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NMR as a local probe of magnetic anisotropy: The possibility of orbital ordering and orbital liquid states in colossal magnetoresistance manganites

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^{139}La rf enhancement experiments are shown to be an excellent tool for detecting changes of the local magnetic anisotropy in colossal magnetoresistance manganites. Based on this, we discuss the possibility of orbital ordering in ferromagnetic (FM) $La_{1-x}Ca_xMnO_3$, and provide evidence about the formation of an unusual kind of phase separation in the low temperature regime of the FM conductive (FMC) phase for $0.25 \leqslant x < 0.5$. We show that by lowering temperature, an extra NMR signal is formed in the FMC phase, which originates from regions with vanishingly small magnetic anisotropy. We anticipate that this feature is due to the formation of regions with strong orbital fluctuations within an orbitally frozen matrix.

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The origin of the electronic properties of mixed valence manganites with the general formula $R_{1-x}D_xMnO_3$ (R = rare earth, D = Ca, Ba, Sr), poses one of the most exciting open problems in the physics of strongly correlated electron systems. Initially, these properties were determined in the framework of the double exchange (DE) model,[1] which is based on the strong Hund's coupling between hopping e_g electrons in successive $Mn^{4+,3+}$ sites and the underlying t_{2g} electrons. However, in recent years experiments have shown that DE is inadequate for the full description of the complex properties of these systems, and coupling of spin with orbital and lattice degrees of freedom is essential in order to explain the magnetic phase diagram. A basic consequence of this assumption is the possibility of states with simultaneous spin and orbital order (OO).[2,3] In such states, OO gives rise to anisotropy of the electron transfer interaction, therefore DE and superexchange interaction are favored or disfavored in an orbital direction-dependent way.[2] This might explain the origin of the ferromagnetic insulating (FMI) to ferromagnetic conductive (FMC) phase transition, which has been recently verified experimentally in the low doping regime of $La_{1-x}Sr_xMnO_3$,[4] and $La_{1-x}Ca_xMnO_3$.[5–7] According to theory[3,4] and experiments,[8,9] the low-T FMI phase has a staggered orbital configuration, in contrast to the orbitally disordered (OD) FMC phase. It is also worthwhile to notice that in the vicinity of the FMI-FMC phase boundary of $La_{1-x}Ca_xMnO_3$, which takes place at $x_c \approx 0.20$, coexistence of both phases has been observed at low temperatures, by using ^{55}Mn NMR techniques.[7]

In the presence of OO, a fundamental question that arises concerns the stability of the orbital lattice against thermal and quantum fluctuations. Recent theoretical studies have shown that orbital fluctuations in the fully spin polarized FMC state[2,10–12] might explain the anomalous optical conductivity behavior in FM compounds of the $La_{1-x}Sr_xMnO_3$ family.[13] It is also possible that the quasi-two-dimensional nature of the orbital fluctuations enables the quantum OD state to persist down to zero temperature, i.e., an orbitally liquid state is formed, as recently proposed in Refs. 2 and 10.

In this Communication, we provide experimental evidence about the formation of an unusual kind of phase separation occurring in the low temperature regime of ferromagnetic (FM) $La_{1-x}Ca_xMnO_3$. This feature, which persists even in the antiferromagnetic (AFM) spin ordered phase above $x \geqslant 0.5$, is explained as showing the onset of strong orbital fluctuations at low temperatures. Our experimental approach proceeds in two steps: First, we show that by increasing doping, the FMI-FMC phase transition is accompanied by a strong reduction of the local magnetic anisotropy. In the next step, we demonstrate that in the doping range $0.25 \leqslant x \leqslant 0.55$ and at low temperatures, FM clusters with vanishingly small magnetic anisotropy are formed within the ''homogeneous'' high-T FMC phase.

In order to resolve electronic phases, which differ in their local magnetic anisotropy, we have employed ^{139}La NMR radio frequency (rf) enhancement techniques. In FM materials, very strong NMR signals are produced at very low rf irradiation fields, H_1, due to coupling of the rf field with the magnetic moments of the electrons.[14] In this way, the effective irradiation field at the nuclear sites is sufficiently stronger than the applied H_1. Correspondingly, the emitted NMR signal is amplified by the oscillating electron moments, thus giving rise to the strong NMR signals that characterize FM materials. It is thus straightforward that any change in the magnetic anisotropy will modify the response of the electronic moments to the applied external rf field, i.e., an increase (decrease) of the magnetic anisotropy field H_A will increase (decrease, respectively) the rf field $H_{1,max}$ that is required to attain the maximum NMR signal.[15,16] Hence, NMR signals from coexisting regions with different magnetic anisotropy are expected to cause multiple maxima in the signal intensity I vs H_1 curves.

Experiments were performed on polycrystalline samples prepared by annealing stoichiometric amounts of the corresponding oxides in air at 1300 to 1400 °C. All samples were then characterized structurally at room temperature with a D500 Siemens x-ray diffractometer, and magnetically with a superconducting quantum interference device (SQUID) mag-

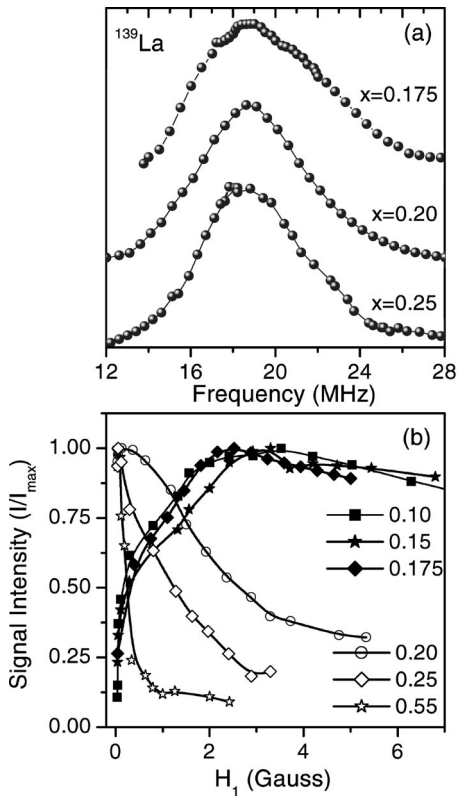

FIG. 1. (a) ^{139}La NMR spectra for the systems $La_{1-x}Ca_xMnO_3$, $x=0.175$, 0.20, and 0.25 at 5 K. (b) ^{139}La NMR signal intensity I as a function of the rf field H_1 for $x=0.1$, 0.15, 0.175, 0.20, 0.25, and 0.55 at 5 K.

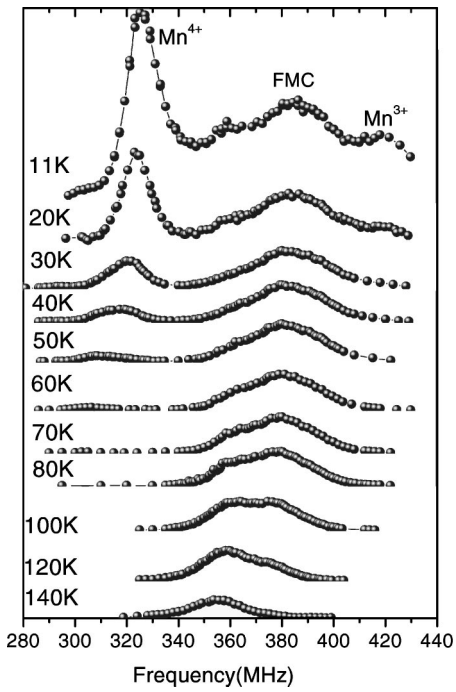

FIG. 2. ^{55}Mn NMR spectra of $La_{0.825}Ca_{0.175}MnO_3$, as a function of temperature.

netometer. The obtained crystallographic and magnetic data were found to be in accordance with literature. ^{139}La NMR spectra of $La_{1-x}Ca_xMnO_3$ in zero external magnetic field were acquired by applying a two pulse spin-echo technique, with pulse widths $t_{p1}=t_{p2}=0.6$ μsec as described elsewhere.[17] The rf enhancement experiments were performed by recording the ^{139}La NMR signal intensity I as a function of H_1 at the peak of the NMR spectra. The obtained curves follow an asymmetric bell-shaped law with maximum at $n\gamma H_{1,max}\tau=2\pi/3$, which allows the calculation of the rf enhancement factor n.[17]

The sensitivity of the rf enhancement to the FMI-FMC phase transition is clearly shown in Figs. 1(a) and (b), which show ^{139}La NMR spectra and signal intensity I vs H_1 curves of $La_{1-x}Ca_xMnO_3$ as a function of x at 5 K. The NMR spectra [Fig. 1(a)] exhibit a peak at ≈ 20 MHz, which corresponds to fully FM polarized Mn octants,[18,19] and remain almost unchanged by crossing the critical doping at $x_c \approx 0.20$. On the contrary, by increasing x and for $x \geqslant x_c$, $H_{1,max}$ shifts rapidly to lower values [Fig. 1(b)] in agreement with recent results by Dho *et al.*[20] Such a rapid increase of the rf enhancement by crossing the phase boundary is explicable if we consider that the OO FMI phase has a sufficiently higher magnetic anisotropy than the OD FMC phase.

However, a clear demonstration of the relation between rf enhancement and the local magnetic anisotropy, i.e., OO, is given by the FMI $La_{0.825}Ca_{0.175}MnO_3$. In reality, this system exhibits a mixed FMI-FMC phase, as deduced from the ^{55}Mn NMR spectra of Fig. 2.[21] At low temperatures, spectra show the coexistence of localized $Mn^{4+,3+}$ (peaks at 320 and 420 MHz, respectively[7]), and delocalized Mn states [peak at 370–380 MHz (Ref. 7)], whereas by increasing temperature the $Mn^{4+,3+}$ signal intensities reduce rapidly, and finally disappear above 80 K. The disappearance of the $Mn^{3+,4+}$ NMR signals deep into the FMI phase for $T>80$ K is puzzling. Apparently, this effect is related to the reentrant structural transition, recently detected by neutron scattering experiments[22] at the same temperature range for $0.1 \leqslant x \leqslant 0.2$, which is characterized by a strong reduction of the orthorhombicity in the low-T phase. At the same time, electron and neutron scattering experiments on $La_{0.85}Ca_{0.15}MnO_3$ have revealed an unconventional layered and staggered OO, which becomes more profound below 70–80 K.[9] In the case of $La_{0.825}Ca_{0.175}MnO_3$, the transition at 80 K is associated with a rapid increase of the ^{139}La NMR rf enhancement on heating, as shown in Figs. 3(a) and (b). At low temperatures, the maximum of the I vs H_1 curves is located at $H_{1,max}=2.4$ G [Fig. 3(b)], and corresponds to the majority FMI phase. By increasing temperature the ^{139}La NMR signal intensity from FMI regions decreases rapidly and disappears at $T=80$ K, in accordance with the ^{55}Mn NMR results. This behavior is clearly seen in the inset of Fig. 3(b), which demonstrates the ^{139}La NMR signal intensity I as a function of temperature, after correcting the influence of the spin-spin relaxation time T_2. Apparently, for $T>80$ K the NMR signal from the FMI phase is so fast relaxing that only the NMR signal from the minority FMC phase component is observable. At the same time $H_{1,max}$ shifts to lower values, and becomes minimum $H_{1,max}\approx 0.3$ G at $T\approx 80$ K, which is characteristic for the FMC phase component. *The system*

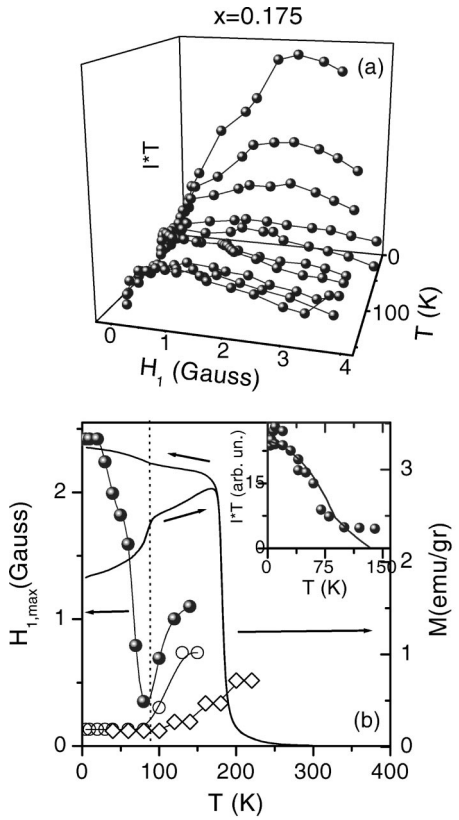

FIG. 3. (a) ^{139}La NMR signal intensity I as a function of the rf field H_1 for $La_{0.825}Ca_{0.175}MnO_3$ at various temperatures. The signal intensities are corrected by the Boltzmann factor. (b) $H_{1,max}$, i.e., the position of the maximum on the I vs H_1 curves, as a function of T for $x=0.175$ (●), 0.20, (○), and 0.25 (◇). The solid line is the magnetization M vs T curve for $x=0.175$. The inset exhibits the ^{139}La NMR signal intensity I vs T after considering the influence of T_2. The solid line in the inset is the corresponding magnetization M vs T curve in the FC route.

thus comprises two strongly intermixed phase components with different rf enhancements that reflect the different local electronic properties, and specifically the different OO of the two subphases. Remarkably, at ≈80 K, the magnetization M vs T curve (obtained at 50 G) exhibits a slope change in both the zero field cooling (ZFC) and field cooling (FC) branches. For $T>80$ K the ZFC branch shows a rapid increase of the magnetization, which—considering the reduced OO above 80 K (Refs. 5, 7, and 9)—may be explained as showing better alignment of the electron spins into the external magnetic field due to a decrease of H_A. On the other hand, in the FC route, the electron spins are already aligned into the external magnetic field and the slight increase of the magnetization below 80 K is in agreement with the formation of the OO state, as pointed out by Endoh and coworkers.[4] It is also observed that the magnetization increase below 80 K in the FC route nicely follows the variation of the NMR signal intensity with T, as shown in the inset of Fig. 3(b). *This confirms that the high $H_{1,max}$ values at low temperatures reflect the establishment of a low-T OO state.* For reasons of comparison, we have also plotted in Fig. 3(b) the $H_{1,max}$ vs T curves for $x=0.20$ and 0.25. In both systems and at low

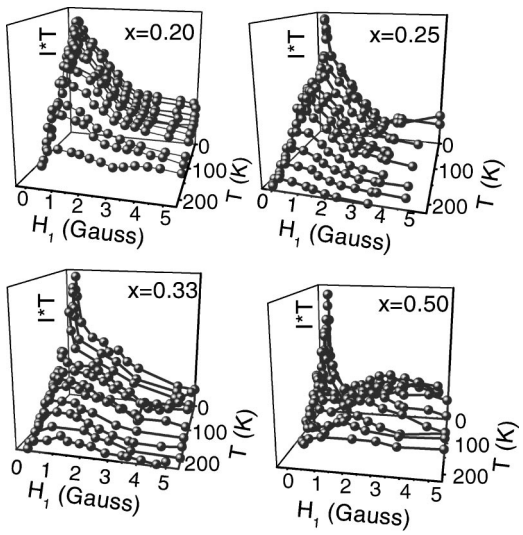

FIG. 4. ^{139}La NMR signal intensity as a function of the rf field H_1 at various temperatures, for $x=0.20$, $x=0.25$, 0.33, and 0.5. The signal intensities are corrected by the Boltzmann factor.

temperatures, $H_{1,max}\leqslant 0.2$ G, whereas at high temperatures $H_{1,max}$ increases slightly in a way similar to $x=0.175$. The relatively higher $H_{1,max}$ values of the 0.175 system in comparison to those of the $x=0.20$, and 0.25 systems for $T>80$ K, might indicate a slight increase of the high-T magnetic anisotropy for $x=0.175$, due to enhanced orbital correlations.

An unusual effect was observed by performing detailed I vs H_1 measurements on $La_{1-x}Ca_xMnO_3$ for $x=0.20$, 0.25, 0.33, and 0.5 as a function of temperature (Fig. 4). At high temperatures, the I vs H_1 curves exhibit the FMC maximum, which in the doping range $0.20\leqslant x\leqslant 0.33$ takes values of $H_{1,max}\approx 0.4-1.0$ G. Remarkably, for $x\geqslant 0.25$ and by lowering temperature, a second maximum appears at $H_{1,max}\approx 0.05$ G. Such an extremely low $H_{1,max}$ value is indicative of an NMR signal produced in FM regions, where the electron spins are almost freely responding to the external rf field. It is also worthwhile to note that this feature persists even in the AFM phase, as implied by its appearance in the low temperature regime of $x=0.5$, and $x=0.55$ [Fig. 1(b)]. In the case of $x=0.5$, two maxima at $H_{1,max}\approx 0.05$ and 2.3 G are observed, whereas neutron diffraction[23] and resistivity[24] data show the presence of a minority FM phase down to the lowest measured temperature. However, for the $x=0.55$ sample, only the $H_{1,max}\approx 0.05$ G maximum was detected (Fig. 1), whereas no FM peaks are observed in the corresponding neutron diffraction pattern performed on the sample used in the present work.[23] This implies that for this doping concentration, the detected ^{139}La NMR signal is produced in FM clusters with a very short correlation length, which are finely dispersed within the AFM matrix in agreement with previous electron microscopy results.[25] It is thus tempting to argue that t_{2g} electrons within such FM nanoclusters do not possess any energetically preferential orbital orientation, thus enabling the obtainment of extremely high rf enhancement. This picture is in compliance with recent calculations,[26] which show that by increasing x

the FMC state may vary among different orbital configurations. Remarkably, the calculated energy difference of these configurations is very small,[26] suggesting the presence of strong orbital fluctuations. In such a case, the formation of islands of an orbital liquid with extremely low H_A cannot be ruled out. The possibility of orbitally liquid states may explain the appearance of the puzzling I vs H_1 maximum at the extremely low $H_{1,max} \approx 0.05$ G. In this scenario, by increasing temperature, the onset of Jahn-Teller distortions[27] lifts the degeneracy of the various states, and the orbital liquid would freeze in the high temperature FMC orbital configuration. This causes the 0.05 G maximum in the NMR signal intensity to decrease rapidly on heating.

In conclusion, ^{139}La rf enhancement experiments provide evidence about the presence of FMI states in $La_{1-x}Ca_xMnO_3$ for $0.1 \leqslant x \leqslant 0.2$, which at low temperatures exhibit sufficiently higher local magnetic anisotropy than the FMC states for $0.2 \leqslant x < 0.5$. This difference may be attributed to the OO nature of the FMI states in comparison to the OD FMC states. Experiments also indicate that by increasing temperature, the NMR signal from the low temperature OO FMI phase ''wipes out.'' This effect accompanies the structural phase transition recently detected by neutrons.[22] For $x \geqslant 0.25$ and at low temperatures, experiments show the formation of regions with extremely low magnetic anisotropy, presumably due to strong orbital fluctuations as predicted by theory.[10–12,26] Remarkably, this feature appears to persist even into the AFM phase for $x \geqslant 0.5$.

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