Phase separation in polycrystalline $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$

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In this work we present electrical resistivity and magnetization (M) data as a function of temperature T and magnetic field H of polycrystalline $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ ($x = 0.1$ and 0.2). Within a large T range we have observed the coexistence of the ferromagnetic (FM) and charge-ordered antiferromagnetic phases. From the spontaneous magnetization in the $M(H)$ curves we obtained the fraction of the FM phase X_{FM}. We found that X_{FM} is ~20% at low T, and increases by increasing both T and H. Through a simple free-energy model driven by random disorder, we reproduce the T and H evolution of the phase-separation phenomena. We also show that a low-energy difference between the competing states is responsible for the dramatic effects that the disorder has on the physical properties.

In recent years, the coexistence of several magnetic phases, such as, for example, the charge-ordered antiferromagnetic (CO-AFM) state with a ferromagnetic (FM) metallic one has attracted great interest. This phenomenon is known as phase separation (PS).[1] Direct observations of nanometer sized FM clusters inside an AFM matrix and vice versa have been performed in transmission electron microscopy (TEM) experiments.[1,2] Some recent papers have associated the occurrence of PS with the existence of disorder that controls the size of the clusters.[3–8] This disorder could compensate a small energy difference between the competing states, inducing the formation of clusters of both phases.[9]

We focus our attention on those Mn perovskites that exhibit the coexistence of the FM and CO-AFM phases. It is known[2,10] that the fraction of FM phase increases with the magnetic field H, and in most cases increases with the temperature T. Moreover, it has been shown that a high enough field induces a metamagnetic transition from the mainly CO-AFM to the FM state.[11,12]

In particular, in $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ the complex competition between FM and AFM interactions is related to the increase of the bandwidth of the e_g electrons when the Ca atoms are replaced by Sr. At low T, the $Pr_{0.5}Ca_{0.5}MnO_3$ compound is a CO-AFM insulator with a CE-type spin arrangement.[13] In contrast, in the other limit the also AFM compound $Pr_{0.5}Sr_{0.5}MnO_3$ is A-type with a two-dimensional (2D) metallic band, and increasing T becomes FM metallic.[14] For the intermediate region, Damay *et al.*[15] have suggested the possibility of the coexistence of the FM and CO phases. Recently, in the $Pr_{0.5}Sr_{0.3}Ca_{0.2}MnO_3$ compound (our $x = 0.2$ sample), Savosta *et al.*[16] by NMR studies have found evidence of PS within the CO-AFM and in the FM phases.

Here we study the electric and magnetic properties of ceramic samples of $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ for $x = 0.1$ and 0.2. Through magnetization measurements we show that both samples present PS and we obtain the fraction of the FM phase. We describe the temperature and field evolution of the PS phenomena in the frame of a simple free-energy model driven by random disorder.

The sample preparation and characterization was described elsewhere.[14] Magnetization (M) data were taken in a commercial superconducting quantum interference device (SQUID) magnetometer with a 50-kOe magnet in the 5–300-K temperature range. Electrical resistivity (ρ) measurements were performed by the usual four probe method between 5 and 300 K with applied magnetic fields up to 9 T.

Figure 1 shows $M(H)$ data at several (increasing) T for both samples (similar curves were obtained decreasing T). It is evident the presence of a FM component at all temperatures, including below 200 K where the samples are in the CO-AFM phase.[14] Then, we conclude that this FM component is a clear signature of PS in this compound, so that the CO state is not a pure phase. Such a FM component inside the mainly CO state was also observed in other phase-separated manganites.[1,11]

Below 200 K the $M(H)$ curves present a remarkable hysteresis. At low fields, normal FM curves of the already mentioned FM component are observed. These curves tend to saturate, but at high fields the magnetization begins to increase more rapidly. This complex behavior is related to the
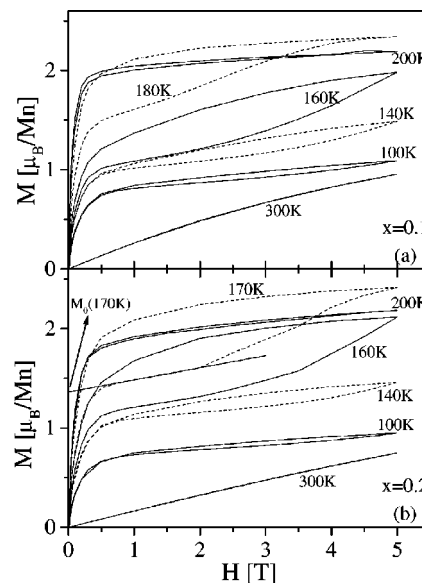

FIG. 1. $M(H)$ data at different temperatures for both samples, (a) $x = 0.1$ and (b) $x = 0.2$. The straight line in (b) shows an extrapolation to zero field to obtain $M_0(T)$.
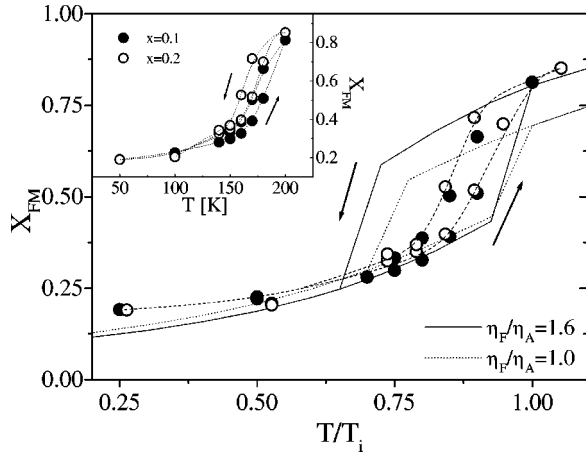
FIG. 2. FM phase fraction at $H=0$ vs T/T_i for the $x=0.1$ (●) and 0.2 (○) samples. Two lines were obtained from the free-energy model with different values of parameters. Solid line: $\eta_F = 0.96\Delta E_0$, $\eta_A = 0.60\Delta E_0$. Dotted line: $\eta_F = \eta_A = 1.2\Delta E_0$. In both cases $\gamma = 0.20\Delta E_0$. Inset: the same experimental data shown as a function of T. Dashed lines are a guide to the eye.

increase of the volume of the FM phase against the CO-AFM one.[11] When H is decreased from 5 T a wide hysteresis is generated until the low-field region is reached again. We name the temperature where the irreversibility disappears as T_i (200 and 190 K for the samples with $x=0.1$ and 0.2, respectively).

To quantify the FM component we have obtained the spontaneous magnetization $M_0(T)$ by extrapolating the $M(H)$ curves to $H=0$ T from the field increasing branch (see the example in the lower panel of Fig. 1). The AFM phase has zero spontaneous magnetization, thus M_0 is proportional to the fraction of the FM phase X_{FM}.

In the case that the whole sample were FM, the M_0 at very low T should be $3.5\mu_B$ (Mn^{3+} and Mn^{4+} ions in a 1:1 relation), and it should decrease with increasing T. On the contrary, as it is obvious in the curves of Fig. 1, M_0 increases with T. This feature undoubtedly demonstrates that also X_{FM} increases with T. To obtain X_{FM}, we have estimated the spontaneous magnetization M_{0FM} of a totally FM sample ($X_{FM}=1$). We obtained this estimation[17] from the Brillouin function using a saturated magnetization $M_s = 3.5\mu_B$. Then

$$X_{FM}(T) = \frac{M_0(T)}{M_{0FM}(T)}. \quad (1)$$

We note that although the Brillouin function is based on a mean-field approach, the qualitative behavior of X_{FM} (increasing with T) is not modified.

The resulting X_{FM} for $x=0.1$ and 0.2 as a function of T/T_i are shown in Fig. 2 (the inset presents the same data as a function of T). At low T the FM phase includes $\approx 20\%$ of the sample. The experimental observation of PS in charge-ordered manganites has been the subject of extensive studies. By neutron powder-diffraction[10,12] and NMR (Ref. 18) measurements, the FM fraction in other half doped polycrystalline manganites have been estimated as $\sim 20\%$ at low T, in

remarkable agreement with our magnetic estimation for the Pr$_{0.5}$Sr$_{0.5-x}$Ca$_x$MnO$_3$ samples.

It is important to note that although the way to obtain X_{FM} in the present paper is not direct, this simple procedure correctly reproduces the phase transition from charge ordering to ferromagnetism. This transition is related to the large increase of X_{FM} near T_i, and the observed hysteresis is generated by the first-order character of the transition. At low temperatures the CO state dominates, covering $\sim 80\%$ of the sample. We suggest that the minority FM phase is immersed in the CO-AFM matrix in the form of clusters, as observed before.[1] On the other hand, the high-T phase is dominated by the FM state [$X_{FM}(T_i) \approx 82\%$]. Therefore in this transition the FM phase must percolate, and consequently a simultaneous change in the resistivity should be observed. This is indeed the case, as we will show below.

Katsufuji et al.[3] showed that Cr impurities in the Mn site of charge-ordered manganites induce the appearance of FM clusters. They associated this effect with the random disorder introduced by the Cr atoms, that produces the clustering of the system.[9] In a recent paper, Moreo et al.[4] have also shown that the disorder induces PS in systems with two phases with similar free energies. This disorder could be related to some structural inhomogeneities, strain,[5] cationic disorder,[3,6] non-uniform oxygen distribution,[7] surface effects, or grain boundaries.[8] The effective action of the disorder is a randomness in the parameters that dominate the energies of the competing states, as, for example, the hopping energy t, the superexchange coupling, etc.

Several theoretical papers[19–21] considering different interactions leading to CO have been published. In all cases, the energy gain due to that interaction is comparable to the loss of kinetic energy ($\sim t$). In this condition, the energy difference between the FM and the CO states ($\Delta E_0 = E_{FM} - E_{CO}$) is expected to be small. This is in fact the result obtained in some recent papers,[20] where ΔE_0 was found as a small fraction of t. Considering the local Jahn-Teller (JT) distortions with a characteristic energy $E_{JT} \sim 2t$, in the CO state a gap $\Delta_{CO} \sim E_{JT}$ opens at the Fermi level.[21] With a Hamiltonian containing the JT distortions, similar to that used in Ref. 21, ΔE_0 can be estimated as $\sim 0.02t$ to $0.05t$ per Mn site, with $t \sim 0.2$ eV. These values imply that even when Δ_{CO} is as high as 400 meV, the energy difference between both states could be as small as 4 meV per Mn site, so that a critical field $H_c \sim 20$ T breaks the CO and transforms the sample to the FM metallic state. This low-energy difference provides a unique opportunity to the disorder to induce the appearance of PS. If ΔE_0 were much greater the effect of disorder would be negligible.

In order to describe the effect of the disorder we refer to a previous paper of Imry and Ma[9] to obtain a free energy of phases coexistence. In that paper, a $V^{1/2}$ dependence was stated for the energy gain of a given phase due to random fluctuations, where V is the volume of that phase. A domain-wall energy must also be included that in the Ising case has a $V^{2/3}$ dependence.[9]

Also a T dependence must be introduced, and for simplicity we have taken the difference in the free energies between the FM and CO phases as $\Delta E_0(1-\tau)$, where $\tau = T/T_0$ is a
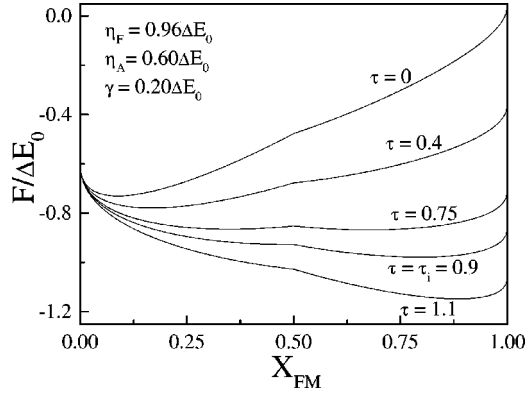
FIG. 3. Free energy vs FM phase fraction at different temperatures, containing the effect of random disorder.

reduced temperature and T_0 the transition temperature in the absence of disorder. Then, the simplest free energy for PS in zero field takes the form

$$F(X_{FM},T) = \Delta E_0(1-\tau)X_{FM} - \eta_F X_{FM}^{1/2} - \eta_A(1-X_{FM})^{1/2}$$
$$+ \gamma(0.5 - |X_{FM}-0.5|)^{2/3}, \quad (2)$$

where the parameters η_F and η_A represent the strength of the disorder that favor the FM metallic and the CO-AFM state, respectively. The last term gives the domain-wall energy, with strength γ, and is written in the simplest way to select the wall surface of the smaller volume. We note that the free energy of Eq. (2) does not imply charge segregation, as expected for half doped manganites with large clusters, in which the Coulomb energy would destroy the PS. It is clear that our phenomenological model is a very simple one, but the main features of the system are contained and we expect that the principal result of phases coexistence can be reproduced.

In Fig. 3 we show the F vs X_{FM} curves at several temperatures τ for a given set of parameters (indicated in the figure). As can be observed, even at $\tau=0$ the system presents a fraction $X_{FM}>0$. This state is not a metastable state; on the contrary, the system has only one minimum of F at $X_{FM}\approx 10\%$. Another important feature is the appearance of a second minimum at $X_{FM}>0.5$ when τ increases. This high X_{FM} state corresponds to the mainly FM (mFM) phase. Both minimums have the same energy at $\tau\approx 0.75$, indicating that a first-order phase transition takes place at this T, where the order parameter X_{FM} has a discontinuous jump. Of course, this transition exhibits hysteresis due to the energy barrier generated at $X_{FM}=0.5$, and the transition at $\tau=0.75$ should not be observed. An appreciable thermal hysteresis in the physical properties of the system is the expected behavior, as it was indeed observed in M and ρ vs T measurements.[2,8,10,16] The phase transition should be then characterized by the temperatures where the irreversibility disappears. In Fig. 3 it is shown that the temperature where the minimum at X_{FM} <0.5 disappears is $\tau_i\approx 0.9$ for this set of parameters.

From the $F(X_{FM})$ curves we obtained the FM fraction as a function of T as the position of the minimum of the free energy. The resulting X_{FM} vs T/T_i curves are plotted in Fig.

2 for two different sets of parameters, together with the experimental results. To obtain the hysteretic behavior we have taken the X_{FM} at $T=0$ and in the increasing T branch we have followed the position of that minimum of the free energy until it disappeared above T_i. For $T>T_i$ the X_{FM} value was extracted from the position of the second minimum. In the decreasing T branch, the position of this minimum was taken as the X_{FM} value, until again it disappeared at low T. Of course, near the irreversibility temperatures where the energy barrier at $X_{FM}=0.5$ is small enough, the thermal activation makes the system jump to the second (first) minimum before the first (second) minimum disappears, thus reducing the real hysteresis. However, even with this simple model the agreement between the experimental data and the calculated $X_{FM}(T)$ is quite fair.

Some relevant features are observed in Fig. 2. First, the data of the $x=0.1$ and $x=0.2$ samples collapse on a single curve when are shown as a function of T/T_i. Second, the energy provided by the disorder (η) to produce the PS is comparable to ΔE_0, the energy difference between the FM-metallic and the CO-AFM phases. The solid line in Fig. 2 was obtained with the same parameters values used in Fig. 3, where $\eta_F=0.96\Delta E_0$ and $\eta_A=0.60\Delta E_0$. In this way, the disorder can revert the energy difference between both states in some regions of the sample, thus producing the PS. Third, in our model the unbalanced disorder ($\eta_F>\eta_A$) produces an asymmetry between the low T and high T states. As the ratio η_F/η_A increases the X_{FM} above T_i also increases and is closer to 1, as shown by the solid curve in Fig. 2. Although a symmetric disorder is the simplest case, it does not seem to be a strong reason to assume this condition.

We have also investigated the effect of a magnetic field on the phase-separated state. In Fig. 4(a) we present $\rho(T)$ data for the $x=0.1$ sample (the results for $x=0.2$ are similar). For $H=0$ an insulator to metal transition appears at $T_C=268$ K, related to the paramagnetic (PM) to FM transition. On further cooling ρ shows a clear break, increasing abruptly below $T_{CO}\sim 185$ K. This temperature coincides with that T where X_{FM} changes notably (see Fig. 2). Above T_{CO} the predominating phase is the low-resistive FM one. On the other hand, below T_{CO} the CO-AFM state dominates, thus the resistivity exhibits a strong insulating behavior.

The charge-ordering temperature T_{CO} depends on the thermal process, presenting an appreciable hysteresis between the cooling and heating $\rho(T)$ curves in Fig. 4(a). The temperature where the irreversibility disappears and both curves collapse on a single one is labeled as $T_i(H)$ for each field. The $T_i(H=0T)$ remarkably coincides with that T_i where the system turns to the mFM phase and the $M(H)$ curves become reversible.

In the inset of Fig. 4(a) we show the magnetoresistance (MR$=[\rho(H)-\rho_0]/\rho_0$) vs H. These data also exhibit a wide hysteresis at $T<200$ K, being totally reversible above that T, as do the $M(H)$ data. The field $H_i(T)$ where the irreversibility disappears is indicated for each T. It can be noted that for $T<200$ K the MR is greatly increased, as shown by the $\rho(T)$ data at $H=9$ T. This behavior is related to the increase of the FM volume, thus at high fields a metamagnetic
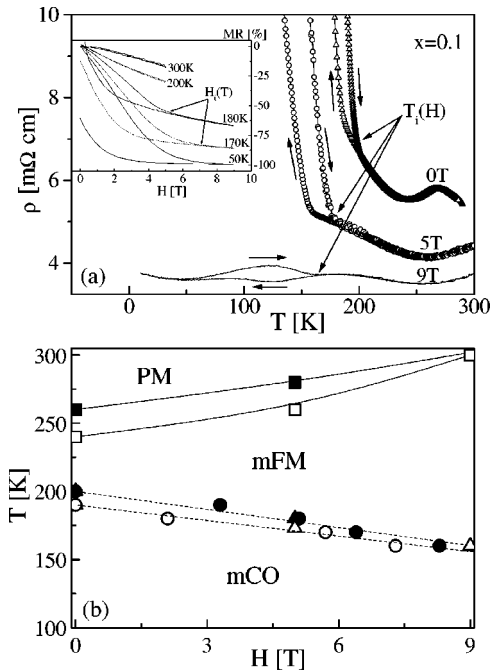
FIG. 4. (a) $\rho(T)$ curves at several H and magnetoresistance (inset) vs H at several T for the $x=0.1$ sample. (b) Phase diagram obtained from resistivity data. Filled and open symbols correspond to the $x=0.1$ and 0.2 samples, respectively. $T_C(H)$ (squares) and $T_i(H)$ (triangles) data were extracted from $\rho(T)$. The $H_i(T)$ data (circles) were obtained from $MR(H)$. The dashed lines indicate the phase boundary between the mainly CO-AFM (mCO) phase and the mainly FM (mFM) state, calculated from the free-energy model.

transition to the mFM phase takes place, where the high resistive CO-AFM state is replaced by the low resistive FM phase.

In Fig. 4(b) we present a T-H diagram that summarizes the resistivity results of both samples. From $\rho(T)$ we obtained the $T_C(H)$ (squares) that indicates the boundary between the PM and FM states. The triangles represent the

H-dependent temperatures where the irreversibility in $\rho(T)$ disappears [$T_i(H)$ in Fig. 4(a)]. By other way, from the MR(H) data, we extracted the fields $H_i(T)$ where also these curves become reversible (circles).

It is clear that both $T_i(H)$ and $H_i(T)$ describe the same phenomena. This boundary separates the mFM phase above the $T_i(H)$ line from the also phase-separated mainly CO-AFM (mCO) phase below it. To describe this boundary we have added to the free energy of Eq. (2) the magnetic term $F_m(X_{FM}, H) = -M_s H X_{FM}$. With this new term we obtained the irreversibility temperature as a function of H [the boundary $T_i(H)$]. This calculation is represented in the diagram of Fig. 4(b) with dashed lines. To reproduce the experimental results, we used the same parameters of Fig. 3 and the values $\Delta E_0 = 0.05t$ and $0.055t$ for the $x=0.1$ and 0.2 samples, respectively, and $t=0.2$ eV, in good agreement with the expected values.

In summary, in the $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ compound we observed the coexistence of the FM and CO phases. From magnetization measurements we estimated the FM fraction X_{FM}, being $\sim 20\%$ at low T, similar to other half doped manganites. By increasing T, the system presents a first-order phase transition to the mainly FM phase, generating an appreciable hysteresis in $X_{FM}(T)$ and in the electrical properties. The application of a magnetic field increases the FM volume, producing the high magnetoresistance exhibited by this compound in the low T (low X_{FM}) phase-separated state. Assuming cluster formation in our samples, as observed in other manganites, we construct a simple free-energy model containing the effect of random disorder. With this model we describe the temperature evolution of X_{FM} and the field-dependent boundary between the low and high X_{FM} states. In this frame, the only condition for the appearance of PS is that the competing states have to present a small energy difference that the disorder can counteract.

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