Field-induced segregation of ferromagnetic nano-domains in Pr$_{0.5}$Sr$_{0.5}$MnO$_3$, detected by $^{55}$Mn NMR

G. Allodi, R. De Renzi, M. Solzi

Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

K. Kamenev, G. Balakrishnan

Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

M. W. Pieper

Institut für Angewandte Physik, D-20355 Universität Hamburg, Germany.

(March 24, 2022)

The antiferromagnetic manganite Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ was investigated at low temperature by means of magnetometry and $^{55}$Mn NMR. A field-induced transition to a ferromagnetic state is detected by magnetization measurements at a threshold field of a few tesla. NMR shows that the ferromagnetic phase develops from zero field by the nucleation of microscopic ferromagnetic domains, consisting of an inhomogeneous mixture of tilted and fully aligned parts. At the threshold the NMR spectrum changes discontinuously into that of a homogeneous, fully aligned, ferromagnetic state, suggesting a percolative origin for the ferromagnetic transition.

75.30.Kz, 75.25.+z, 76.60.-k

Manganites R$_{1-x}$A$_x$MnO$_3$ (R = rare earth, A = alkali-earth metal) display correlated magnetic and transport properties, which include a colossal magnetoresistance (CMR) near $T_C$ for the metallic ferromagnetic compositions (around $x = 1/3$). The complexity of the physics in manganites is witnessed by a very rich phase diagram, which comprises various magnetic structures and regions of phase coexistence at $x < 0.1$ and at $x \approx 0.5$. The magneteto-transport properties of these materials are generally understood in terms of the double exchange interaction, arising from spin-polarized carriers coupled to localized electronic moments by a strong intra-atomic exchange. The underlying physics, however, is probably more complex, and other competing interactions are relevant. Among these, the narrow bands, nesting effects of the peculiar Fermi surfaces, and the electron-lattice coupling through the Jahn-Teller (JT) active Mn$^{3+}$ ion play perhaps a major role.

Recently the focus of studies has moved to non-CMR compositions, in particular to the 50% substituted compounds, where the itinerant ferromagnetic (F) state becomes unstable and electronic localization with antiferromagnetic (AF) order take over at low temperature. Manganites at half band filling display in fact two magnetically ordered states: a F metallic state at $T > T_C > T_N \approx 150$K, and an AF insulating phase at lower temperature. The AF phase can be accompanied by the ordering of Mn$^{3+}$ and Mn$^{4+}$ on two distinct sublattices, like in La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. We have recently shown that in La$_{0.5}$Ca$_{0.5}$MnO$_3$ the charge ordered state sets in at $T_N$ by nucleation of mesoscopic AF domains from the ferromagnetic bulk in a first order transition. However, in Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ charge ordering (CO) does not take place and the magnetic structure is of the layered A-type. Both AF ground states can be destroyed by suitably strong applied fields, which restore the metallic F phase: this can be viewed as another regime of CMR.

In this paper we present an investigation of the AF-F transition in Pr$_{0.5}$Sr$_{0.5}$MnO$_3$, carried out by means of $^{55}$Mn NMR, a.c. susceptibility, and magnetization measurements. The sample is a random assembly of small single crystals obtained from crushing a floating zone specimen. Magnetization and a.c. susceptibility were measured by means of an Oxford Instruments Maglab$^{2000}$ System ($\mu_0 H_{dc} = 0 - 7$ T, $T = 1.5 - 400$ K), equipped with a d.c. extraction magnetometer and an a.c. induction susceptometer. NMR was performed in liquid He at 1.3 K with a home built spectrometer and a variable field superconducting solenoid.

A.c. susceptibility ($H_{ac} = 1$ Oe, $\nu = 1$ kHz) in zero d.c. field was measured as a function of temperature. The $\chi'(T)$ and $\chi''(T)$ curves, reproducible on cooling and warming, are shown in figure. The magnetization curve in a d.c. field of 500 Oe was measured as well, and it reproduces closely the features of $\chi'(T)$. The curves show clearly the two magnetic transitions of the sample: the Curie point $T_C = 270$ K, observed as a steep rise of $\chi'$ and the sharp peak on $\chi''$, and the F-AF transition at $T_N \approx 150$ K, where the susceptibility drops by two orders of magnitude. This behavior is qualitatively similar to that encountered in La$_{0.5}$Ca$_{0.5}$MnO$_3$ where, however, in all reported works, a comparatively high remanent susceptibility (approximately 5-20% of maximum, depending on the author) was found in the CO-AF phase. In the present case the susceptibility saturates below $T_N$ at the value $\chi' = 1.5 \times 10^{-4}$ emu/g Oe, only a factor 10 larger than expected in a simple AF state by Curie-Weiss law,
suggested a very weak ferromagnetic term. Moreover, no appreciable thermal hysteresis was observed here, in contrast again with La$_{0.5}$Ca$_{0.5}$MnO$_3$ \[14\].

Magnetization at constant temperature as a function of the applied field is shown in fig. 1b for several temperatures below $T_C$. At $T_N < T < T_C$ an applied field of a few kOe fully saturates the magnetization $M(H)$. Below $T_N$, the initial slope of $M(H)$ drops abruptly, corresponding to the onset of AF order. In both cases the initial d.c. susceptibility $\chi_d = dM/dH$ is in good quantitative agreement with $\chi'_\text{ac}(T)$. In addition at $T < T_N$ a first order metamagnetic transition takes place at larger fields: $M(H)$ deviates from the linear behavior, with a steep rise at a threshold field $H_\theta(T)$ (marked by arrows in the figure). This agrees with results from Tomioka et al. [15]. The threshold field, determined as the knee of the curve, increases with decreasing temperature, as shown in the inset of fig. 1b. The magnetic moment right of the curve, increases with decreasing temperature, as et al. [15]. The threshold field, determined as the knee in the figure). This agrees with results from Tomioka et al. [15]. The threshold field, determined as the knee of the curve, increases with decreasing temperature, as shown in the inset of fig. 1b. The magnetic moment right above $H_\theta(T)$ is roughly 2/3 of the apparent saturation value $\mu_n(T) \approx 3\mu_B$/formula unit, which is approached at higher fields. Such a large moment demonstrates that the magnetic order is close to that of a full ferromagnet above $H_\theta$. (Fig. 1. a) Real, $\chi'(T)$, and imaginary, $\chi''(T)$, a.c. magnetic susceptibility. Measurements performed during cooling and warming are marked with closed and open symbols, respectively. Inset: $M(T)$ in 500 Oe. b) Magnetization $M(H)$ at several temperatures ($H$ swept from 0 to 7T). Inset: threshold field $H_\theta(T)$ (see text). $H_\theta$(48K) is extrapolated from the data; the point at 1.3 K is from the NMR measurements.

In order to obtain microscopic information on the field induced transition we employed $^{55}$Mn NMR at 1.3 K in variable magnetic fields as a local probe of magnetization and of magnetic structure. The local field experienced by $^{55}$Mn arises from dipolar, transferred, and the Fermi contact fields, and is proportional to the electronic moment $g\mu_B(S)$:

$$B = \frac{2\pi}{\gamma} g\mu_B A(S) + \mu_c H. \tag{1}$$

Here $\mu_B H$ is the external field, and $\gamma/2\pi = 10.501$ MHz/T for $^{55}$Mn. The hyperfine coupling tensor $A$ is found to be negative and isotropic within the experimental resolution \[4\]. The resonance frequency determines with this equation only the product $Ag(S)$. We use below the resonance frequencies in homogeneous Mn compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\]. Similar frequencies have also been observed in CO manganites \[4\]. In the conducting CMR compounds as a reference to assign local moments and a valence to different sites in our spectra. The nuclei of the 3$\mu_B$ Mn$^{4+}$ ions resonate at low temperatures around 300 MHz in several single valence insulating Mn compounds \[16,17\].
Although the sample is antiferromagnetic at $H = 0$ the high frequency NMR signal originates entirely from a ferromagnetic fraction, as it is demonstrated by the sizeable enhancement $\eta \approx 100$ and by the field dependent frequency shifts. The slope of the full line in fig. 3a shows that the high frequency peak shifts with field according to the full nuclear gyromagnetic ratio $(\mu_c^{-1} d\Delta\nu / dH = \gamma / 2\pi$, from eq. 1). This implies that the electronic moments on the Mn sites are constant and fully aligned to the external field, as expected in a saturated ferromagnet.

The low frequency peak exhibits only a fractional shift (fig. 3a), which implies a partial alignment of the Mn moments giving rise to this signal. Assuming for the sake of simplicity a constant angle between external field and the Mn moments one finds for this angle $\theta \approx 65$ degrees from the slope $d\nu / \mu_c dH \approx \gamma \cos \theta / 2\pi \approx 4.5 \text{ MHz/T}$. We shall refer to this contribution as a tilted F ($tF$) component and to the former as fully F ($fF$).

Fig. 3b shows the area $I(H)$ under the full spectrum, corrected for $\eta(H)$, which is proportional to the number of resonating nuclei. The zero field signal has a tiny intensity, hence the F fraction is initially a minority phase. Its presence may account for the enhanced macroscopic d.c. susceptibility in the AF state discussed above. However, $I(H)$ increases rapidly with field, and the intensity ratio of the two peaks remains constant, of order one, independent of the field. The rapid increase of $I$ with field rules out an impurity phase. No signal from the majority AF phase is observed, probably due to extremely fast relaxation, as it is suggested by comparison with the related compound La$_{0.5}$Ca$_{0.5}$MnO$_3$, where $^{55}\text{Mn}$ relaxes two orders of magnitude faster in the AF phase than in the F phase [4].

The field induced magnetic transition was easily located at 1.3 K and 7.7(1) T by an abrupt change in $\chi'$ and $\chi''$ which induces a severe detuning and rf-mismatch of the probe head. The transition also shows up in the NMR spectrum, which at 8 T (the topmost in fig. 2) consists of a narrower single high frequency peak, whereas the low frequency peak, still well resolved at 7 T, has completely disappeared. No additional peak was found between 210 and 420 MHz. The mean frequency of the 8 T spectrum lies on the same line of the $fF$ peak in fig. 3a. The $tF$ peak is not recovered by setting the field back to 7 T: the hysteresis demonstrates that this is a first order transition, clearly corresponding to that detected by $M(H)$ at higher temperatures. Although instrumental limitations prevented direct verification by magnetometry, the value of 7.7 T at 1.3 K is in good agreement with the $H_\theta(T)$ curve extrapolated from magnetization data (see inset to fig. 1b). The identification is also supported by the steep rise of the NMR amplitude $I(H)$ near 7 T, in qualitative agreement with the $M(H)$ curve at the lowest temperature (cfr. fig. 1b and fig. 3b).

From our NMR data we can conclude, therefore, that on a microscopic scale the increase of $M(H)$ below $H_\theta$ is not due to homogeneously increasing induced moments or a field induced homogeneous canting of the AF structure, since both are incompatible with the slope of the
fF-line in fig. 3a. Instead, the simultaneous increase in the tF- and fF-line intensities shows that $M(H)$ develops by inhomogeneous nucleation of fF- and tF-phases from the AF matrix. The strong correlation between the intensity of the fF- and the tF-line while both change with field by more than an order of magnitude strongly suggests a growth of both phases in spatially connected volumes. It is tempting to associate the two lines with the inner core and with the outer surface layers of ferromagnetic clusters within the AF matrix respectively. At the threshold field the tilted component vanishes, indicating that the ferromagnetic volume fraction becomes homogeneous (AF-regions may still exist).

If we follow this idea we may discuss some further consequences of our data for the properties of these clusters. First, the fact that the intensity ratio is constant means that the volume fraction of the mixed phase (tF + fF) increases by growth in the number of clusters rather than in their size. Second, the ratio $I_{tF}/I_{fF} \approx 1$ implies a very large surface to volume ratio, corresponding to a very small size of the clusters. Assuming for simplicity a cubic shape, the core contains $(N - 2)^3$ unit cells, covered by a layer of $6(N - 2)^2$ unit cells (not counting the edges). The NMR intensity ratio then implies nearly equal volumes or $N = 8$, that is a size of the core in the order of six lattice constants. Finally, comparison with the zero field frequencies of the reference materials described above provides information on the local valence: 370 MHz for the fF-line corresponds to Mn$^{+3.3 \leq v \leq +3.5}$ in a metallic ferromagnet, while 290 MHz for the tF-line is close to the value of Mn$^{+4}$ in antiferromagnetic insulators.

The peculiar nature of these clusters brings to mind a static version of magnetic polarons, often invoked by theories as the excitations of either magnetic JT [21] or magnetic semiconductor [22] systems. Unfortunately, we cannot distinguish from our NMR data between the two cases of a tF core surrounded by a fF layer or vice versa, the ferromagnet being surrounded by a tilted structure. From a magnetic point of view the second possibility is more intuitive, but it implies some electrostatic overshielding of the core hole state ($v \leq +3.5$) in the surface layer ($v \approx +4$), followed by the surrounding AF ($v \approx +3.5$). In the other case the valence decreases nearly monotonically from the center of the cluster where Mn$^{+4}$ forms an AF structure, canted due to the field and frustrated magnetic bonds, to the fully aligned ferromagnetic surface of the cluster. An interface layer between fF surface and the surrounding AF matrix might well be unobservable in NMR. In both cases the metamagnetic transition at $H_0$ indicates a change of topology in this phase. Its coincidence with a large mean magnetic moment strongly suggests the crossing of a percolation threshold by F domains at $H_0$. This view is also supported by the abrupt increase of electrical conductivity accompanying the transition [12].

A similar intrinsic phase separation was encountered in La$_{0.5}$Ca$_{0.5}$MnO$_3$, where a minority F fraction coexists with the majority AF phase at all temperatures below 150 K [1]. In that sample, however, the large thermal and magnetic hysteresis and the single fF peak in the $^{55}$Mn NMR spectrum indicate a bulk F phase. Recent TEM imaging actually showed that the size of F domains in La$_{0.5}$Ca$_{0.5}$MnO$_3$ is mesoscopic rather than nanoscopic [3]. In this respect Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ is more similar to low doped La$_{1-x}$Ca$_x$MnO$_3$ ($x < 0.1$), where the nanoscopic dimension of spontaneously segregated hole-rich F droplets was demonstrated by small angle neutron scattering [4]. It is worth noting that both Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ and under-doped La$_{1-x}$Ca$_x$MnO$_3$ present the same A-type AF structure, [11,15], whereas the AF phase of La$_{0.5}$Ca$_{0.5}$MnO$_3$ is charge ordered CE-type. Such a difference might be relevant: since the CO phase is far more insulating than the A-type phase [11,15], the latter may provide a screening mechanism sufficiently effective to cut the long range tails of the Coulomb interactions and to accommodate charged clusters, whereas such a mechanism is ruled out in the insulating CO state.

In conclusion, $^{55}$Mn NMR in the AF state of Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ demonstrates the segregation of nanoscopic ferromagnetic clusters, dressed by a modulation of local spin and charge density at the interface with the host AF matrix. Evidence is provided that the field-induced transition to a ferromagnetic state, detected also by magnetization measurements, is percolative in nature.

This work was partially supported by MURST-Cofin 1997 and EPSRC GR/K95802 grants. Support by Prof. J. Kötzer (IAP, Universität Hamburg) is gratefully acknowledged.

[1] S. Jin et al., Science 264, 413 (1994)
[2] M. Hennion et al., Phys. Rev. B 56 R497 (1997); J. Rodriguez-Carvajal et al., Phys. Rev. B 57, R3189 (1998)
[3] G. Allodi et al., Phys. Rev. B 56, 6030 (1997)
[4] G. Allodi et al., Phys. Rev. Lett. 81 4736 (1998)
[5] S. Mori et al., Phys. Rev. Lett. 81, 3972 (1998)
[6] P. Calvani et al., Phys. Rev. Lett. 81, 4504 (1998)
[7] C. Zener, Phys. Rev. 82, 403 (1951)
[8] A. J. Millis et al., Phys. Rev. Lett. 74, 5144 (1995); A. J. Millis et al., Phys. Rev. Lett. 77, 175 (1996)
[9] Guo-meng Zhao et al., Nature 381, 676 (1996); A. Shengelaya et al., Phys. Rev. Lett. 77, 5296 (1996)
[10] P. G. Radaelli et al., Phys. Rev. B 55, 3015 (1997)
[11] H. Kawano et al., Phys. Rev. Lett. 78, 4253 (1997)
[12] G. Balakrishnan et al., J. Phys.: Condens. Matter 9, L471 (1997)
[13] M. W. Pieper et al., Rev.Sci.Instr. 65, 517 (1994)
[14] P. G. Radaelli et al., Phys. Rev. Lett. 75, 4488 (1995); G. Papavassiliou et al., Phys. Rev. B 55, 15000 (1997)
[15] Y. Tomioka et al., Phys. Rev. Lett. 74, 5108 (1995)
[16] V. Jaccarino, in Magnetism IIA, eds. G. T. Rado, H. Suhl, Academic Press, New York (1965)
[17] M. Sonobe et al., J. Phys. Soc. Japan 61, 4193 (1992)
[18] M. M. Savosta et al., Phys. Rev. Lett. 79, 4278 (1997)
[19] A. Anane et al., J. Phys.: Cond. Matt. 7, 7015 (1995); G. Matsumoto, J. Phys. Soc. Japan 29, 615 (1970)
[20] P. C. Riedi, Hyperfine Int. 49, 335 (1989)
[21] S. Yunoki et al., Phys. Rev. Lett. 81, 5612 (1998)
[22] E. L. Nagaev, Phys. Rev. B 58, 2415 (1998)
[23] E. O. Wollan et al., Phys. Rev. 100, 545 (1955)