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Coexistence of two types of spin glass phases in polycrystalline films of $La_{2/3}Ca_{1/3}MnO_3$

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Abstract

The magnetoresistance (MR) and magnetization of $La_{2/3}Ca_{1/3}MnO_3$ films with controllable grain sizes have been studied. Both quantities show differences between their zero-field cooled (ZFC) and field cooled (FC) states at low temperatures. The results indicate the coexistence of two types of spin glass phase at and nearby the grain boundaries: one forms a shell of a certain thickness and manifests itself in both MR and magnetization, and the other is nearly volume-less, manifesting itself only in MR.

1. Introduction

The research on the colossal magnetoresistance phenomenon in manganite compounds was partially motivated, at least at its early stage, by the need to seek for sensitive readhead materials in magnetic data storage. However, it turned out that the low-field magnetoresistance (MR) of single crystals of manganite is quite insignificant compared to that of the traditional hetero-structured materials. Recently, particular attention has been drawn to polycrystalline manganite samples where improved sensitivity of MR is reached at low fields [1–3]. To understand the mechanism of low-field MR behaviour, many experiments with different configurations of grain boundaries have been designed and performed [4–10], and two pictures have been proposed. The first is known as the tunnelling magnetoresistance (TMR) picture. It assumes that the grain boundary acts as a tunnelling barrier: the tunnelling conductance is determined by the relative misorientation in magnetization of the two adjacent grains [1, 4–7]. The second is the so-called spin-dependent scattering picture, in which the grain boundary and nearby area are considered as a spin-misorientated region that contributes to the MR [2, 3, 8, 11–13]. To further clarify the issues of spin arrangement at the boundaries and spin-dependent scattering processes across the boundaries, MR and magnetization investigations on polycrystalline samples with well-controlled grain size and enhanced boundary contribution are preferred.

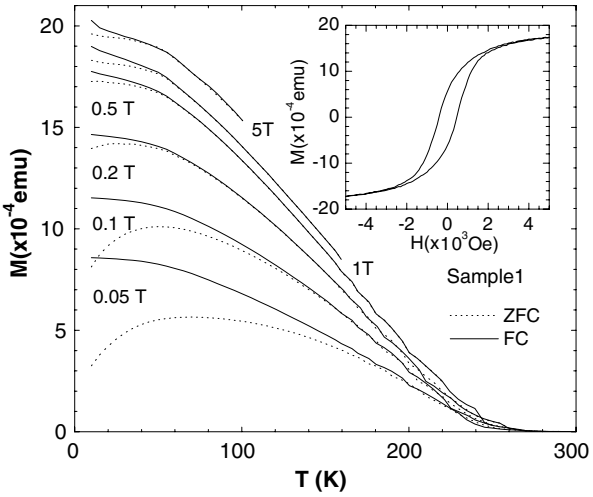

Figure 1. Magnetization of sample 1 in warming-up measurements after it is cooled in zero magnetic field (dotted lines) or in a field the same as that used for the warming-up measurement (solid lines). The inset shows the M–H curve of the sample at 10 K.

In this paper, we report our investigations on the MR and magnetization of a new type of $La_{2/3}Ca_{1/3}MnO_3$ film sample in which the manganite grains with controllable size form a ring-like network (see the insets in figure 2). By comparing the ZFC and FC states of the MR and magnetization of these samples, we are able to distinguish two spin glass phases. One presumably occupies a shell with a certain thickness near the grain surface, manifesting itself in both MR and magnetization, and the other arises at the grain surface, manifesting itself only in MR.

2. Experiments

$La_{2/3}Ca_{1/3}MnO_3$ films were deposited onto porous alumina substrate by a pulsed-laser deposition method [14]. By choosing porous alumina with numerous holes at the sub-micrometre scale as the substrate, the deposited manganite film forms a thin ring-like network composed of a series of grains that sit one by one on top of the 'ridge' of the substrate. The grain size can be adjusted via controlling the film thickness. The magnetization of the samples was measured on a Quantum Design SQUID magnetometer, and the resistance was measured by utilizing the low-temperature and high-field conditions of a Quantum Design Physical Properties Measurement System. Two samples with different grain size were studied: one, denoted as sample 1, had a film thickness of 180 nm and an averaged grain size of 60 nm; the other, denoted as sample 2, had a thickness of 36 nm and an averaged grain size of 20 nm. For sample 1 both the resistance and magnetization were measured. For sample 2, however, only its resistance was measured. We were unable to resolve its magnetization signal correctly because of the extremely small volume fraction of the film compared to that of the substrate.

3. Results and discussion

Figure 1 shows the magnetization of sample 1 as a function of temperature. The data were taken in warming-up processes after the sample was first cooled down to the base temperature either with (FC) or without (ZFC) a magnetic field. The low-field ZFC curves exhibit a

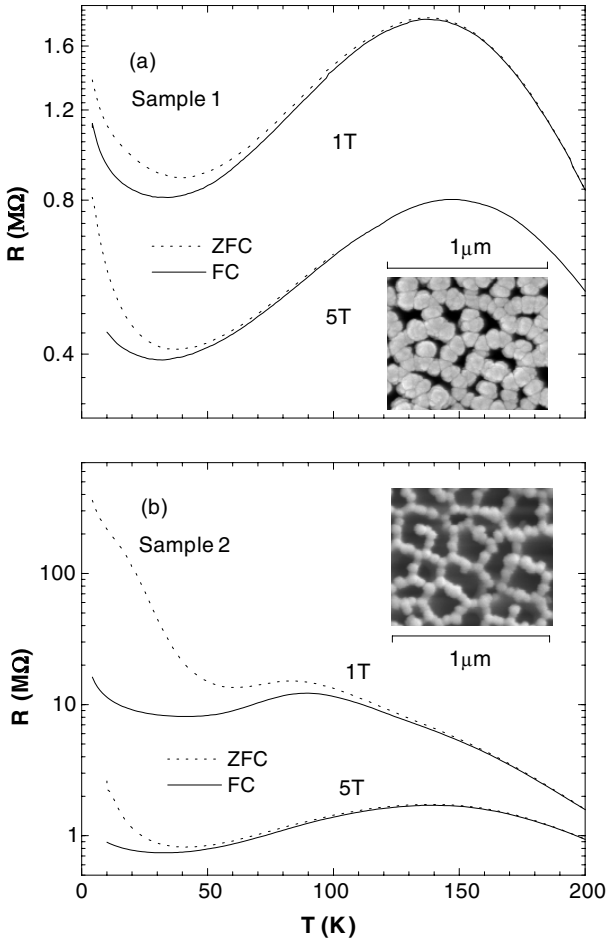

Figure 2. Resistance of sample 1 (panel (a)) and sample 2 (panel (b)) measured in warming-up processes after they are cooled either in zero magnetic field (dotted lines) or in a field the same as that used for the warming-up measurement (solid lines). For sample 1 both four- and two-probe measurements are used, all giving the same results, whereas for the highly resistive sample 2 only two-probe measurement configuration with a picoampere meter located at the lower voltage side is used, to guarantee the measurement accuracy. The insets are the scanning electron microscopy images of the corresponding samples.

broad maximum, whereas its FC counterpart shows a monotonic increase with decreasing temperature. The two curves overlap at high temperatures but split off at low temperatures. The splitting becomes smaller and its onset temperatures shifts to the lower side with increasing magnetic field, but is still recognizable in a field of 5 T.

Splitting in magnetization between the ZFC and FC curves has previously been observed in polycrystalline samples [15–17]. It is believed that the big splitting observed in low fields should mainly reflect the difference in domain orientation between the ZFC and FC states [15]. And the small splitting that remained in high fields, much higher than the coercive field, should merely reflect the difference in the spin glass phase between the ZFC and FC states [16, 17]. Due to the close relationship between magnetic and transport properties in manganite systems, one would naturally expect that the resistivity of the sample also shows a spin glass behaviour,

i.e., the R versus T curves in the ZFC and FC states should split off at low temperatures and in high fields. To our knowledge, however, such behaviour has not yet been observed. Ziese and co-workers were able to observe a time relaxation of the resistance after a sudden field change from 1 T to 70 G [18]. However, in a field of only 70 G the relaxation of the resistance could be caused either by a spin glass mechanism or by a TMR mechanism via domain rotation.

We have measured the resistance of the samples in both ZFC and FC states in fields of 1 and 5 T where domains are almost aligned up so that the TMR mechanism can be ruled out in resistive behaviour, and observed for the first time the splitting of the R versus T curves at low temperatures (figure 2). This result, together with the splitting of magnetization in the same fields as shown in figure 1, provides evidence of the existence of spin glass phases in our samples. Note that the upturn in resistance at low temperatures is possibly caused by a Coulomb blockade effect in granular systems [19], and will be discussed elsewhere [20].

It is known for ferromagnetic metals and some manganites near the Curie temperature, as well as for some spin glass systems below the glass transition temperature, that their MR and magnetization follow the empirical relation [21, 22]:

$$(R_0 - R)/R_0 = C(M/M_s)^2 \tag{1}$$

where R_0 is the resistance at temperature T in completely spin disordered state, M, the magnetization, M_s, the saturation magnetization, and C, a weakly temperature-dependent coefficient. It would be interesting to check if the MR and magnetization of the spin glass phases alone also follow this relation. For this purpose, we need to subtract the contributions of the ferromagnetic core from the total MR and magnetization of the sample. The magnetization of the spin glass phases can be written as M–$M_{\rm core}$. According to the M–H curve at low temperatures (inset of figure 1), we assign 2000 G as the averaged saturation field for the cores, and estimate according to the approaching saturation behaviour in [1] that the magnetization of the cores should already reach 99% of its saturation value at $T = 10$ K and $H = 2000$ G, i.e., $M_{\rm core} = M(B = 2000\,{\rm G}) \approx 1.45 \times 10^{-3}$ emu. For the resistance side, at low temperatures and when $H > 2000$ G, the cores' contribution to the total MR is negligible because of the perfect alignment of spins inside each core as well as the perfect alignment of all cores to the field direction. Therefore, we can roughly assign $R_0(T) = R(T, B = 2000\,{\rm G})$ as the resistance of the spin glass phases at a given temperature T in a full spin-disordered state. Then, if (1) still holds for the spin glass phases, we can write for both the 1 and 5 T cases:

$$\frac{R_0(T) - R_{\rm ZFC}(T)}{R_0(T)} = C\left(\frac{M_{\rm ZFC}(T) - M_{\rm core}}{M_\infty - M_{\rm core}}\right)^2 \tag{2}$$

$$\frac{R_0(T) - R_{\rm FC}(T)}{R_0(T)} = C\left(\frac{M_{\rm FC}(T) - M_{\rm core}}{M_\infty - M_{\rm core}}\right)^2 \tag{3}$$

where M_∞ represents the magnetization of the samples in an infinitely large field, and $M_\infty - M_{\rm core}$ denotes the saturation magnetization of the spin glass phases. By subtracting (2) from (3) we have:

$$\frac{R_{\rm ZFC}(T) - R_{\rm FC}(T)}{R_0(T)} = \alpha[M_{\rm FC}(T) - M_{\rm ZFC}(T)][M_{\rm FC}(T) + M_{\rm ZFC}(T) - 2M_{\rm core}] \tag{4}$$

where $\alpha = C/(M_\infty - M_{\rm core})^2$.

In figure 3 the differences in MR and magnetization between the ZFC and FC states in fields of 1 and 5 T are plotted according to (4). Any data point that sits away from (0, 0) should arise from a spin glass state. Two regimes can be recognized: one is a linear regime at low temperatures where substantial difference in magnetization between the ZFC and FC states is seen. This regime is presumably originated from a spin glass shell of a certain thickness

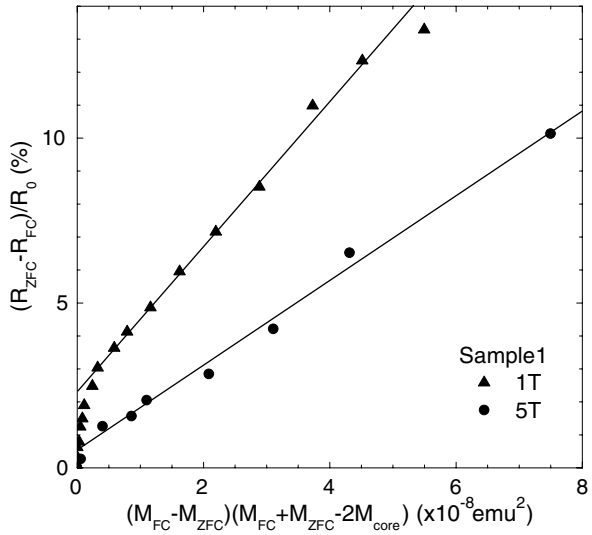

Figure 3. The difference in MR between the ZFC and FC states as a function of the difference in magnetization. The solid lines are guides to the eyes.

near the grain surface. The linearity proves that the MR and magnetization of the shell can still be described by (1). The coefficient C is 1.2 for the 1 T case and 0.7 for the 5 T case, if taking $M_\infty = 2.2 \times 10^{-3}$ emu according to figure 1. These values are close to that of the conventional spin glass systems [21] but significantly lower than the ones observed in bulk samples of $La_{2/3}Ca_{1/3}MnO_3$ (where $C = 6$–8 [22]).

The thickness of the spin glass shell can be estimated as follows. Since $M_{\rm core} \approx 1.45 \times 10^{-3}$ emu and $M_\infty \approx 2.2 \times 10^{-3}$ emu, the spin glass shell should contribute about 34% to the total magnetization. This would yield a shell thickness of ∼3 nm for sample 1 with averaged grain size of 60 nm.

We can also recognize a second spin glass regime near the ordinate in figure 3, which is almost volume-less in magnetization but contributes significantly to the MR splitting at relatively high temperatures. We attribute this part of the spin glass behaviour to the spin misalignment at the grain surface, i.e., a surface spin glass phase.

Surface spin glass has previously been found in $NiFe_2O_4$ nanoparticles and later also studied in manganites. In the case of $NiFe_2O_4$ nanoparticles [17], the magnetization hysteresis loop opens up to 16 T, and a time-dependent magnetization is observed in a field of 7 T. A model consisting of ferromagnetically aligned core spins and spin-glass-like surface layers was proposed, in which the surface spin disorder arises from reduced coordination and broken exchange bonds at the surface layers of the grains. For manganites [18, 23], it is believed that the ferromagnetic double-exchange interaction via Mn^{3+}–O^{2-}–Mn^{4+} bonds will be interrupted or bent at the grain surface, leading to the spin glass state thereby.

Therefore, our overall picture for sample 1 at low temperatures is: each of its grain has a ferromagnetic core, surrounded by a spin glass shell of 3 nm in thickness. At the outmost surface of the shell there is another layer of surface spin glass with much less volume occupation, presumably only one or two atomic layers in thickness. It survives to much higher temperatures compared to the shell phase.

It is known for a spin glass that, upon a sudden change of magnetic field, both its magnetization and resistance will relax with time in a logarithmic law [24, 25]. We have

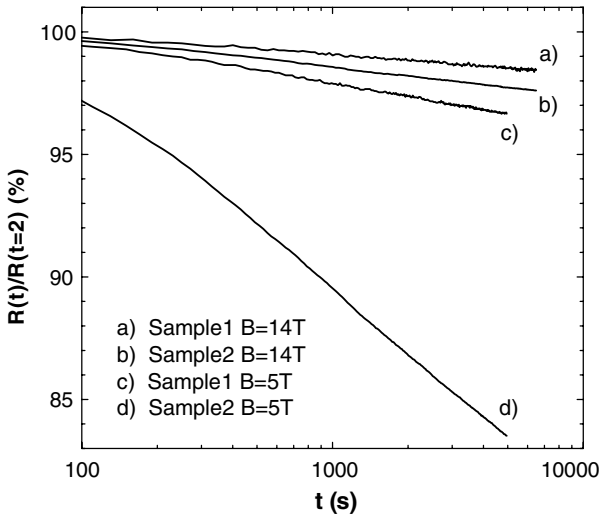

Figure 4. The resistance of the samples as a function of time in fields of 5 and 14 T at 10 K.

also investigated the time dependence of the MR of our samples in high magnetic fields. After ZFC to 10 K, the field is increased at a fixed rate of 100 Oe s^{-1} to a value much higher than the coercive field. Then, the resistance of the sample is recorded as a function of time. After the first few hundred seconds of transient time, we find that the resistance of both samples follows a logarithmic time relaxation, as is plotted in figure 4. This provides additional evidence for the existence of spin glass states in our samples.

4. Conclusions

In summary, through combined measurements on the ZFC and FC resistance and magnetization of polycrystalline $La_{2/3}Ca_{1/3}MnO_3$ samples, we have recognized besides the ferromagnetic core two spin glass phases. One phase is presumably related to the spin misalignment at the grain surface, manifesting itself only in MR but not in magnetization. The other is presumably a shell of a certain thickness formed near the spin-misaligned surface, manifesting itself in both MR and magnetization. We find that the shell phase follows the same empirical quadratic relation between MR and magnetization as for a conventional spin glass phase. Upon a sudden change in magnetic field, the high-field resistance of our samples follows a logarithmic law of time relaxation as is expected for a spin glass phase. Further experiments are needed to verify the shell–surface picture assigned for the two spin glass phases.

Acknowledgments

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