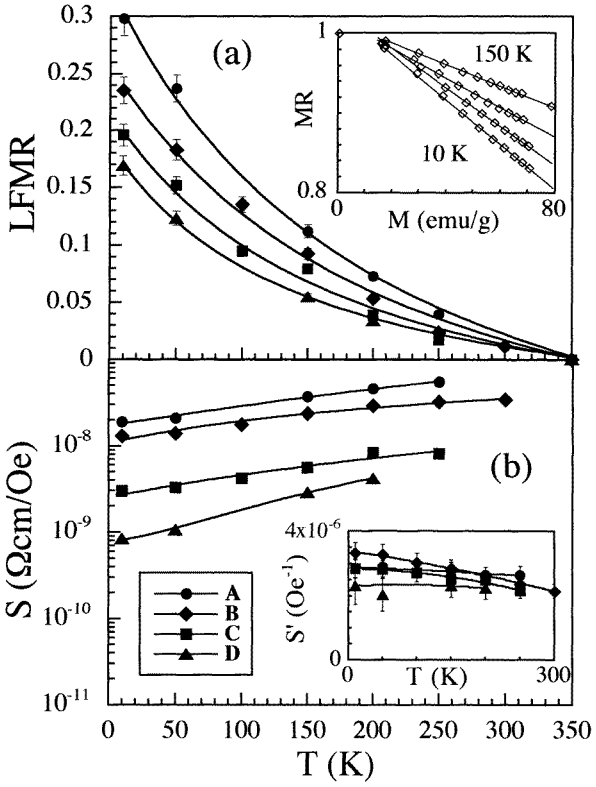


**Figure 3.** (a) Low-field magnetoresistance LFMR, defined as $1 - \lim_{H\to 0}[R(H)/R(0)]$, against temperature. Inset: MR($H$) against M($H$) for sample B. (b) High-field dependence of $S = \mathrm{d}R(H)/\mathrm{d}H$ against temperature. Inset: temperature dependence of the normalized high-field slope $S' = [\mathrm{d}R(H)/\mathrm{d}H]/R(H = 0)$. The symbols corresponds to the four samples having different particle size (A $\approx$ 0.5–1 $\mu$m, B $\approx$ 2–5 $\mu$m, C $\approx$ 10–20 $\mu$m, D $\approx$ 50–100 $\mu$m).

$a + b/(T + q)$ (solid lines through the data in figure 3(a)) and the fitting parameter $q$ increases monotonically when decreasing the particle size.

We recall here that the intergrain contribution to the overall magnetoresistance (MR), particularly the LFMR fraction, is additive to the intrinsic MR associated with each grain, which should be similar to that observed in single crystals, thus displaying a maximum close to the Curie temperature. These additive contributions can be clearly observed in figure 4 where we include the resistivity, and the magnetoresistance (10 kOe) for sample B.

The slope $S$ of the high-field linear portion of $R(H)$ for these samples can be seen in figure 3(b). A systematic trend is observed: $S(H)$ becomes progressively reduced when increasing the particle size. Thus it is clear that even the high-field region of $R(H)$ is affected by grain boundary effects. More precisely, the intergrain resistivity is strongly field dependent, both in the low- (below 1 kOe) and high-field regions. A significant difference however exists: whereas in the first case the normalized magnetoresistance LFMR strongly depends on the particle size, the normalized high-field slope $S' = [\mathrm{d}R(H)/\mathrm{d}H]/R(H = 0)$ is almost insensitive to the particle size, in the range investigated in the present work, and weakly temperature dependent (see inset of figure 3(b)). Even more, it is relevant that inspection of data from the literature—see for instance [9]—also lead to $S(H)/R(H)$ values that are coincident with the present data.

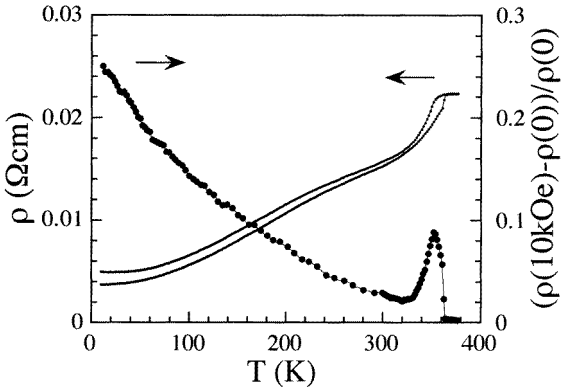


**Figure 4.** Thermal behaviour of the electrical resistivity (left) measured at $H = 0$ and 10 kOe, and magnetoresistance (10 kOe) (right) for sample B (particle size ≈2–5 $\mu$m).

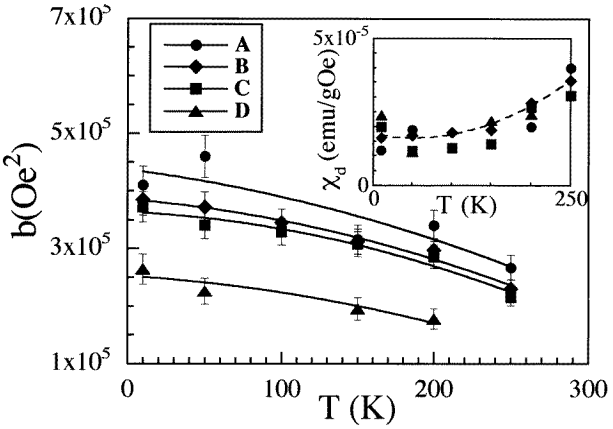


**Figure 5.** Evolution with temperature of parameter $b$ in (1). Inset: high-field differential susceptibility $\chi_d$ for the four samples used in this work. (A ≈ 0.5–1 $\mu$m, B ≈ 2–5 $\mu$m, C ≈ 10–20 $\mu$m, D ≈ 50–100 $\mu$m.)

On the other hand, the isothermal field dependence of the magnetization has been analysed in terms of the so-called 'law of approach to saturation' (LAS) [10]:

$$M(H) = M_S[1 - a/H - b/H^2] + \chi_d H \tag{1}$$

where $M_S$ is the saturation magnetization and $\chi_d$ is the high-field differential susceptibility. This equation gives a proper description of magnetization curves (solid lines in figure 2(b)) for fields larger than about 5–6 kOe. The most relevant parameters, $b$, that contains the contribution of the magnetic anisotropy, and $\chi_d$ are depicted in figure 5. It is clearly shown in this figure that $b$ decreases as the particle size increases while $\chi_d$ remains almost constant and, therefore, no further information about possible influence of particle size in the magnetic ordering can be obtained from it. A naive estimate of the upper limit of magnetic anisotropy energy in these samples may be obtained by assuming the expression

of $K_1$ for uniaxial systems [10]:

$$K_1 = \left[\frac{105}{8} b M_S^2\right]^{1/2} . \tag{2}$$

It is not expected that surface effects will lead to a cubic magnetic anisotropy and consequently the uniaxial approximation should provide a first-order estimate of the anisotropy energy. Using the values of $b$ of figure 5(a) we obtain for $K_1$ very large values that are around $1.0 \times 10^7$ erg cm$^{-3}$ at 10 K. This magnetic anisotropy energy is surprisingly large for a transition metal oxide; in fact it is even larger than that measured in the very anisotropic hexagonal ferrites ($\sim 5 \times 10^6$ erg cm$^{-3}$ [11]) and arises several questions about its origin. Nevertheless, it should only be considered as an upper limit for the anisotropy in these materials since several factors may disturb the determination of $K_1$ from (1) and (2). (a) The values obtained for $K_1$ are sensitive to the field interval of the $M(H)$ curves used in the fitting with (1) since the contribution from the terms $a/H$ and $b/H^2$ is difficult to separate and variations of about 15% are found. This error becomes larger as the magnetic hardness of the sample increases and larger fields are necessary in order to be able to separate both contributions. (b) Fields very much larger than the anisotropy field are required in order to correctly determine $\chi_d$ and subtract its contribution to $K_1$.

Apart from these sources of error, intrinsic to the use of (1) for the determination of $K_1$, other factors may also disturb the determination of the anisotropy such as, for example, the possible existence of antiferromagnetic clusters and the magnetic frustration due to the disorder and competition of interactions at grain boundaries. The contribution of the latter is expected to increase dramatically as particle size decreases [8] and may, therefore, represent a major contribution to the observed increase of the magnetic hardness of the samples as the particle size decreases.

Even though there are no measurements of the magnetic anisotropy in single crystals yet, recent magnetization measurements of $La_{2/3}Sr_{1/3}MnO_3$ thin films on top of $SrTiO_3$ substrates give values of the anisotropy constant that are also very large ($K_1 \approx 2 \times 10^6$ erg cm$^{-3}$ at 5 K [12]). In this case, it was argued that this anisotropy arises mainly from the stress induced by the temperature dependent lattice mismatch between the film and the substrate. Nevertheless, the observation of even large anisotropy values in the present ceramic compounds, even having in mind the fact that our estimates correspond to an upper limit, appears to rule out the substrate induced stress as the origin of the large anisotropy observed in thin films.

At this point the observation of an enhancement of the magnetic hardness for smaller particles follows nicely the recent observation in nanoparticle systems [7, 8], where surface induced spin disorder was also found to play a fundamental role in the magnetization and relaxation processes.

It is worth mentioning here that the absence of explicit particle-size dependence on $\chi_d$ may be understood on the basis of the bulk character of this magnitude that should be much more insensitive to the surface disorder than the electrical resistance since electrons necessarily have to cross surfaces from one grain to another. Nevertheless, possible errors in the determination of $\chi_d$, as particles become smaller and the magnetic hardness increases, due to the impossibility of fully saturating the magnetization with the maximum available field, may not be disregarded.

Therefore, in principle, $S(H)$ should explicitly depend on particle size while the dependence of $\chi_d$ is not so clear. Similarly, recent results by Gupta *et al* [13], of magnetoresistance and Kerr measurements on manganite thin films, suggested that disorder induced canting of spins should exist at the grain-boundary regions. On the other hand,

the comparison between the MR in the ferromagnetic phase in single crystals and ceramics clearly rules out any significant contribution of intragrain magnetic domain scattering as a source of negative MR.

The proposal of spin polarized tunnelling through grain boundaries in sintered ceramics [2] becomes extremely attractive although it faces several difficulties. In principle, the theory was first developed for a non-percolating network of single-domain ferromagnetic particles, having a ferromagnetic interaction between them [4]. In the present case, particles in the $\mu$m range and ceramics of high density ($\approx$70%) are expected to form a percolating network of metallic conduction unless the grain boundaries (GBs) have an insulating character. This is a point that has not been investigated for ceramics of compositions close to $La_{2/3}Sr_{1/3}MnO_3$. If this quenched spin disorder at the particle surface leads to a quasi-insulating behaviour of the GB, then the use of the spin polarized tunnelling mechanism [4] to analyse the present results may be justified. In that case, the appropriate expression is given by:

$$\frac{\Delta\rho}{\rho} = \frac{-JP}{4k_BT}[M^2(H,T) - M^2(0,T)] \tag{3}$$

with $P$ the magnetic polarization degree of the spins. It follows that a negative magnetoresistance corresponds to a $J > 0$, that means a ferromagnetic coupling between the grains [14]. From the definition of magnetic coupling energy EM of [4], it is clear that the parallel spin alignment always results in a lower energy than the antiparallel if $J > 0$. This conclusion contrasts with that derived by Hwang *et al* [2].

According to (3) the maximal $\Delta\rho/\rho$ should be of the order of $JP/4k_BT$. Estimates of $J$ can be made from the stiffness constant of the spin waves. It turns out that $J \approx 1$ meV [14, 15]. Therefore, assuming $P = 1$ as appropriate to these fully polarized electronic systems, at 10 K, one obtains $\Delta\rho/\rho \approx -(JP/4k_BT) \approx 0.33$. The close similarity of this limiting value to our data of figure 2(a), as well as the data of other authors [2, 9] is extremely suggestive and it may provide additional support to the tunnelling model. However, it is important to recognise that our experimental data show a clear linear $\Delta\rho$–$M(H,T)$ relationship (see inset of figure 3(a)) spanning almost all the range of investigated fields, which is in contrast with the predictions of (3). This experimental behaviour is also in disagreement with the spin dependent scattering mechanism that also predicts a quadratic dependence on the magnetization.

In summary, we have shown that the low-field magnetoresistive response of ceramic manganese perovskites clearly depends on the particle size. At the same time we have also observed an increase of the magnetic hardness of the samples as the particle size decreases. This increase may, in principle, be attributed to a reinforcement of the magnetic anisotropy, that turns out to be very high. Nevertheless, other contributions, such as, for instance, the magnetic frustration at grain boundaries or the existence of antiferromagnetic clusters, cannot be disregarded, implying, therefore, smaller values of the anisotropy constant. Even though our results cannot elucidate whether spin polarized intergrain tunnelling or spin dependent scattering at the grain boundaries is the actual mechanism lying behind the low-field magnetoresistive response, they clearly show the major role played by interfaces and surface effects in this range of fields. Thus, the low-field magnetoresistive response may originate in part from the field suppressed magnetic disorder at the particle surface layer. Under these circumstances, strategies for further improvement of the low-field MR can be easily envisaged. Enhancement of the surface magnetic disorder appears to be a very attractive approach.

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