Magnetoresistance induced by low-field control of phase separation in La$_{0.5}$Ca$_{0.5}$MnO$_3$

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The effect of low magnetic fields on the transport properties of a manganite compound with magnetic phase separation is studied. The different behavior obtained in samples of La$_{0.5}$Ca$_{0.5}$MnO$_3$ related to the way in which the low field is applied is consistent with a picture of changes in the metallic fraction induced by the magnetic field in a field-cooled cycle. Using a simple model of conduction through a binary mixture, the interrelation between magnetoresistance, metallic fraction, and percolation temperature is accounted for. A different physical coefficient relating magnetic field and metallic fraction emerges as the relevant parameter in the description of phase separated manganites.

I. INTRODUCTION

The hole-doped rare-earth manganites $L_{1-x}A_x$MnO$_3$, where $L$ is a lanthanide and $A$ a divalent alkaline earth, display a wide variety of spin, charge, and orbital states. The close interplay between them gives rise to different electronic, magnetic, and structural phases, such as paramagnetic insulator (PI), ferromagnetic metallic (FMM), or charge ordered antiferromagnetic insulator (COAF) phases. That interrelation leads to many unusual physical properties, of which the negative magnetoresistance (MR) effect is perhaps the most spectacular one.

The MR effect has been extensively studied, and it has been associated, in general, to a magnetic transition. In particular, the MR of a homogeneous and single crystalline system displaying a PI to FMM transition shows a peak close to the transition temperature $T_C$. This was explained on the basis of the double exchange mechanism, as the result of the thermally induced spin disorder suppression by an external magnetic field, with the consequent shift in $T_C$. Far below $T_C$ the magnetic field has no influence in the (homogeneous) state of the system, and the MR is negligible below $T/ T_C < 1/2$. For granular manganites, instead, the effect of the magnetic field is appreciable even at very low temperatures, due to the role played by intergrain barriers. A similar scenario accounts for homogeneous systems showing a FMM-COAF transition. In this case, the presence of a low magnetic field can only introduce a little shift in $T_C$, with a consequent peak in MR; neither single crystals nor granular materials show an appreciable value of the MR far below $T_C$. However, at fields high enough to induce the COAF-FMM transition (or to suppress the FMM-COAF one) the MR can achieve high values in a wide temperature range below $T_C$.4

The above described scenario has now an unexpected ingredient: the fact that the low-temperature state of some of the manganites consists of coexisting ferromagnetic (FM) and COAF phases has introduced new degrees of freedom into the problem. In this context, the physical properties of the system are strongly dependent on the fraction of the FM phase and its spatial distribution (percolative or not) to account for transport behavior.

Despite the fact that the reason for the existence of the phase separated (PS) state is not yet well understood, theoretical and experimental results agree that the competition between different phases, which is resolved in a short length scale, is very sensitive to the particular kind of disorder in the compound: site $A$ disorder in La$_{0.5}$Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, site $B$ disorder in Nd$_{0.5}$Ca$_{0.5}$Mn$_{0.98}$Cr$_{0.02}$O$_3$, and grain-size effects in La$_{0.5}$Ca$_{0.5}$MnO$_3$, or intragranular strain in Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. The conduction through percolative paths of the FM phase in PS systems has opened a different scenario for the MR effect. The fourfold orders of magnitude in the drop of the resistivity below 100 K found in La$_{0.5}$Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ under a magnetic field as low as 0.4 T is far away from typical values of the low-field MR in homogeneous systems. The role played by the magnetic field in this phenomena was interpreted as related to the interplay between the percolative nature of the phase separation and the domain alignment mechanism, since the field was considered too low to modify the coexisting phase balance.

Crucial effects of the magnetic field on PS systems suggesting a different interpretation were recently reported. In La$_{0.5}$Ca$_{0.5}$MnO$_3$ scanning tunneling microscopy experiments gave direct evidence of changes of the FM fraction by the applied magnetic field for temperatures just below $T_C$. In Nd$_{0.5}$Ca$_{0.5}$Mn$_{0.98}$Cr$_{0.02}$O$_3$, it has been shown that the low-temperature fraction of the FM phase is highly dependent on the magnetic field $H_{ann}$ under which the system is cooled (annealing field): a nonpercolative-percolative transition is induced for $H_{ann} \approx 2$ T, with the consequent changes of several orders of magnitude in the resistivity. That transition can be only accounted for by the change of the FM fraction $f$ induced by the magnetic field, a fact also reflected in the linear $H_{ann}$ dependence of the low-temperature magnetization $M$.

The effects of applying moderate magnetic fields ($H \geq 5$ T) has been also studied in other PS compounds. It has been shown that a magnetic field of 6 T produces the melting of the CO phase in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, inducing a structural transition and rendering the material FMM mostly. The possibility of controlling the relative phase fractions with...
magnetic fields was also claimed in Ref. 13. They have shown that different FM fractions can be tuned as a function of \( H \) in \(^{18}\)O rich samples of \((\text{La}_{0.25}\text{Pr}_{0.25})_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) when \( H \) exceeds a temperature-dependent value \( H_c \) of a few teslas. Specific-heat measurements on charge ordered compounds \( \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \) (0.3 \( \leq x \leq 0.5 \)) reveals also that a magnetic field \( H=8.5 \text{ T} \) is able to modify the relative phase fractions.\(^{14}\)

The gap existing between the magnitude of the magnetic field used in the low-field MR work \( \sim 0.4 \text{ T} \),\(^{6}\) and those needed for inducing changes in the relative fractions of the coexisting phases \( (\geq 2 \text{ T}) \),\(^{7,12,13}\) seems to enforce the idea of two different mechanisms to explain the MR effects in PS systems: domain alignment effect at low fields (under 1 T), the fraction change at moderate ones.

The aim of this paper is to give some insight into this subject by analyzing the simple idea that even when applying a low magnetic field in a field-cooled experiment it is possible to affect the fraction of the coexisting phases, a process we call field-induced fraction enlargement. We have performed MR measurements on \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \), a suitable compound for studying PS effects due to its PI-FM-COAF phase transitions sequence\(^{15}\) and the coexistence of the COAF phase with nanodomains of the FM one below \( T_{co} \approx 150 \text{ K} \) (on cooling).\(^{16}\) As we previously reported,\(^ 9\) changing the grain size through consecutive thermal treatments allow us to control the fraction of FM and COAF phases. This fact opens the possibility for studying the magnetic-field effects for different FM fractions below \( T_{co} \). The measurements were performed with low magnetic fields, in a way that we claim the two effects, alignment (suppression of thermal disorder, intergranular coupling, domain orientation) on one hand, and field-induced fraction enlargement on the other one, are clearly distinguished. Doing this, we could establish the relevance of the fraction enlargement mechanism over the magnetic domain alignment in percolative PS systems at low field. With this result in hands, we analyze the general issue of MR in PS systems, and show that the relation between MR and the FM fraction can be accounted for within this framework with a simple model of conduction by a binary mixture.

II. EXPERIMENT

Polycrystalline samples were obtained by a citrate/nitrate decomposition method as described in Ref. 9. Powder x-ray diffraction was used to check the phase purity; unit-cell dimensions and structural parameters were analyzed using the Rietveld method. Four-probe resistivity measurements were performed in the temperature range 30–300 K on polycrystalline pellets previously pressed and sintered. The two samples used in this work are those labeled C and EII in Ref. 9; the FM fractions were determined through magnetization measurements following the procedure explained there.

III. RESULTS

In Fig. 1 we show the resistivity \( (\rho) \) curves for the two samples under study as a function of temperature. Sample I, with 55% of FM phase at low temperatures, displays a metallic behavior below 80 K, indicating the existence of percolative paths of the FM phase. In sample II, with 9% of FM phase at low temperatures and an insulating behavior, no signal of transport percolation was found down to 40 K, were its resistance exceeded our instrumental detection limit. In Fig. 2(a) we sketch two curves showing the magnetoresistance \( \text{MR} = \rho(0) - \rho(H) / \rho(0) \) of sample I, with each result corresponding to a particular measurement process. In the first procedure, hereafter referred to as field-cooled (FC) mode, the low field \( (H=0.65 \text{ T}) \) was applied throughout the thermal cycle as the sample is cooled. In the second one, the field was turned on and turned off periodically (TOTO mode) while cooling the sample; the data points were ob-
tained after the field was fully established in each step. These procedures were used with the aim of distinguishing the two above-mentioned mechanisms involved in the field dependence of the resistivity: the alignment and the field-induced fraction enlargement effects. If the local free energy describing the FM and COAF states is adequately accounted for by a double-well potential with almost identical minimums, the main idea is that a low magnetic field can, in the FC mode, prevent the formation of otherwise COAF regions. In this case both mechanisms are expected to be present in the FC mode, and this fact would be reflected by the MR. On the other hand, if a low magnetic field is applied after the fraction of the phases was established, the energy barrier between the wells would prevent the change of the populations if the field is applied for a short time. Therefore the only effect in the resistivity would be related to domain orientation. Following this argument, we have taken a period of 60 sec for the switching off the field in the TOTO mode, which is short compared with relaxation times observed through similar processes in another PS system, and also confirmed by careful relaxation experiments performed on our samples.

Comparing the temperature dependence of the obtained MR’s measured on cooling with the different procedures on sample I, plotted in Fig. 2(a), we can see that both MR have their onset around $T_C$, and the curves increase close together with decreasing temperature down to $T\approx200$ K. Bellow this temperature both curves depart. Remarkably, this temperature is close to that at which the onset of a structural phase separation has been reported. The TOTO curve has a peak near $T_C$, and below $T_{co}$ increases almost linearly towards a low-temperature value of 0.25, resembling the behavior of an homogeneous granular FMM compound. On the other hand, the FC curve rises steeply below $T_C$, reaches a peak (MR=0.75) around $T_{co}$, and also increases almost linearly towards a low-temperature value as high as 1.2.

The different response of the compound to the magnetic field regarding the way it was applied gives us a starting point for the understanding of the MR effect in PS systems. When the role of the magnetic field is only that of magnetic moments alignment, as in the TOTO mode, the MR of a PS compound is, irrespective of its PS nature, the same as that of an homogeneous FMM one, due to the intensive character of the MR. The split of the curves when the compound becomes unstable against phase separation and the large values of the MR in the FC mode point to the fact that the low magnetic field is able to modify the relative volumes of the coexisting phases when applied throughout the thermal cycle. In this situation the resistivities with and without applied field correspond to media with different amount of FM phases, which is a distinctive feature that can only be obtained in PS systems.

In order to support the above described scenario we have measured the MR in the FC and TOTO modes on sample II [Fig. 2(b)]. This sample is just below the percolation threshold of the FM phase, as the lack of metallic behavior at low temperatures indicates (see Fig. 1). The MR in the TOTO mode goes to zero for low temperatures, as expected in a nonpercolative sample. However, the applied low field in the FC mode induces an increase of the fraction of the FM phase, leading to its percolation, with the consequent change of more than two orders of magnitude in resistivity below 60 K. Thus the low field plays an unbalancing role in the FC mode, inducing a qualitative change, from nonpercolative to percolative transport, giving the colossal values of the MR displayed in Fig. 2(b). It is also worth noting that the differences found in the MR figures obtained by the FC mode for samples I and II seem to follow a definite relation among the FM fractions and the MR values: high MR are obtained when the sample has a low FM content.

IV. DISCUSSION

The presented results point to the fact that field-induced enlargement of the FM phase is responsible for the observed low-field MR in this PS perovskite. In the discussion that follows we show that this fact is a suitable candidate to give an explanation for the relation between MR and FM fraction at a given temperature. We also show that within this framework it is possible to account for the MR values at the insulator-metal transition temperature ($T_{im}$) in the prototypical PS system La$_{3}$S$_{8}$-yPr$_{y}$Ca$_{3}$S$_{8}$MnO$_{3}$, an experimental observation not yet properly understood.

To do this we use as main framework the general effective medium theory, which describes the resistivity $\rho_c$ of a binary mixture through the relation

$$f \frac{(\rho^{\mu\nu}_c - \rho^{\mu\nu}_{FM})}{(\rho^{\mu\nu}_c + A_c \rho^{\mu\nu}_{FM})} + (1-f) \frac{(\rho^{\mu\nu}_c - \rho^{\mu\nu}_{CO})}{(\rho^{\mu\nu}_c + A_c \rho^{\mu\nu}_{CO})} = 0,$$

where $\rho_{FM}$ and $\rho_{CO}$ are, respectively, the resistivities of homogeneous FM and CO phases, explicitly including their particular field and temperature dependence and granular effects. $t$ is the critical exponent (we assume $t=2$), $f$ is the fraction of the FM phase, and $A_c = 1/f_c - 1$, where $f_c$ is the critical percolative fraction of the FM phase.

Through Eq. (1) we can obtain an expression for the MR of a PS system in terms of the resistivities of the constitutive mediums and the corresponding FM fraction $f$, under the assumption that the magnetic field induces small changes in $f$. As $\rho_{FM}$, $\rho_{CO}$, and $f$ are, in general, temperature and field dependent, we obtain an intricate dependence of the MR with the external parameters. An important simplification can be introduced by neglecting the dependence of $\rho_{FM}$ with the magnetic field (the MR arising from that dependence is, at most, 10% for low fields at $T_{co}$, as shown by the TOTO curves of Fig. 2). With this approximation, the calculated MR is defined by the ratio of the resistivities of the sample when the FM fraction is changed by $\Delta f$, so that

$$MR = \frac{\rho_c(f,\rho_{CO},\rho_{FM})}{\rho_c(f+\Delta f,\rho_{CO},\rho_{FM})} - 1,$$

where $\Delta f$ is the actual field-induced fraction enlargement value. It is worth noting that Eq. (2) is, in some sense, a generalization of the MR concept, as it describes a MR obtained between resistivity curves at fields $H$ and $H+\Delta H$, where in this case the FM fraction enlargement effect is induced by $\Delta H$. 
FIG. 3. Measured (symbols) and calculated (lines) magnetoresistance MR = \( \rho_s(H)/\rho_s(H+\Delta H) - 1\) for (a) samples I \((f_0 = 0.55)\) and II \((f_0 = 0.09)\) of \(La_{0.5}Ca_{0.5}MnO_3\) at \(T=150\) K as a function of \(\Delta H\); the calculations were done taking \(r = 2\) and \(\rho_{co}/\rho_{FM} = 1000\) in Eq. (2); the values \(\alpha_f = 0.20\) and \(0.11\) \(^\circ\) \(T\) \(^{-1}\) were obtained for samples I and II, respectively, by adjusting the experimental data points; and (b) \(La_{58-\delta}Pr_{\delta}Ca_{38}MnO_3\) as a function of \((\rho_{co}/\rho_{FM})^{1/2}\); experimental data points were extracted from Refs. 6 and 20, corresponding to samples with \(y\) values of 0.30, 0.35, 0.375, and 0.40; \(f_c = 0.17\) was taken in Eq. (2), and \(\alpha_f = 0.13\) \(^\circ\) \(T\) \(^{-1}\) was obtained.

We may now compare the predictions arising from this simplified model with the experimental results of the MR of two prototypical PS compounds: \(La_{0.5}Ca_{0.5}MnO_3\) and \(La_{58-\delta}Pr_{\delta}Ca_{38}MnO_3\). As a distinctive feature, in the case of \(La_{0.5}Ca_{0.5}MnO_3\) we can study the MR in samples with different values of \(f\) at a constant temperature, for instance, the temperature at which the MR peaks. In this case the value of \(\rho_{co}/\rho_{FM}\) is fixed, and the only unknown parameter is the field dependence of \(\Delta f\). In order to gain some insight into the relation between \(f\) and \(H\) we have measured the resistivity of samples I and II for several magnetic fields \(H\) in the FC mode, between 0 and 0.8 T, and calculated the MR at the peak temperature, \(T=150\) K, for all the intervals \(\Delta H\) between these fields. With this procedure we obtain the MR for different values of \(\Delta f\) as a function of \(\Delta H\). The zero-field data was ruled out in order to partially exclude the neglected field effect on \(\rho_{FM}\). The results are shown in Fig. 3(a). The calculated curves were obtained following the experimental results of Ref. 7, assuming a linear relation between \(f\) and \(H\), i.e., \(f = f_0 + \alpha_f H\), where \(f_0\) is the zero-field FM fraction and \(\alpha_f\) a field-independent factor, hereafter referred to as the fraction expansion coefficient. We have taken the value \(\rho_{co}/\rho_{FM} = 1000\) and the zero field FM fraction of the samples I and II from Ref. 9. The only free parameter for the adjustment of the experimental results is \(\alpha_f\). The \(\alpha_f\) values obtained, 0.20 and 0.11 \(^\circ\) \(T\) \(^{-1}\) for samples I and II, respectively, indicate a small dependence of \(\Delta f\) with the initial FM fraction \(f_0\). The agreement between the experimental data and calculated curves reveals that the simplified model we are dealing with is able to account for the relation between the MR and FM fraction at a constant temperature, giving a quantitative basis for the understanding of the MR effect in PS systems.

In order to obtain an additional insight on the results that are expected for PS systems in the fraction enlargement scenario, we have used Eq. (2) to describe the MR effect occurring in \(La_{58-\delta}Pr_{\delta}Ca_{38}MnO_3\), a compound with a very distinct behavior.\(^6\) In this system, and as a function of \(y\), a sharp change in the insulator-metal transition temperature \(T_{im}\) is obtained in the \(y\) region near 0.3. In the high \(y\) region, a net separation between \(T_{im}\) and \(T_c\) can be observed.\(^{20}\) Below \(T_c\) the state of the system is characterized by the coexistence of isolated FM clusters embedded in charge ordered regions. Unlike what happens in \(La_{0.5}Ca_{0.5}MnO_3\), in the Pr based compound the FM fraction increases as the temperature decreases below 80 K, and the insulator-metal transition is achieved when the fraction of the FM phase reaches the percolation threshold.\(^{20}\) As \(y\) approaches 0.41 from below, \(T_{im}\) is lower and the maximum of the MR curve is higher.\(^6\) We have studied the MR obtained by Eq. (2) as a function of the percolation temperature \(T_{im}\) by varying the relation \(\rho_{co}/\rho_{FM}\), which is a monotonous function of \(T_{im}\). The analytical description of this situation can be done within the following scheme: (i) At \(T_{im}\) the FM fraction is close to \(f_c = 0.17\),\(^{20}\) and is fixed by definition for all samples; (ii) the temperature \(T_{im}\) enters in the calculations through the ratio \(\rho_{co}/\rho_{FM}\), which can change several orders of magnitude as a function of temperature; (iii) at \(T_{im}\), the fraction enlargement \(\Delta f\) is the same for all samples, and it is only determined by the value of the magnetic field. In Fig. 3(b) we show the results corresponding to the MR values at \(T_{im}\) of different samples obtained from resistivity curves measured with \(H = 0\) and 0.4 T. The raw experimental data was extracted from Refs. 6 and 20, and the MR calculated as a function of \((\rho_{co}/\rho_{FM})^{1/2}\). The calculations were made taking into account that the maximum of the MR in Eq. (2) is obtained, for a fixed \(\Delta f\), when \(f = f_c - \Delta f/2\). The only free parameter in the calculations is \(\Delta f\), which was found equal to 0.054; this corresponds to a value of \(\alpha_f = 0.13\) \(^\circ\) \(T\) \(^{-1}\), although the relevance of this coefficient is not proved in \(La_{58-\delta}Pr_{\delta}Ca_{38}MnO_3\) compounds. The main fact to be noted is that only one parameter is sufficient to account for the MR at \(T_{im}\) through several orders of magnitude, the huge changes of MR being a consequence of the variation of the \(\rho_{co}/\rho_{FM}\) ratio as the percolation temperatures change. This can be taken as a clear indication on behalf of the role played by the magnetic field in PS systems.

V. CONCLUDING REMARKS

We have shown some important aspects concerning the effects of magnetic fields in PS systems. On one hand, we have presented evidence that even a low magnetic field has the capability of modifying the volume fractions of the coexisting phases in a field-cooling process. This effect seems
to be the one that drives the colossal magnetoresistance observed in these systems. On the other hand we have shown that the response of the system is highly dependent on the way in which the magnetic field is applied. The fact that the large values of MR are obtained only in FC experiments put strong restrictions to the use of PS systems in practical applications: magnetic devices taking advantage of the MR effect are actually exposed to processes like our magnetic field turn-on-turn-off experiment. In such a case, the MR response of the PS compound will be rather similar to that obtained in an homogeneous FM system, i.e., displaying values far away from being considered "colossal." Another interesting point related to the measurement methods we dealt with is the fact that, combining them, we can determine the onset temperature at which a system gets into the phase separated state.

Finally, using the fraction enlargement picture we have been able to account for the relation between the FM volume fraction and the MR in La$_{0.5}$Ca$_{0.5}$MnO$_3$, and between MR and $T_{im}$ in La$_{5/8}$Pr$_{3/8}$Ca$_{3/8}$MnO$_3$. In this scenario the fraction expansion coefficient $\alpha_f$ appears as the main parameter to characterize the PS systems, as it governs the interrelation between transport properties and magnetic fields. The interesting question arising from the last point is related to the dependence of $\alpha_f$ with some physical parameters, namely, $f$, $H$, and $T$. We obtained only partial information about that dependence in the PS systems mentioned here, although the similar values of $\alpha_f$ found in all them, with very different conditions with respect to $f$, $H$, and $T$, give some confidence on the physical entity of $\alpha_f$. Further experimental and theoretical work is indeed needed to corroborate this point.

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