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# NMR Probe of Phase Segregation in Electron Doped Mixed Valence Manganites

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A $^{55}$Mn and $^{139}$La NMR study of $La_{0.35}Ca_{0.65}MnO_3$ is reported. The zero field $^{55}$Mn spectra consist of two lines centered at 290 and 375 MHz. Their behavior under an applied magnetic field makes it possible to attribute them to regions of antiferromagnetically and ferromagnetically coupled Mn spins, respectively. This gives evidence for the existence of electronic phase segregation of microscopic ferromagnetic regions of double exchange coupled Mn spins over a charge ordered antiferromagnetic background. The behavior of these ferromagnetic regions in the applied magnetic field is related to the magnetoresistive properties of the manganites.

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A great deal of renewed interest in mixed valence manganites has recently been brought about by the extraordinary magnetoresistive properties exhibited by many compounds of the $La_{1-x}Ca_xMnO_3$ perovskites, called colossal magnetoresistance (CMR). The effect occurs mostly in the vicinity of a magnetic ordering temperature which is usually also the temperature of an insulator-to-metal transition. The decrease of electrical resistivity in an applied magnetic field can be as large as 3 orders of magnitude [1]. Although the magnetic properties of the compounds have been studied experimentally and theoretically since the early 1950s [2–4], it was only recently that their microscopic magnetic properties could be understood and a reasonable theoretical description of the CMR effect could be given.

The magnetic phase diagram of the $La_{1-x}Ca_xMnO_3$ system has been reported in [5,6]. In the low Ca doping region, $x < 0.2$, the compounds are antiferromagnetic and insulating, owing to the superexchange interaction between the $Mn^{3+}$ ions. For $0.2 < x < 0.5$ the compounds exhibit ferromagnetism and a metallic conductivity owing to the double exchange (DE) interaction between $Mn^{3+}$ and $Mn^{4+}$ ions. The $Mn^{4+}$ ions are generated by the substitution of a divalent alkaline earth for trivalent lanthanum which corresponds to the creation of holes at the $Mn^{3+}$ sites (hole doping). In the high doping regime, $0.5 < x < 1$, the superexchange interaction $Mn^{4+}$-$Mn^{4+}$ and $Mn^{3+}$-$Mn^{3+}$ prevails and the compounds are antiferromagnetic and insulating. The compound $La_{0.35}Ca_{0.65}MnO_3$ exhibits charge ordering below $T_{CO} = 275$ K and antiferromagnetism below $T_N = 160$ K [7]. The recent neutron study of $La_{0.33}Ca_{0.67}MnO_3$ has shown that the antiferromagnetic structure is noncollinear and the charge ordering is of Wigner crystal type rather than stripe domainlike [8].

Nuclear magnetic resonance (NMR) allows the study of the properties of magnetic materials at the microscopic level via hyperfine interactions. In zero field NMR the hyperfine fields, probed by the resonant response of nuclear magnetic moments at individual atomic sites, provide information on the local magnetic states. Resonance occurs at a frequency $\nu$ when $2\pi\nu = \gamma B_e$, where $\gamma$ is the gyromagnetic ratio and $B_e$ is the effective internal magnetic field, arising largely from the hyperfine interactions. In a recent paper [9] we reported on the state of Mn ions in a series of compounds with $x$ of $1/3$ and found that ferromagnetic clusters of double exchange coupled Mn spins can survive to temperatures much higher than the magnetic ordering temperature obtained from magnetization measurements. Up to now magnetic phase segregation (dynamic [9–13] or static [14–16]) has been observed in the hole doped region of the La-Ca phase diagram.

The lack of colossal magnetoresistance in the electron doped part pointed out the stability of the insulator phase in the whole range of temperature. Despite the large number

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of experimental reports on this concentration region there has so far been no evidence for the existence of phase segregation in the charge ordered state. By using NMR under applied field in $La_{0.35}Ca_{0.65}MnO_3$, we have discovered the coexistence of ferromagnetic microscopic regions with the charge ordered antiferromagnetic state.

The measurements have been carried out on a polycrystalline powder sample, the same as studied in [7], using an automated, computer controlled, frequency swept spectrometer [17]. Measurements were made in zero magnetic field and in applied fields up to 3 T at temperatures between 3 K and 77 K. Spin echo spectra were obtained by measuring the integrated echo intensity versus frequency. A two pulse sequence, consisting of two radiofrequency pulses of the length $\tau$ and $2\tau$, $0.2\ \mu\text{s} < \tau < 8\ \mu\text{s}$, adjusted to a maximum echo signal in a given field, was used. The relaxation time $T_2$ was measured at the central frequencies of the lines by varying the pulse separation.

The spectra are shown in Figs. 1 and 2. The $^{55}$Mn spectra, Fig. 1, consist of two lines. In zero external field they are centered at 290 MHz ($B_e = 27.5$ T) and 375 MHz ($B_e = 35.5$ T). These two lines evolve quite differently as a function of the external field: while the upper frequency line shifts towards lower frequencies with increasing field, the line at 290 MHz broadens but shows only a slight variation of its central frequency, Fig. 3. The shift of the upper line corresponds to the full $^{55}$Mn gyromagnetic ratio as expected in a ferromagnetic material where the moments, the hyperfine field, and the external field are aligned (actually, for 3d moments the hyperfine field is antiparallel to the moment). As a matter of fact, the central frequency and the shift of the high frequency line in the applied field are indeed similar to those of the resonance line observed for the metallic and ferromagnetic $La_{0.67}Ca_{0.33}MnO_3$ [9]. By contrast, the broadening, and the very slight shift, of the lower frequency line is characteristic of an antiferromagnetic material where the moments and the hyperfine field are either randomly oriented with respect to the external field or perpendicular to it after a spin flop: indeed this results in a distribution of the internal field at the nuclei and only a small variation of its average value. Therefore we have here the first evidence for the coexistence of ferromagnetic and antiferromagnetic regions in the sample. A second proof is given by the measurement of the enhancement factor of the two lines.

In a magnetically ordered material the actual radio frequency field acting on the nuclei is enhanced with respect to that observed in para- or diamagnetic materials. This enhancement arises from the oscillation of the magnetic moments in the rf field of the pulses. In turn the NMR signal is enhanced the same way as the rotating nuclear spins produce oscillations of the electronic magnetization. The enhancement is thus proportional to the transverse magnetic susceptibility of the local magnetic moments. It is rather weak for an antiferromagnetic system (inversely proportional to the exchange interaction), larger for a single domain ferromagnet (inversely proportional to the anisotropy field) and, usually, much larger in ferromagnetic domain walls (proportional to the domain wall mobility). The present measurements show that the enhancement factor in zero field is 10 times larger for the 375 MHz line than for that at 290 MHz. Moreover, the enhancement factor of the upper line decreases by a factor of 5 with the application of a 3 T field, *whereas the enhancement factor of the lower line is field independent*. This is again exactly what is expected for ferromagnetic and antiferromagnetic regions, respectively, since the transverse susceptibility of a ferromagnet

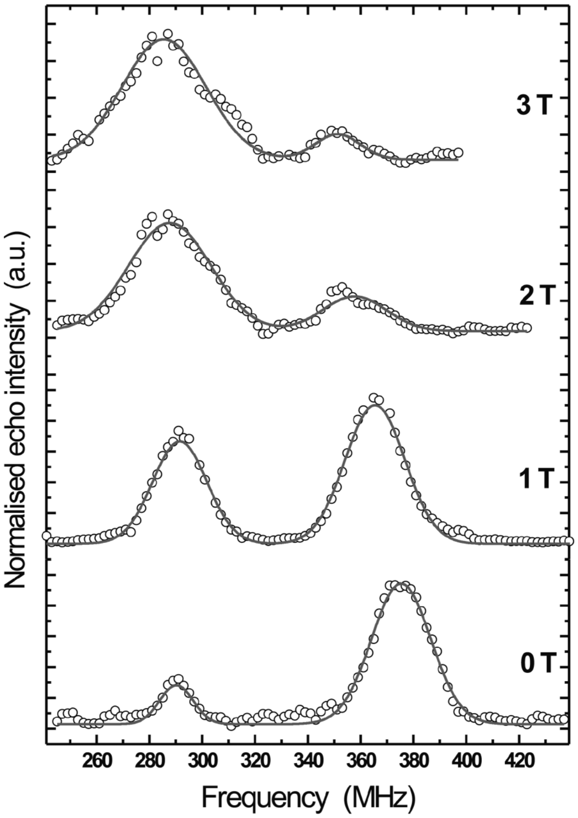

FIG. 1. $^{55}$Mn spin echo spectra at 3 K at various applied fields and the optimum rf pulse lengths chosen at the center of the upper line. Solid lines are Gaussian fits. The spectra are normalized to the maximum signal within each spectrum.

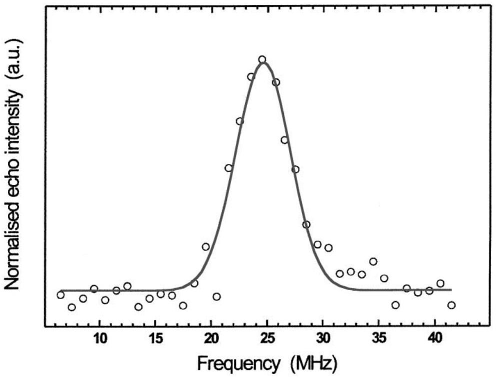

FIG. 2. $^{139}$La spin echo spectrum at zero field and 3 K. Solid line is a Gaussian fit.

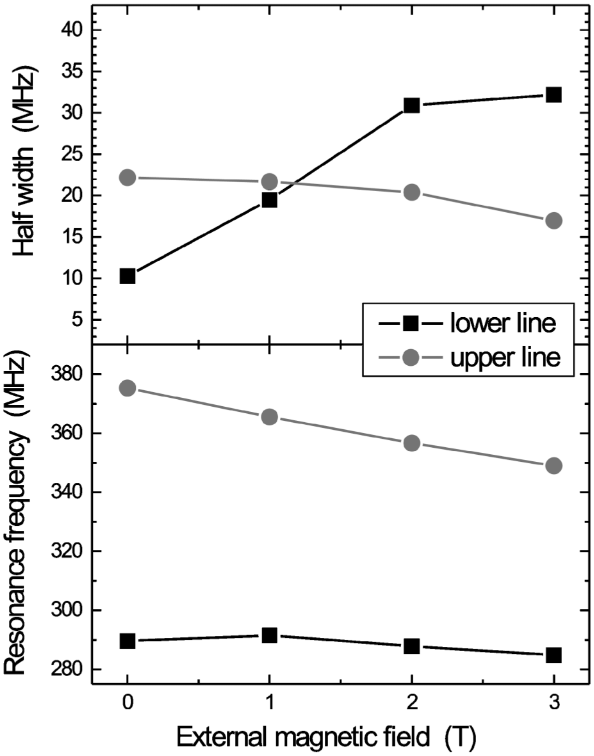

FIG. 3. Dependence of the central frequencies and linewidths on the applied field for the $^{55}$Mn spectra shown in Fig. 1. Solid lines are guides for the eye.

does decrease with increasing external field, whereas, in an antiferromagnet, it is essentially field independent.

Thus, the 290 MHz line is unambiguously assigned to $\mathrm{Mn}^{4+}$ moments in antiferromagnetic regions whereas the 375 MHz line is attributed to regions of ferromagnetically coupled Mn spins. The presence of a single line for the ferromagnetic regions is related to a DE controlled hopping between adjacent $\mathrm{Mn}^{3+}$ and $\mathrm{Mn}^{4+}$ ions with the hopping time $\tau_h$ much shorter than the period of Larmor precession of nuclear spins, $\tau_L$, so a single "motionally narrowed" line is observed. When $\tau_h > \tau_L$, separate lines corresponding to the distinct $\mathrm{Mn}^{3+}$ and $\mathrm{Mn}^{4+}$ states are observed at about 430 and 320 MHz, respectively [18,19]. The NMR signal of $\mathrm{Mn}^{3+}$ ions in the antiferromagnetic regions could not be observed due to their low abundance and much faster relaxation than for $\mathrm{Mn}^{4+}$.

The $^{139}$La resonance line at zero field is centered at 24.4 MHz ($B_e = 4.1$ T) and its linewidth amounts to 5 MHz (Fig. 2). The line exhibits a large enhancement factor, comparable to that of the 375 MHz line of manganese. Thus, it must originate from the ferromagnetic regions. The hyperfine field at the lanthanum nuclei is produced by the neighboring Mn spins. Their contributions largely cancel in the antiferromagnetic phase so the corresponding zero field lanthanum NMR signal cannot be detected.

In order to estimate the relative amount of the ferromagnetic regions the areas under the ferromagnetic and antiferromagnetic lines, corrected for the enhancement factor, Boltzmann factor, and the frequency response of the spectrometer have been determined. A comparison of them leads to the relative amount of the ferromagnetic regions of $8(\pm 3)\%$. From the enhancement factor of the ferromagnetic line, which is an order of magnitude smaller than the domain wall enhancement in the ferromagnetic and metallic $\mathrm{La}_{0.67}\mathrm{Ca}_{0.33}\mathrm{MnO}_3$, it can be deduced that the ferromagnetic regions are small enough to be single domainlike. This would explain why in neutron diffraction experiments no long range ferromagnetic contribution was observed [7]. Within these ferromagnetic regions the Mn ions are double exchange coupled, which is consistent with small angle neutron scattering experiments [10]. Even under the application of a field of 3 T for which the magnetic moments in the ferromagnetic regions are aligned along the field direction, the volume fraction of the ferromagnetic phase does not increase. Thus the concentration of this phase is far from the percolation limit in a three-dimensional system. This is in good agreement with the macroscopic measurements of transport properties, which are not affected by the application of a magnetic field even up to 12 T [7] and constitutes a clear indication of the stability of the low temperature phase segregated state in this compound. A different behavior was reported in [19] for $\mathrm{Pr}_{0.7}\mathrm{Ca}_{0.3}\mathrm{MnO}_3$ where a percolation transition from the isolated DE clusters in a charge ordered state into a macroscopically metallic state was observed by $^{55}$Mn NMR. A growth of the DE clusters in the applied magnetic field was found in the hole doped $\mathrm{LaMnO}_{3+\delta}$ [19]. Considering also the significant population of DE clusters found above the magnetic ordering temperature of the optimally doped compounds [9], this indicates their crucial role in the high field low temperature magnetoresistance and in the CMR.

Summarizing, small ferromagnetic clusters of Mn spins have been found to exist in the antiferromagnetic, charge ordered structure of $\mathrm{La}_{0.35}\mathrm{Ca}_{0.65}\mathrm{MnO}_3$. The clusters do not expand or increase their population in the applied field, in contrast to the low hole doped compounds, which indicates that the antiferromagnetic, charge ordered structure of the compound is stable in the applied field and the compound does not show high field magnetoresistance.

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