Coexistence of paramagnetic-charge-ordered and ferromagnetic-metallic phases in La$_{0.5}$Ca$_{0.5}$MnO$_3$ evidenced by electron spin resonance

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Throughout a complete electron spin resonance (ESR) and magnetization study of La$_{0.5}$Ca$_{0.5}$MnO$_3$, we discuss about the nature of the complex phase-segregated state established in this compound below $T \sim 210$ K. Between $T_N \leq T \leq T_C$, the ESR spectra shows two lines characteristic of two different magnetic phases. From the resonance field ($H_r$) derived for each line, we argue that the incommensurate-charge-ordering phase (ICO) which coexists with ferromagnetic–metallic (FMM) clusters in this temperature interval, is mainly paramagnetic and not antiferromagnetic. The FMM/ICO ratio can be tuned with a relatively small field, which suggests that the internal energy associated with those phases is very similar. Below $T_N$, there is an appreciable ferromagnetic (FM) contribution to the magnetization and the ESR spectra indicates the presence of FM clusters in an antiferromagnetic matrix (canted). Our results show that ESR could be a very useful tool to investigate the nature of the phase-separated state now believed to play a fundamental role in the physics of mixed valent manganites. © 2002 American Institute of Physics.

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I. INTRODUCTION

Since the possibility of an intrinsically phase-separated ground state in mixed-valent manganites was suggested by theoretical studies, much experimental effort has gone into determining the exact nature of this inhomogeneous state. As a consequence, although early work focused around the optimum doping level for $T_C$ of $x \sim 3/8$, present work is now moving toward $x \sim 1/2$, where the competition between these phases can be better studied. At the 1:1 Mn$^{3+}$:Mn$^{4+}$ composition, charge ordering (CO), that inhibits the electron transfer associated with double exchange-ferromagnetism in manganites, is particularly feasible, leading to a rich variety of charge/orbital ordered (CO/OO) structures.

For example, previous studies showed that, upon cooling, La$_{0.5}$Ca$_{0.5}$MnO$_3$ first becomes ferromagnetic (FM) at $T_C \sim 225$ K and then antiferromagnetic (AF) at $T_N \sim 155$ K (180 K upon warming). Its low temperature ground state shows a complex CO/OO-AF (CE-type) in which only anisotropic superexchange interactions, associated with Jahn–Teller (JT) distorted Mn$^{3+}$O$_6$ octahedra, are active. Couplings along the [001] direction are AF, while in the (001) plane Mn$^{3+}$–O–Mn$^{4+}$ superexchange is FM (AF) when the occupied (unoccupied) $e_g$ orbitals are directed toward empty Mn$^{3+}$–$e_g$ orbitals. Neutron powder diffraction revealed two different coherence lengths for the two interpenetrating Mn$^{3+}$–Mn$^{4+}$ magnetic sublattices in the CE structure, which implies the presence of structural/magnetic domain boundaries associated with the CO domain boundaries observed by electron diffraction. On the other hand, x-ray synchrotron and electron diffraction experiments showed that the first-order AF transition at $\sim 150$ K is associated with an incommensurate-to-commensurate-CO transition (ICO-to-CCO), and that ICO and FM do coexist between 160 K $\leq T \leq 210$ K as a finite spatial mixture of two competing phases (mutually exclusive). Moreover, the simultaneous presence of multiple phases (their relative proportion varying with temperature) with different degrees of orientational order of the JT distorted Mn$^{3+}$O$_6$ octahedra, has been demonstrated in this transition region. All these experiments show the extreme complexity of the magnetic/orbital structures in La$_{0.5}$Ca$_{0.5}$MnO$_3$, and demonstrate that much more work is still needed for a deep understanding of the mixed-phase state in manganites.

To investigate the nature of the magnetic phases in La$_{0.5}$Ca$_{0.5}$MnO$_3$ at different temperatures, we carried out a detailed electron spin resonance (ESR) study in a broad temperature interval. The ESR technique is very sensitive to magnetic heterogeneity, even if it involves a relatively small number of spins. Here, we argue that the ICO is associated with a paramagnetic (PM) structure, which coexists with ferromagnetic–metallic (FMM) regions. The ratio FMM/ICO-PM is strongly field dependent, even for relatively small fields ($\sim 0.5$ T).

II. EXPERIMENT

Ceramic samples used for this study were synthesized by solid state reaction. Room temperature x-ray diffraction pat-
terns indicate that the samples are single phase (orthorhombic, \textit{Pnma}). Lattice parameters derived from Rietveld analysis ($a = 5.4241(5)$ Å, $b = 7.6479(1)$ Å, and $c = 5.4353(1)$ Å) are in perfect agreement with available data. 15 ESR measurements were performed at 9.4 GHz (X-Band) with a EMX Bruker spectrometer between 100 and 400 K. A small quantity of sample (~1 mg) was used for ESR experiments in order to avoid overloading of the cavity. Magnetization (versus temperature and field) was measured in a superconducting quantum interference device magnetometer.

III. RESULTS AND DISCUSSION

In Fig. 1(a), we show the thermal evolution of the magnetization measured on warming and cooling at 3.3 kOe (the resonance field for a free electron at X-Band, in order to compare it with ESR data). The strong thermal hysteresis (~30 K) resembles the first-order character of the transition. On the other hand, a sudden increase of resistivity (not shown) is also observed at $T_N$, indicating the appearance of CO associated to the AF structure. 16

Above $T_C$, the ESR spectra consist of a single Lorentzian line centered at $g = 2.00$ independent of temperature [Figs. 1(b) and 2]. As a function of $T$, both ESR linewidth and intensity showed a behavior similar to that described for other manganites in the paramagnetic state: the linewidth decreases with temperature on approaching $T_C$ from above, goes through a minimum at ~1.1 $T_C$ and increases again.17,18 The intensity follows a Curie–Weiss law in this regime, i.e., all the spins contribute to ESR.

In Fig. 2, we show some ESR lines, representative of the general behavior in the different temperature intervals. When reducing temperature below ~215 K, the spectra split in two lines [low field, (LF); and high field, (HF), lines] that are observable down to ~160 K where the long-range AF develops ($T_N$).

Below this temperature, a single (apparently) broad line is recovered with a significant increment of the resonance field. When the ESR spectrum is recorded increasing temperature, the broad line characteristic of the low temperature AF phase is maintained up to ~170 K, following the hysteric behavior observed in $M(T)$.

We have fitted the ESR spectra keeping the resonance field ($H_r$), the linewidth, and the intensity of each line (when more than one line is employed in the fitting procedure) as adjustable parameters. Some of these fits are shown in Fig. 3. Above $T_C$, the ESR spectra can be successfully reproduced with a single absorption line (Lorentzian). On the other hand, as mentioned, between $T_N$ and $T_C$ the spectra splits in two lines, (LF and HF) characteristic of two magnetic components, their relative proportions varying with temperature. Below $T_N$, a single line is recovered, but only apparently, as again two lines are needed to reproduce the experimental data. When three or more lines were employed to fit the ESR spectra, the goodness of fit does not improve, demonstrating the validity of our fits with two lines in this temperature range. Between 150–160 K only, the presence of three different phases can not be discarded from our data. In fact, Radaelli et al. 8 suggested the possibility of four different
values of resonance condition for a fixed frequency is reached at lower FM region, the internal field adds to the applied field and the T_N ropy constant and M_S order approximation yields a system of randomly oriented and noninteracting spherical magnetic resonance and effective internal field (H_r). This effect of applied external field. In Fig. 4 magnetization iso-

therms are shown at different temperatures. Between T_C and T_N, the slope of the M(H) curves increases at a critical field of ~0.5 T. The sudden increase in the magnetization marks the increasing volume fraction of the FM phase as the ICO-PM phase is melted by the applied field. This effect increases the number of free carriers (via itinerant de Gennes double exchange)\(^{21}\) and hence produces a diminution of the resistivity. To check this hypothesis, we measured the magneto-resistance (MR) at different temperatures (Fig. 5). It is clear from the large values obtained between T_C and T_N that the metallic fraction is nicely increased by a small applied field in this temperature interval, while only small values of MR are reached below T_N. In fact, Roy et al.\(^{22}\) previously found an appreciable MR for H=all Oe in La_{1-x}Ca_{x}MnO_3 with Mn^{4+}~52.8%-53.2%. Iodometric analysis in our samples gave Mn^{4+}~51.4%, which coincides satisfactorily well with their results.

Extrapolating to H=0 from the initial magnetization curves before the critical field and comparing with the theoretical FM value of 3.5 \(\mu_B\) for Mn^{3+}/Mn^{4+}=1, we have obtained the fraction of the FMM phase at H=0 and its temperature dependence (Fig. 6). From the values of M(H=1 T), it follows that the percentage of FM phase increases dramatically with applied field between T_C and T_N, leading to the large values of MR at relatively small fields here presented. The relative fraction of the FM phase extracted from ESR experiments is also proportional (no absolute values were obtained) to those from M(H), at least between T_C and T_N.

FIG. 4. Field dependence of the magnetization of La_{0.5}Ca_{0.5}MnO_3 between T_C and T_N (main panel). There is a critical field around 0.5 T which produces a sudden increase of magnetization. Inset: well above T_C, the expected linear (PM) behavior is observed, while the curves below T_N indicate the presence of a net magnetic moment in the AF phase.

FIG. 5. Magnetoresistance at different temperatures. Note the large values of MR obtained between T_C and T_N, where the effect of the applied field over magnetization is stronger. The large hysteresis and the anomalies in the R(H) curves reproduce the M(H) behavior.

FIG. 6. Experimental percentage of the FM phase obtained from M(H) (\(\bullet\)). Data from ESR experiments (\(\circ\)) are also plotted to show the proportionality with magnetic data, although we could not get absolute values from the ESR experiments.
It is clear that even in the low temperature AF state, there is a FM contribution to the magnetization which is about 3% of the full FM moment at \( H = 0 \). To elucidate whether this ferromagnetism comes from a canted AF state or from small metallic clusters embedded in the AF matrix, we have studied the ESR spectra at \( T < T_N \).

Below \( T_N \), the broad ESR lines can be decomposed as the sum of two independent lines (see Fig. 3) one at \( H \approx 3100 \text{ Oe} \) and other that varies from \( H \approx 4150 \text{ Oe} \) at 150 K to \( H \approx 4750 \text{ Oe} \) at 100 K [Fig. 1(b)]. The line at LF indicates the presence of FM clusters even at these low temperatures, in a similar configuration as it was recently suggested for \( \text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3 \) by \(^{55}\text{Mn} \) and \(^{139}\text{La} \). On the other hand, as we have indicated in the introduction of this article, the low temperature ground state in \( \text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3 \) is AF. Normally, AF resonance is observed at very high frequencies, around 100 GHz or more, far beyond the resonance frequencies used in this experiment, and hence no line should be observed at 9.4 GHz. However, in the Pnma structure, the oxygen atoms that mediate the interaction between Mn ions do not occupy inversion symmetry centers of the crystal, due to the cation of MnO$_4$ octahedra. In this situation, antissymmetric superexchange interaction (Dzialoshinsky–Moriya coupling) between Mn produces spin canting and the appearance of a weak ferromagnetic moment. In this situation, two nondegenerate resonance modes appear, one at very high frequencies (not observed in our experiments at 9.4 GHz) while the other one will occur at ordinary microwave frequencies, and can be considered similar to a ferromagnetic mode. For this reason, the resonance observed at high fields below \( T_N \) can be attributed to the weak ferromagnetic component. The fact that the line is observable in the AF state is an indication of the existence of canting between antiparallel sublattices.

Let us now compare our experimental findings with recent theoretical results about phase separation in \( x = 0.5 \) manganites. Yunoki et al. obtained the magnetic phase diagram for \( x = 0.5 \) as a function of electron–phonon coupling (\( \lambda \)) and \( J_{\text{AF}} \) spin exchange. For intermediate values of \( \lambda \), as it is the case for \( \text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3 \), their results indicate the of CO and FM phases in an intermediate temperature range. [see Figs. 3(b) and 3(d)] in Ref. 23. Moreover, the CE-AF structure is developed at lower temperatures, when the CO is well established, then supporting our hypothesis of an intermediate CO-PM state between \( T_C \) and \( T_N \). A systematic study of a \( A_2B_{1.5}\text{MnO}_3 \) series covering a wide \( (\delta_A) \) interval, and hence a \( J_{\text{AF}} \) range, will be very useful to elucidate the nature of the phase separation mechanism in half doped manganites, as well as the different phases implicated.

### IV. CONCLUSIONS

In summary, we have demonstrated that the magnetic structure of the incommensurate CO state stabilized between \( T_N \) and \( T_C \) in \( \text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3 \) is PM and not AF. This ICO state can be melted by an external applied field (\( \sim 0.5 \text{ T} \)) that grows the FM regions and increases the number of free carriers, leading to considerable values of MR. On the other hand, ESR and \( M(H) \) at \( T < T_N \) indicate that the low temperature AF state in \( \text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3 \) is also inhomogeneous. Our results are in perfect agreement with recent theoretical estimations. Finally, ESR is presented here as a useful tool to investigate the magnetic structure of the phase-separated state in manganites.

After submission of this article, we performed resistivity, thermoelectric power, and thermal expansion experiments in \( \text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3 \). The results indicate that the FM/CO-PM phases between \( T_C \) and \( T_N \) are hole-poor (\( x \approx 0.4 \)) conductive clusters and a hole-rich matrix, respectively. The conductivity in the matrix (with larger Mn–O bond lengths) takes place through thermal activation of small polarons. These results will be present in another article.  

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24. From resistivity data, and with \( \epsilon_R \approx -1.5 \text{ eV} \), we have derived a value of \( \lambda \approx 3.4 \) for \( \text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3 \).