First Order Nucleation of Charge Ordered Domains in $La_{0.5}Ca_{0.5}MnO_3$ Detected by ^{139}La and ^{55}Mn NMR

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The local magnetism and charge ordering of $La_{0.5}Ca_{0.5}MnO_3$ was investigated between room temperature and 1.3 K by means of ^{139}La and ^{55}Mn NMR. Antiferromagnetic and ferromagnetic domains are assigned unambiguously to the insulating charge ordered and the metallic state respectively. The phases are found to coexist at all temperatures below the first formation of a charge-ordered state. The two signal fractions display thermal and magnetic hysteresis, while their local fields and relaxations do not. These features and the absence of any critical behavior are characteristic of a first order F-AF transition, with ferromagnetic domains microscopically identical to the bulk metallic phase of the OMR manganite. [S0031-9007(98)07678-9]

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Lanthanum manganites $La_{1-x}A_xMnO_3$ (A = alkali-earth metal) have attracted increasing interest in recent years since the discovery of a *colossal* magnetoresistance (CMR) in suitably substituted members of this family (around $x = 0.3$) [1], and, more generally, due to their intriguing magnetic and transport properties. Substitution of La leads manganese ions to a mixed valence state Mn^{3+x}, or, equivalently, to the injection of holes into the valence band; as a consequence, the ground state of the compound is driven from insulating A-type antiferromagnetism [2,3] (according to Goodenough's nomenclature) in the stoichiometric compound, to metallic ferromagnetism at the optimum doping for CMR. In the $La_{1-x}Ca_xMnO_3$ series, however, as the fraction x of substituted ions approaches $1/2$, electronic correlations drive a second transition from the metallic to an insulating, charge ordered (CO) state below the temperature T_{CO}, with Mn^{3+} and Mn^{4+} ions localized on two distinct sublattices [4,5]. The metallic ground state is restored by a very strong applied field, which makes the delocalization of the electrons energetically more favorable; this may be viewed as another regime of CMR. The magnetic order in the charge ordered state has been shown to be CE-type antiferromagnetic [2,3]. Nevertheless, both magnetometry [6,7] and neutron diffraction [2] detect a weak ferromagnetic moment of a fraction of Bohr magneton per ion in the charge ordered state, which could be explained either within a homogeneous model (e.g., a canted state) or by a phase separation into an inhomogeneous state.

In this Letter, we present an investigation of the magnetism of $La_{0.5}Ca_{0.5}MnO_3$ by means of ^{139}La and ^{55}Mn NMR. The sample was obtained as sintered powders by solid reaction at 1200 °C of La_2O_3, $MnCO_3$, and $CaCO_3$, weighed in stoichiometric amount, and subsequent annealing in air at 1350 °C; the mean valence of Mn was determined by iodometric titration, yielding $x = 3.51 \pm 0.01$. The details of sample preparation and characterization are described elsewhere [8]. NMR experiments were performed both in zero field (ZF) and in the applied field of a superconducting solenoid ($\mu_0 H$ up to 7 T); radio-frequency (rf) susceptibility was measured by means of a Hewlet Packard impedance bridge and a coil.

Magnetic resonance of both nuclei constitutes a local probe of magnetization, since the nuclear spins are coupled to the surrounding electronic moments by the hyperfine interaction (we neglect the comparatively small dipolar fields). The local field experienced by the nuclear spin of isotope $\alpha = 55\,139$ has the form

$$\mathbf{B}_i^{\alpha} = \frac{2\pi}{{}^{\alpha}\gamma}\, g\mu_B \left[\mathcal{A}_i^{\alpha} \langle \mathbf{S}_i \rangle + \sum_j \mathcal{B}_j^{\alpha} \langle \mathbf{S}_j \rangle \right] + \mu_0 \mathbf{H} . \quad (1)$$

Here $\langle \mathbf{S}_i \rangle$, $\langle \mathbf{S}_j \rangle$ are the on-site and nearest-neighbor electron spin ($\langle \mathbf{S}_i \rangle = 0$ for La), $\mathcal{A}_i^{\alpha}$, $\mathcal{B}_j^{\alpha}$ are their respective hyperfine couplings, ${}^{\alpha}\gamma/2\pi = 6.014$ and 10.5 MHz/T for ^{139}La and ^{55}Mn, respectively, are the gyromagnetic constants, and $\mathbf{H}$ is the external field. In agreement with experimental results from manganites with lower Mn valence [9,10], we assume isotropic couplings ($\mathcal{A}, \mathcal{B}$ are scalar), independent of the small structural changes at the CO transition.

We shall denote resonances of nuclei from ferromagnetically or antiferromagnetically ordered domains by a superscript F or AF, respectively. They are easily distinguished experimentally. First, both La^F and Mn^F signals show the typical ferromagnetic enhancement, an amplification

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of the applied radio-frequency field H_1 at the nucleus owing to its coupling with the electronic magnetization, and a corresponding amplification of the signal induced in the probe coil [11]. The rf power required for the maximum echo signal provides a measure of this enhancement. The second distinction between AF and F resonances is based on Eq. (1). ^{139}La has eight equal transferred couplings $\mathcal{B}_j^{139} = \mathcal{B}^{139}$ with the nearest Mn neighbors. The transferred fields cancel in the AF domains, and since the same holds for the electric field gradient in the nearly cubic symmetry of the La site, the La^{AF} signal is not observable in zero field. The zero-field La^{F} signal, in contrast, is found at $\nu_F(H = 0) \approx 8g\mu_B|\mathcal{B}^{139}|\langle \mathbf{S} \rangle$. In an applied field the La^{AF} resonance occurs close to the Larmor frequency appropriate to the external field, $\nu_A(H) \approx {}^{139}\gamma\mu_0 H/2\pi$, whereas the La^{F} resonance is shifted by $\nu_F(0)$, since the hyperfine coupling is isotropic, hence the local field is collinear to the external field [12]. On ^{55}Mn, on the other hand, the on-site hyperfine coupling $\mathcal{A}^{55}\langle \mathbf{S} \rangle$ is by far the dominant contribution to the local field. Thus, zero field AF and F resonance lines occur at comparable frequencies. An external field shifts the Mn^{F} resonance frequency by $-{}^{55}\gamma\mu_0 H/2\pi$ as $\mathcal{A}^{55}$ is isotropic and the Mn spin aligns with the field [9]. The Mn^{AF} line broadens without shift owing to the vector composition of the randomly directed hyperfine field with the much smaller external field.

Zero-field spectra of ^{139}La, recorded at several temperatures [13], are shown in Fig. 1a. All of these spectra have a large ferromagnetic enhancement, roughly constant for $T < T_C$, which allows a quantitative comparison of their NMR intensities at different temperature. The spectra consist of a single inhomogeneously broadened peak centered at frequencies ranging from approximately 14 MHz at 210 K to 21 MHz at 90 K. The observation of a signal implies that $T < T_C$ for all of the spectra. The position and width of the lines coincide with those detected in the fully ferromagnetic CMR compound $La_{0.7}Ca_{0.3}MnO_3$ [10,14]. This coincidence suggests that the Mn moments are in the full ferromagnetic state at all of these temperatures. The signal falls below the instrument sensitivity approaching T_C at $T > 210$ K. The mean precession frequency $\nu_F(H = 0)$ is proportional to the local moment $\langle S \rangle_T$ and *increases* monotonically for $T \to 0$ throughout the whole temperature range (Fig. 2a). The frequency, still high at 210 K, in contrast with the greatly reduced amplitude, indicates that the local moments build up discontinuously in a first order transition. A first order transition to the ferromagnetic metal was observed also at lower doping by Savosta *et al.* [15] in $Pr_{0.7}Ba_{0.3}MnO_3$.

The ZF NMR *amplitude* decreases rapidly below T_{CO}, the temperature corresponding to the charge ordering transition (Fig. 2b). Note that this transition does not influence the line position. The rf susceptibility χ'_{rf} as well as the NMR intensity exhibit a marked thermal hysteresis below T_C (Fig. 2b); for this reason all reported NMR experiments

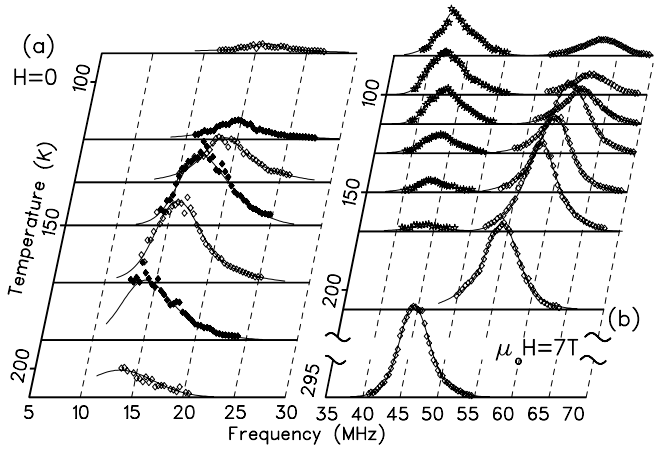

FIG. 1. ^{139}La spectra from $La_{0.5}Ca_{0.5}MnO_3$ at several temperatures. The intensities have been corrected for the nuclear Boltzmann factor and for the NMR sensitivity. (a) La^{F} zero-field spectra at $T < T_c$. (b) 7 T ZFC and spectra of La^{AF} (stars) and La^{F} (diamonds) in a temperature interval including $T_C \approx 230$ K and $T_{CO} \approx 150$ K.

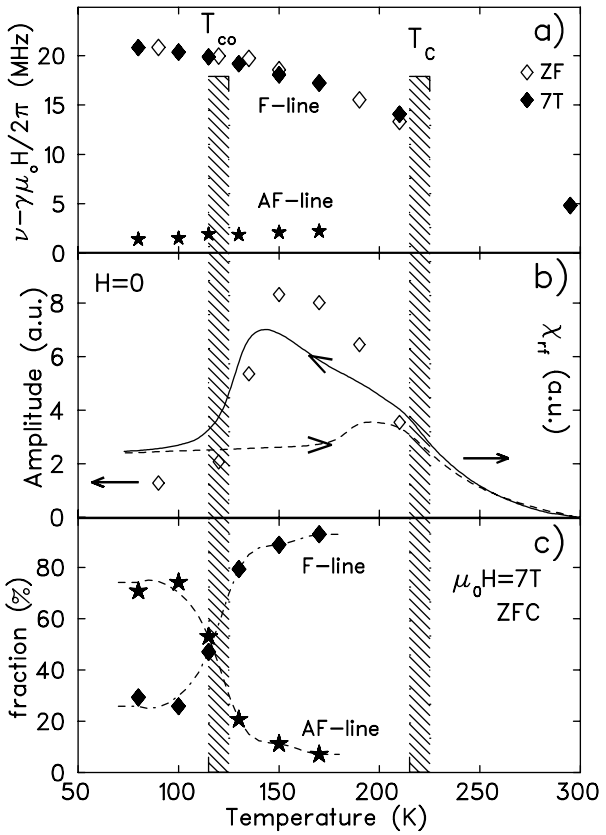

FIG. 2. (a) Mean frequency shift of the La^{AF} and La^{F} resonance lines in zero field, and in 7 T with respect to the external field resonance frequency $\mu_0 H = 42.08$ MHz. (b) Filled symbols: integrated amplitude $I(T)$ (see the text) of the zero field La^{F} spectra, as a function of temperature. For comparison, the rf susceptibility curves recorded in cooling (solid line) and warming (dashed line) are also plotted. (c) Relative integrated amplitudes of the two 7 T ZFC La peaks as a function of temperature.

were carried out by *cooling* the sample to the operation temperature. $I(T)$ and $\chi'_{\rm rf}(T)$ are both related to the ferromagnetic volume fraction in the sample, and their cooling behavior in the figure shows good qualitative agreement, including the drop at $T_{\rm CO}^{\rm rf} \leq 150$ K.

The hysteresis below T_C and the fact that the size of the local moments is unchanged at $T_{\rm CO}$ are strong evidence that the charge ordering is also a first order transition, the hysteresis being due to a phase coexistence below T_C. To further clarify this conclusion we turn to the ^{139}La resonance in field. We recall that observation of the La$^{\rm AF}$ signal requires a large applied magnetic field. The spectra plotted in Fig. 1b were recorded in an external field of 7 T, applied after zero-field cooling (ZFC): in this way the insulating charge ordered phase is preserved at low T. Below $\approx$170 K they consist of two distinct peaks: one centered at $\nu_F(H) = {}^{139}\gamma\mu_0 H/2\pi + \nu_F(0)$, where $\nu_F(0)$ coincides with the resonance frequency in zero field (see Fig. 2b), and one at $\nu_A(H) \approx {}^{139}\gamma\mu_0 H/2\pi = 42.08$ MHz. From the discussion of Eq. (1) it is clear that the former originates in a ferromagnetic and the latter in an antiferromagnetic phase [16].

The properties of the La$^{\rm F}$ line are nearly unchanged by the external field: The intensity drops below $T_{\rm CO}$ and the mean frequency is shifted according to ${}^{139}\gamma H$, showing that the coupling constant $\mathcal{B}^{139}$ in the ferromagnetic phase is positive and $\mathcal{B}^{139} \approx 2.7$ MHz/Mn moment. In Fig. 2a we plot, in addition, the *decrease* of the frequency shift $\delta\nu_A = \nu_A - {}^{139}\gamma\mu_0 H/2\pi$ with temperature. The shift is proportional to a powder average of the AF susceptibility $\bar{\chi}^{\rm AF}$ ($\delta\nu_A = 8\mathcal{B}\bar{\chi}^{\rm AF}H/nS$), consistent with $\chi_\perp^{\rm AF}$ constant and $\chi_\parallel^{\rm AF}$ increasing with T. The highest temperature value agrees with this expression, if one assumes $T_N \approx 200$ K and a Curie constant larger by a factor of 3 than the single ion value $C_0 = (g\mu_0)^2 S(S+1)/3k_B$. A large Curie constant was also measured from ^{139}La NMR on other manganites [10].

The two peaks at ν_A and ν_F actually coexist throughout most of the magnetically ordered state, showing that the inhomogeneous phase mixture discussed above is present in 7 T ZFC experiments as well as below 170 K. The relative amplitudes of the two resonance lines in 7 T are plotted in Fig. 2c as a function of temperature, showing a continuous growth of the AF phase below 170 K from a minority phase in a ferromagnetic matrix to a majority phase with a small ferromagnetic volume fraction at 110 K and below. Note that the minority antiferromagnetic fraction at 170 K would be difficult to detect by other techniques.

The ratio of the integrated amplitudes of the antiferromagnetic and the ferromagnetic phase, $R = I_A/I_F$, depends strongly on thermal history. For instance, FC vs ZFC yields $R = 0.1$ vs $R = 3$; furthermore, a ZFC cycle 150 $\rightarrow$ 80 $\rightarrow$ 150 K enhances the AF amplitude by a factor of 2. This hysteretic dependence of the resonance amplitude on thermal and magnetic history indicates that the coexistence of phases is not due to chemical inhomogeneity of the samples but to a phase equilibrium in a first order transition.

^{55}Mn NMR confirms that the two phases coexist in the ground state as well. The ^{55}Mn spectrum at 1.3 K in zero field, shown in Fig. 3, consists of two signals. They are distinguished by their behavior in an external field and by their enhancement [17].

The Gaussian peak at 380 MHz is attributed to Mn$^{\rm F}$, since this signal exhibits the large enhancement appropriate to ferromagnets, and it is shifted in the field according to the full gyromagnetic ratio of ^{55}Mn, as predicted by Eq. (1) for $\langle \mathbf{S} \rangle \parallel \mathbf{H}$ (Fig. 3a). The rest of the signal, consisting of a peak at 310 MHz and a broad background from 270 to 400 MHz, is attributed to Mn$^{\rm AF}$, as it does not show significant enhancement and the main peak at 310 MHz is broadened but unshifted in an applied field (Fig. 3a). Comparison with NMR of the related compounds $LaMn_{0.5}Ni_{0.5}O_3$ [18] and $Pr_{0.7}Ba_{0.3}MnO_3$ [15] indicates that this Mn$^{\rm AF}$ peak is to be ascribed to the nuclei of localized Mn^{4+} ions. We can, therefore, associate antiferromagnetism with charge ordering. The corresponding peak from Mn^{3+} ions in the AF-CO environment should fall in the range 370–400 MHz [19], where the broad and largely enhanced Mn$^{\rm F}$ peak prevents its observation. The small shoulder of the Mn$^{\rm F}$ line near 360 MHz, which is unshifted by the field, may be associated with this signal. A very similar spectrum is observed at slightly higher doping in $La_{0.47}Ca_{0.53}MnO_3$ (Fig. 3b). This compound should be fully AF-CO, according to a homogeneous picture, but a sizeable F fraction is present here as well, suggesting that the phase separation takes place not only down to Ca concentrations $x \approx 0.3$ [15] but also to well above $x = 0.5$.

Coexistence of the AF phase with minority F domains was also observed in $LaMnO_3$, where the nanoscopic nature of the F clusters was revealed by strong cross relaxation effects between different ^{55}Mn NMR signals [9],

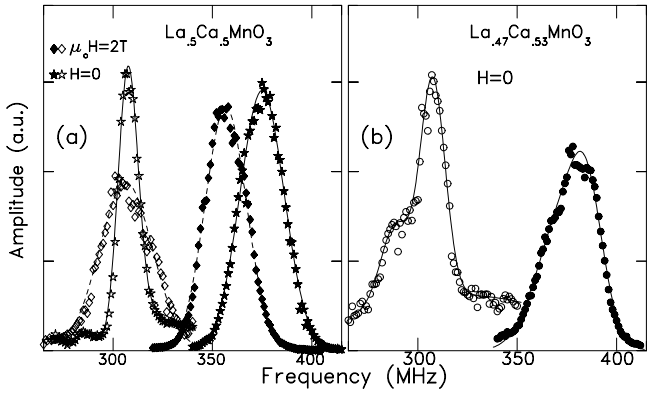

FIG. 3. ^{55}Mn NMR spectra at 1.3 K of $La_{0.5}Ca_{0.5}MnO_3$ (a) and of $La_{0.47}Ca_{0.53}MnO_3$ (b) in a zero and in an applied field. The spectra have been rescaled in amplitude by arbitrary factors. Ferromagnetic lines are marked with filled symbols; antiferromagnetic ones are marked with open symbols.

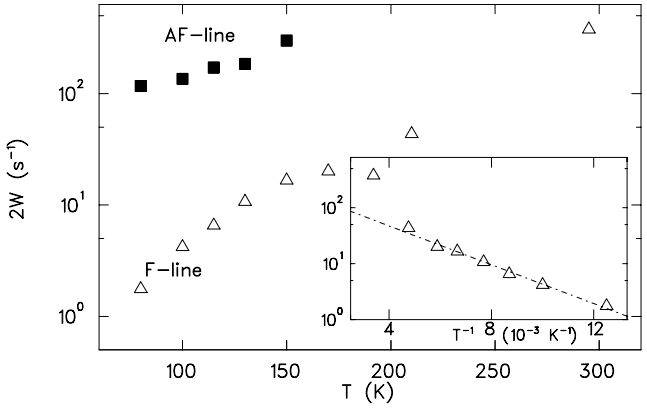

FIG. 4. ^{139}La spin-lattice relaxation rates of $La_{0.5}Ca_{0.5}MnO_3$ in 7 T for the two resonance lines, as a function of T. Inset, the Arrhenius plot for the F relaxations.

and by recent neutron scattering experiments [20]. In the present case, however, we see no evidence for a significant direct coupling between the two phases. In addition, the sum of the intensities of the two La peaks in 7 T, $I_{\mathrm{AF}} + I_{\mathrm{F}}$, is constant with temperature and thermal cycles, which indicates that the fraction of nuclei in AF-F domain walls is negligible. Furthermore, all of the intensive NMR observables (frequencies, line widths, and relaxation rates) are continuous across T_{CO} and show no thermal or magnetic hysteresis. This suggests *mesoscopic* rather than nanoscopic AF and F domains in $La_{0.5}Ca_{0.5}MnO_3$.

Finally, we briefly discuss the La spin-lattice relaxation (SLR) and spin-spin relaxation (SSR). The temperature dependence $2W_F(T)$ of the SLR in 7 T is plotted in Fig. 4, together with $2W_A(T)$. The rates are determined by a fit to a multiexponential Redfield recovery law [21], although the fit is perfectly satisfactory only for F relaxations. The F rate follows an activated law $2W_F \propto \exp(-\theta/T)$ for $T < T_c$. The activation temperature $\theta = 400$ K is considerably higher than T_c. There clearly is an additional contribution to the relaxation above T_C, but no indication of a critical behavior at T_{CO}. The temperature dependence of the SSR is consistent with that of the SLR. Relaxations of the AF line, on the other hand, are faster by orders of magnitude, they display a less pronounced dependence on temperature, and they are nonexponential. Notably, La^{F} relaxations in $La_{0.5}Ca_{0.5}MnO_3$ follow the same functional dependence on temperature as in metallic manganites [10]. Such a behavior, on the other hand, is quite different from those observed both in the AF phase of this compound and in the undoped AF manganite $LaMnO_3$ [10]. This provides strong evidence that the F domains are microscopically equivalent to the metallic bulk.

In conclusion, an electronically driven phase separation, taking place continuously with respect to temperature, magnetic field, and composition, has been demonstrated in $La_{1-x}Ca_xMnO_3$ in the vicinity of $x = 0.5$. This suggests that the sharp metal-insulator transition observed at T_{CO} [4] is due to a crossing of the percolation threshold by metallic F domains.

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