Orbital domain state and finite size scaling in ferromagnetic insulating manganites

G. Papavassiliou1, M. Belesi1, M. Fardis1, M. Pissas1, J. Dolinsek2, C. Dimitropoulos1,2, J. P. Ansermet3,⋆
1Institute of Materials Science, NCSR, Demokritos, 153 10 Agia Paraskevi, Athens, Greece
2Josef Stefan Institute, Jamova 39, 61111 Ljubljana, Slovenia
3Dept. of Physics, University of Illinois, Urbana, Illinois 1801, USA
(Dated: October 27, 2018)

PACS numbers: 75.70.Pa., 76.20.+q, 75.30.Et, 75.60.Ch

Understanding the electronic properties of colossal magnetoresistive manganites has been a challenging subject for both experimentalists and theorists, ever since their discovery almost 50 years ago. There are clearly two types of dominant ground states in these compounds: In \( \text{La}_{1-y}\text{Ca}_y\text{MnO}_3 \) (LCMO) for example, the ground state is ferromagnetic and metallic (FMM) for \( 0 \leq x \leq 0.5 \), and antiferromagnetic insulating for \( x \geq 0.5 \). The establishment of the FMM phase was initially attributed to the double exchange (DE) interaction \( \hbar \), i.e. ferromagnetism via the strong Hund’s coupling between hopping \( e_g \) electrons at neighbouring Mn\(^{4+}\) sites. However, the detection of FM insulating (FMI) \( \hbar \) and AFM metallic \( \hbar \) phases in certain manganites indicates that DE is inadequate for the full description of the magnetic and transport properties in these systems. According to recent theoretical \( \hbar \) and experimental results \( \hbar \) and orbital ordering (OO) is an important factor controlling the \( e_g \)-hole mobility. A characteristic example is \( \text{La}_{1-y}\text{Sr}_y\text{MnO}_3 \) (LSMO), where in the doping range \( 0.1 \leq x \leq 0.15 \) a FMM to FMI transition takes place at low temperatures \( \hbar \). Experiments have shown that this transition is associated with charge ordering, OO, and strong reduction of the cooperative Jahn-Teller (JT) lattice distortions in the low-T phase \( \hbar \). It has been also proposed that the OO phase might contain hole-rich layers \( \hbar \), which sets the stripe of question formation into the FMI phase \( \hbar \).

A similar transition has been observed in LCMO for \( 0.125 \leq x \leq 0.2 \), at \( T_{tr} \approx 70 - 100 \) K \( \hbar \). However, the characteristic resistivity upturn \( \hbar \) \( \hbar \), which marks the onset of the FMI phase is observed at temperatures sufficiently higher than \( T_{tr} \). Experiments show that the resistivity upturn is associated with a diffuse structural transition, characterised by strong reduction of the orthorhombicity \( \hbar \), and a remarkable rotation of the easy magnetization axis \( \hbar \). These characteristics are considered as the hallmark of orbital rearrangements that take place on cooling. At the same time, a number of peculiar features are observed, which are reminiscent of glassy freezing \( \hbar \) especially in the doping region \( 0.17 \leq x \leq 0.2 \): (i) a steep decrease and frequency dependence of the \( \chi \) susceptibility at low temperatures \( \hbar \), (ii) strong difference between the field cooled (FC) and zero field cooled (ZFC) magnetization in low fields \( \hbar \), (iii) the wipe-out of the NMR signal, which has been attributed to ultra-slow fluctuations of the electronic spin, charge, or orbital degrees of freedom \( \hbar \). On the other hand, the sharp, cooling-rate dependent increase of the FM Bragg peaks \( \hbar \), below \( T_{tr} \), and the sudden slope-change in both the ZFC and FC branches of the magnetization at the same temperature \( \hbar \) indicate rather nonequilibrium phenomena and quasinonergodicity (“freezing”) on cooling, than a reentrant spin-glass transition. It is the competition between critical slowing down and spin freezing that makes characterization of the spin and orbital dynamics in this system a nontrivial task.

In this paper we shed light on this intriguing freezing mechanism by using \( \hbar \) and \( 55\)Mn NMR in comparison with recent neutron scattering measurements, performed on the same high quality single crystal of \( \text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3 \). This system exhibits a PM-to-FM transition at \( T_c \approx 180 \) K, and resistivity upturn at \( \approx 150 \) K. We provide clear evidence about a novel thermodynamic phase transition occuring at \( T_{tr} \approx 70 \) K. The high magnetic anisotropy of the low temperature FMI phase and the finite size scaling of \( T_{tr} \) upon increasing hole-doping, are indicative of an inhomogeneous OO state with hole-stripes below 70 K, while the spin-freezing features may arise from the formation of an intermediate FMI orbital domain state at nanometer length scale. This state creates partial magnetic disorder at orbital domain boundaries, while the establishment of long range OO below \( T_{tr} \) gives rise to full magnetic ordering, as deduced from the neutron scattering experiments \( \hbar \).
FIG. 1: $^{55}$Mn NMR spectra of LCMO $x = 0.20$, at various temperatures.

Zero external field $^{139}$La and $^{55}$Mn NMR measurements were acquired by applying a two pulse spin-echo technique, at very low rf power level, due to the very strong rf enhancement that characterizes FM materials [27]. $T_1$ was then measured at the peak of the spectra, by applying a saturation recovery technique and by fitting with a multieponential recovery law as in previous works [22]. Rf enhancement experiments were performed by recording the NMR signal intensity $I$ as a function of the level of the applied rf field $H_1$. In general, the obtained curves follow an asymmetric bell-shaped law with maximum at $n \gamma H_1 \tau = 2\pi/3$, which allows the calculation of the rf enhancement factor $n$ [27]. The neutron scattering data have been recently reported in ref. [3].

Figure 1 exhibits $^{55}$Mn line shape measurements at various temperatures. The maximum signal was obtained for $H_1 || c$-axis, which means that the hyperfine field $H_{hf}$ is lying on the $ab$ plane. A similar result was obtained in $^{139}$La NMR in agreement with previous experiments on low doped LSMO [28]. For $T \geq 70$K spectra consist of a broad single-peaked line at frequency $\approx 375$ MHz, which according to the literature corresponds to delocalized Mn states [14]. However, for $T \leq 70$K new peaks increase rapidly on cooling, which correspond to localized Mn$^{4+}$ states (the narrow peak at $\approx 320$ MHz) and Mn$^{3+}$ states (the broad peak at $\approx 420$ MHz) [14]. At exactly the same temperature a sharp increase of the intensity of certain ferromagnetic Bragg peaks (Figure 3b) is observed on cooling, which implies that the appearance of the localized Mn$^{3+},^{4+}$ NMR peaks is associated with better ordering of the Mn spins. The intensity of these Bragg peaks depends on the cooling rate as recently reported in ref. [13]. The rapid increase of the NMR signal from localized electron states below 70 K is also clearly deduced from the $^{139}$La rf enhancement experiments of Figure 3a. For $T \geq 70$K only a broad peak with maximum at 0.3 Gauss is present in the $I$ vs. $H_1$ curves. However, below 70 K a second peak at $\approx 2$ Gauss appears, which increases rapidly by decreasing temperature. Comparison with Figure 1 implies that this second peak corresponds to localized Mn$^{3+},^{4+}$ states, whereas the 0.3 Gauss peak to delocalized Mn states. There are two possible explanations for the different rf enhancement factors of the FMI and FMM signals: (i) the OO FMI matrix phase has higher local magnetic anisotropy (smaller response to the applied rf power level) than the orbitally disorder FMM minority phase [24], (ii) the system consists of hole-rich FMM domain-walls separating FMI domains. The second argument is based on the fact that the rf enhancement $n \approx 3 \cdot 10^4$ from the FMM regions is sufficiently higher than the FMI $n \approx 2 \cdot 10^2$, as expected for FM domain-walls in comparison to FM domains [27]. Finite size scaling arguments given below, are in favour of the second explanation.

Figure 3 shows $^{55,139}(1/T_1)$ measurements as a function of temperature. In case of $^{55}(1/T_1)$ measurements were performed on the M$^{4+}$ peak and the central FMM peak, whereas in case of $^{139}(1/T_1)$ measurements were obtained at rf power levels 0.3 Gauss and 2 Gauss, which correspond to delocalized and localized Mn$^{3+},^{4+}$ states, respectively. The similar temperature dependence of the corresponding $^{55,139}/T_1$ curves is a proof of the correct assignment of the $^{139}$La NMR signals. The crucial point in Figures 3a,b is that both $^{55,139}/T_1$ from Mn$^{3+},^{4+}$ ions are diverging on approaching 70K from below. Such a behaviour is indicative of critical relaxation enhancement on approaching the phase transition temperature. In a previous work on a series of powder samples the divergence of $1/T_1$ was not observed [22], probably due to inaccurate irradiation conditions in non-oriented powder samples. In contrast, the FMM $1/T_1$ is insensitive to the phase transition while crossing $T_r$. The hump at $\approx 20$K on FMM $^{55}(1/T_1)$ is probably due to partial signal contribution at $\approx 350$ MHz from localized Mn$^{3+}$ states, which induce a broad inhomogeneous signal extending down to $\approx 25$ MHz [14, 29]. At temperatures higher than 70K, where the FMI signal is completely wiped out [22, 23], $1/T_1$ reflects solely the dynamics of the FMM states.

The inset in Figure 3a shows $^{139}(1/T_1)$ as a function of doping obtained in powder LCMO samples at $T = 10$ K. It is observed that in the pure FMM part of the phase diagram ($x \geq 0.25$), $1/T_1$ is almost three orders of magnitude lower than in the pure FMI part ($x \leq 0.15$). It is thus remarkable that for $x = 0.20$ no clear distinc-
FIG. 2: (a) $^{139}$La NMR signal intensity as a function of the rf field $H_1$ for LCMO $x = 0.20$, at various temperatures. (b) The rf field $H_{1,max}$ of maximum signal intensity as a function of temperature (o), together with the integrated intensity of the (110) (or (002)) Bragg peaks vs. temperature (●), from ref. [13].

FIG. 3: (a)$^{139}(1/T_1)$ of LCMO $x = 0.20$, as a function of temperature. The inset shows $^{139}(1/T_1)$ of powder LCMO samples, as a function of Ca doping at $T = 10$ K and rf level 2 Gauss. The arrow indicates the value for the $x = 0.20$ single crystal. (b)$^{55}(1/T_1)$ of La$_{0.80}$Ca$_{0.20}$MnO$_3$ as a function of temperature.

...tion in the $1/T_1$ values from FMI and FMM states is observed at low temperatures, while $1/T_1$'s become particularly different on approaching $T_{tr}$ from below. In a recent neutron scattering study (performed on the same $x = 0.20$ crystal as here) [26] two different FM media were detected, which coexist dynamically in the temperature range $T_{tr} \leq T \leq T_c$, and are stabilized into a periodically arranged collective state below $T_{tr}$. Hence, at low temperatures the system appears to consist of a regular arrangement of OO domains with a uniform relaxation mechanism. In order to envisage how such an orbital domain state could be created, we consider the idea of the random field Ising model [30, 31], where the random field mimics the lattice distortions induced by substitution with Ca ions. By taking into account only the isospin $T = 1/2$ degree of freedom, which describes the twofold $e_g$ orbital degeneracy [21], it can be shown that in strong random fields an intermediate orbital domain state may be realized on cooling [32, 33, 34]. This state is metastable exhibiting anomalous slow relaxation with logarithmic time dependence [35, 36] and strong difference in the orbital and spin ordering between the ZFC and FC branches [32]. The observed cooling rate dependence of the FM Bragg peak intensity below $T_{tr}$ is attributed to nucleation or rearrangement of orbital domains and domain walls, which is connected with the large reduction of orthorhombicity upon cooling [33]. We also note that in case that neighboring orbital domains are arranged in antiphase, stripe-like orbital walls will be formed, where holes are energetically favorable to concentrate [32], in agreement with the neutron measurements [26]. By increasing hole-doping the number of walls will increase [2], whereas above a critical doping $x_c$ the OO phase is expected to be suppressed [33, 34]. Indeed, such doping induced finite size scaling effects are experimentally suggested. Figure 3 shows $T_{tr}$ vs. doping $x$, obtained from NMR and magnetic measurements in a series of LCMO powder samples. The experimental data for $0.1 \leq x \leq 0.25$ are nicely fitted by the expression $T_{tr}(x) = T_{tr}(1 - (x/x_c)^n)$, where $T_{tr} = 110$ K, $x_c = 0.28$, and $n = 2$. Such a power-law dependence is expected from finite size scaling theory [37, 38], which predicts that the effective $T_{tr}$ is limited by the finite size $L$ of the domains according to the formula, $T_{tr}(L) = T_{tr}(\infty)(1 - (L/L^{*})^{n})$. The above equations are consistent with $L(x) = 1/x^{n'}$, which is determined as evidence about the formation of walls separating orbital domains. We also notice that in mean-field approxima-
pressive similarity between our NMR results in LCMO in the layered (2D) structures. We notice the impetitive spin (isospin) ordering under quenched disorder [38, 39]. This is probably due to the similar com-
gogy between the degree of freedom to an isospin, there is a complete anal-
ly that holes are self-assembled - apparently in stripes - in these systems.

This work has been partially supported by the Greek-
Slovenian cooperation project No. 2495. We would like
to thank Dr. M. Hennion, and Prof. Y. M. Mukovskii,
for providing the x = 0.20 single crystal.

* *Institut de Physique Experimentale, EPFL-PH-
Ecuiblens, 1015-Lausanne, Switzerland

[1] C. Zener, Phys. Rev. 82, 403 (1951).
[2] Y. Endoh et al., Phys. Rev. Lett. 82, 4328 (1999).
[3] R. Kajimoto et al., Phys. Rev. B 60, 9506 (1999).
[4] Y. Tokura and N. Nagaosa, Science 288, 462 (2000).
[5] E. Dagotto et al., Phys. Rep. 344, 1 (2001).
[6] T. Mizokawa et al., Phys. Rev. B 61, R3776 (2000).
[7] Y. Yamada et al., Phys. Rev. Lett. 77, 904 (1996).
[8] G.-L. Liu et al., Phys. Rev. B 64, 144414 (2001).
[9] J.-S. Zhou et al., Phys. Rev. B 62, 3834 (2000).
[10] Y. Yamada et al., Phys. Rev. B 62, 11600 (2000).
[11] T. Inami et al., Jpn. J. Appl. Phys., Suppl. 38-1, 212
(1999).
[12] T. Hotta et al., Phys. Rev. Lett. 86, 4922 (2001).
[13] G. Biotteau et al., Phys. Rev. B 64, 104421 (2001).
[14] G. Papavassiliou et al., Phys. Rev. Lett. 84, 761 (2000).
[15] T. Okuda et al., Phys. Rev. B 61, 8009 (2001).
[16] V. Markovich et al., Phys. Rev. B 65, 144402 (2002).
[17] V. Markovich et al., Phys. Rev. B 66, 094409 (2002).
[18] P. Dai et al., Phys. Rev. Lett. 85, 2553 (2000).
[19] R. Laiho et al., Phys. Rev. B 63, 094405 (2001).
[20] C. S. Hong et al., Phys. Rev. B 63, 092504 (2001).
[21] M. Belesi et al., Phys. Rev. B 63, 180406R (2001).
[22] G. Papavassiliou et al., Phys. Rev. Lett. 87, 177204
(2001).
[23] G. Allodi et al., Phys. Rev. Lett. 87, 127206 (2001).
[24] M. M. Savosta et al., cond-mat/0208033 (2002).
[25] You-Quan Li et al., Phys. Rev. Lett. 71, 3527 (1998).
[26] M. Hennion et al., cond-mat/0112159 (2001).
[27] G. Papavassiliou et al., Phys. Rev. B 55, 15000 (1997).
[28] K. Kumagai et al., Phys. Rev. B 59, 97 (1999).
[29] A. Anane et al., Appl. Phys. Lett. 69, 1160 (1996).
[30] S. Fishman and A. Aharony, J. Phys. C 12, 1729 (1979).
[31] R. Bruinsma and G. Aeppli, Phys. Rev. Lett 52, 1547
(1984).
[32] C. Ro et al., Phys. Rev. B 31, R1682 (1985).
[33] Po-zen Wong and J. W. Cable, Phys. Rev. B 28, R5361
(1983).
[34] H. Yoshizawa and D. P. Belanger, Phys. Rev. B 30, 5220
(1984).
[35] T. Nattermann and I. Vilfan, Phys. Rev. Lett. 61, 223
(1988).
[36] J. Villain, Phys. Rev. Lett. 52, 1543 (1984).
[37] M. E. Fisher and M. N. Barber, Phys. Rev. Lett. 28, 1516 (1972).
[38] J. H. Cho et al., Phys. Rev. Lett. 70, 222 (1993).
[39] J. M. Tranquada et al., Nature (London) 375, 561 (1995);
J. M. Tranquada et al., Phys. Rev. Lett. 73, 1003 (1973).
[40] J. Burgy et al., Phys. Rev. Lett. 87, 277202 (2001).
[41] Y. Yoshinari et al., Phys. Rev. Lett. 82, 3536 (1999).

FIG. 4: $T_{tr}$ for LCMO vs. doping $x$. Experimental points were obtained by NMR (•) and magnetic measurements (○). The solid line is theoretical fit as described in the text.