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Field- and temperature-controlled magnetic phase separation in $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}Mn^{18}O_3$ manganite as seen by La NMR and magnetization measurements

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We present a detailed La NMR and magnetization study of $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ manganite, in which an insulator-metal transition can be induced by magnetic field and also by oxygen isotope substitution. NMR results demonstrate directly the presence of magnetic phase separation at a local level. The microscopic magnetic structure of the sample depends on cooling conditions [namely, zero field cooling (ZFC) or field cooling (FC)] and can be continuously controlled through the phase separation range by magnetic field and temperature. The magnetic phase diagrams of the sample have been obtained in a wide ranges of fields and temperatures for both ZFC and FC cases.

I. INTRODUCTION

Rare-earth manganites with a perovskite structure $R_{1-x}M_xMnO_3$ demonstrate, in addition to the well known *colossal magnetoresistance* (CMR), a rich variety of physical phenomena such as metal-insulator transition (MIT), charge ordering (CO), and phase separation (PS). The last one is probably the most interesting aspect of doped manganites[1–3] being an intrinsic feature of many systems with strongly correlated electrons.[4] The PS phenomenon was extensively studied and well established in $x=1/2$ substituted compositions $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Sr_{0.5}MnO_3$,[5–8] which represent the boundary between competing ferro- (FM) and antiferromagnetic (AFM) ground states. At the same time, the compositions of lower doping level with the strongest CMR-effect, especially those with Pr and Nd, which are very sensitive to external magnetic field have attracted less attention.[9–11] It is worth emphasizing that PS in these materials (CMR manganites as such) has a large length scale[9] (~ 0.5 μm) in a sharp contrast with the nanoscale length in $La_{0.5}Ca_{0.5}MnO_3$,[5] which probably means a different origin of the PS.

Magnetization measurements provide a very fast, convenient and sensitive but indirect tool for detecting inhomogeneous states. A reliable identification of PS can be obtained only by the local techniques such as electron microscopy,[9] neutron diffraction,[10,12] and NMR.[5] The advantage of NMR consists in a possibility to obtain the quantitative data (as compared to electron diffraction) and to distinguish clearly between the FM and canted AFM moments (which makes a problem for neutron diffraction). Thus the joint magnetization and La NMR study makes use of advantages of both techniques and allows one to obtain an accurate and reliable information concerning a PS in manganites.

In this paper we present an investigation of the PS in $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$, in which MIT is extremely sensitive to magnetic field, pressure and oxygen isotope substitution.[12,13] The material with ^{16}O shows a charge-ordering transition at $T_{co}=180$ K, AFM ordering at $T_N=150$ K and the FM one at $T_c=120$ K. The isotope substituted material with ^{18}O retains the AFM ordering below T_N till the lowest temperatures after zero field cooling (ZFC). At the same time we have shown that at low temperatures after filed cooling (FC) (at $H=7$ T) this sample is practically identical to the completely saturated FM sample with ^{16}O. So, $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}Mn^{18}O_3$ ensures the attainment of both magnetic ground states depending on the cooling down procedures (ZFC or FC) thus offering an excellent model object for a PS study.

II. EXPERIMENTAL

The ceramic sample preparation and isotope enrichment procedures were described in detail in Ref. 13. Powder x-ray diffraction measurements at room temperature indicate that the investigated material was single phase without detectable impurity. Magnetization was measured by a SQUID (Quantum Design) magnetometer in the temperature range 2–300 K at fields up to 7 T. NMR was performed in both zero magnetic field (ZFNMR) and in magnetic fields up to 8.3 T with a home built field-sweep spectrometer by spin-echo technique.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the examples of $M(H)$ plots measured at 5 K for the ZFC and FC (7 T) samples. Two ranges of the field could be separated clearly for the ZFC case with a very different magnetization behavior. In the first range, below the critical field ($H_c\sim 5.3$ T at 5 K), a field-reversible magnetic state is observed with M independent on time. Above H_c the sample turns into a new state which is characterized by a logarithmic M versus time dependence (M increases by about 2% per hour in $H=7$ T at $T=5$ K) and by a hysteresis $M(H)$ behavior. It should be noted that the field diminishing below H_c allows one to fix an additional magnetic moment in the sample, which depends on the maximum field during the cycle, this new magnetic state being again time-independent below H_c.

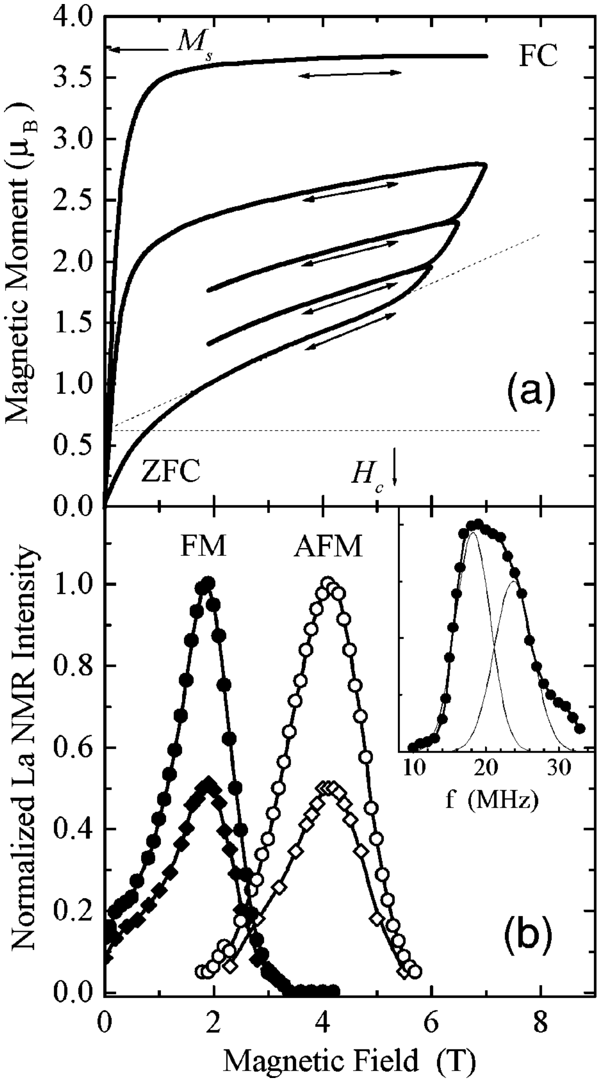

FIG. 1. (a) A hysteresis behavior of $M(H)$ at 5 K in various field cycles. (b) The examples of field-sweep La NMR spectra at 5 K for virgin ZFC sample (open circles), sample cycled to maximum $H=7$ T (open and filled diamonds) and for the FC ($H=8.3$ T) sample (filled circles). In the inset the ZFNMR spectrum of FC sample at 5 K is shown; thin lines represent a double Gaussian fit to the spectrum.

A similar magnetic behavior was first observed in Ref. 14 for $Pr_{0.7}Ca_{0.3}MnO_3$ and later in Ref. 15 for the sample with the same nominal composition as ours.[16] It was proposed in Ref. 15 that the observed ''shifted hysteresis'' and time relaxation behavior of M was ascribed to magnetic PS in the sample. To get a more reliable microscopic proof we undertook a detailed study including traditional magnetometry (SQUID) and La NMR investigation which allowed us to separate unambiguously the signals from the FM and AFM phases in the sample. Taking into account a time relaxation of M above H_c (i.e., in the proposed PS range) and very broad La NMR lines in manganites, we used the following specific measuring procedure. NMR spectra were measured at a fixed operating frequency of 29 MHz while sweeping the magnetic field below H_c. To avoid a possible line shape distortions due to NMR circuit detuning by the sample magnetization (it was important below ~ 1.5 T) we used point-by-point field sweep (in 200 Oe steps) with the periodic tunings of the circuit instead of continuous field sweep. The magnetic phase composition of the sample was changed by a short term field sweep above H_c (to the PS range) and a subsequent decrease of the field down to the stable area with a new magnetic state frozen [see Fig. 1(a)].

The examples of La NMR spectra in our sample at 5 K are shown in Fig. 1(b). The virgin ZFC sample demonstrates an intensive line centered at $H=4.1$ T (the Larmor field is $H=4.8$ T for our operating frequency) with a small rf-enhancement and short spin-lattice ($T_1=10$ ms) and spin-spin ($T_2=50$ μs) relaxation times, which are typical for the AFM state in manganites.[5] At the low-field tail of the line (around $H=2$ T) another signal with very different optimal registration parameters could be separated. The intensity and position of this small peak with a much larger rf-enchancement and longer relaxation times ($T_1=500$ ms, $T_2=200$ μs) could be estimated only roughly (15% of the maximum intensity) due to the overlapping of the lines and the different registration parameters. It is worth noting that the obtained NMR spectrum is independent of any field variations below H_c.

The rise of magnetic field above H_c results in the progressive decrease of the high-field line centered at $H=4.1$ T and the increase of the low-field line at $H=1.9$ T. After cycling the field up to the maximum value ($H=8.3$ T) the high-field line practically disappeared and the low-field one achieved its maximum intensity [Fig. 1(b)]. It is important that only intensities but not the line positions changed during this evolution which proves that only concentrations of the two well defined magnetic phases were changed.

The attribution of the two observed NMR lines is unambiguous and based on different rf-enchancement factors and line positions as discussed in Ref. 5. The low-field line with the large rf-enchancement is originated from the FM phase, where 8 nearest Mn neighbors create the local field of about 3 T at the La site. This internal field value agrees well with the ZFNMR line position measured in the same sample [see inset in Fig. 1(b)]. The high-field line with a smaller rf-enchancement and internal field ($H=0.7$ T) corresponds to the AFM phase.

Figure 2 demonstrates the relative intensities of the two La NMR lines at $T=5$ K as a function of the maximum field in the cycle. The plots show a progressive growth of the FM phase above H_c from a minority phase in the AFM matrix below H_c to a nearly single FM phase at the maximum field with less than 5% of the minor AFM phase contribution. The normalized intensities were obtained by dividing the data to the intensity of the AFM line in the ZFC virgin sample and to the intensity of the FM line in the FC ($H=8.3$ T) sample which is in a completely saturated FM state. A competition between the two phases in the PS range can best be appreciated from the parametric plot, where the concentration of the FM phase is plotted versus that of the AFM phase.

Thus, the La NMR spectra offer a reliable microscopic evidence of magnetic PS in our sample at 5 K. Meanwhile, a NMR experiment is rather complicated and time consuming, especially at higher temperatures. That is why we took NMR data at 5K as a microscopic calibration and used mainly SQUID data for the construction of magnetic phase diagrams. Keeping in mind our NMR results, the $M(H)$ dependence at fixed T in the ZFC sample [see Fig. 1(a)] could be

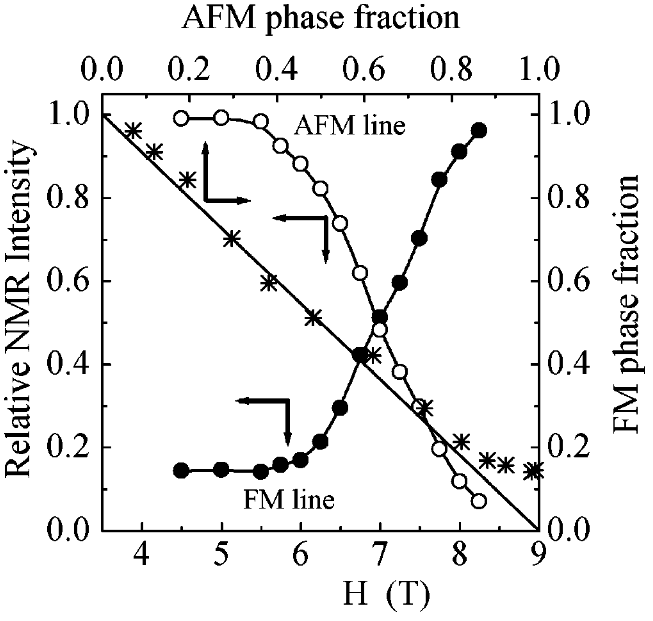

FIG. 2. Relative intensities of the FM and AFM peaks of La NMR spectrum at 5 K for the ZFC sample versus the maximum field in the cycle (left and bottom axis) demonstrating the progressive transformation of the AFM phase to the FM one in a PS state above H_c. The parametric plot (concentration of the FM phase versus that of the AFM one) is also shown (right and top axes).

interpreted in the following way. The initial nonlinear increase of M below ~ 1 T is a consequence of a minor FM phase with a concentration of about 15–20 %, which is in agreement with the NMR data (see above). It is well seen that the concentration of this FM phase decreases with the T-rise. As the field increases above ~ 1 T the FM phase saturates and the $M(H)$ plot has a linear increase as a result of the AFM moment canting. At $H = 4.1$ T, which corresponds to the La NMR line of the AFM phase, this canted moment accounts for 20% of the saturated M_S value in the FM state. This moment should create a local field of $H = 0.6$ T at the La nuclei in the AFM phase. Taking into account a small dipole-dipole contribution of ~ 0.07 T,[17] one has an excellent agreement with the position of the AFM line in Fig. 1(b).

As has already been noted, the linear part of $M(H)$ below H_c implies only an increase of the canted moment in the AFM phase, with concentrations of the main AFM and minor FM phases being field independent. The situation changes drastically above H_c where an additional rise of $M(H)$ means the field stimulated increase of the FM phase concentration at the cost of the AFM one. Eventually, in high fields the virgin AFM phase is nearly suppressed and the sample is completely FM. At 5 K we observed such a saturation of NMR intensity in $H = 8.3$ T and at 40 K it is well seen even in $H = 7$ T on the $M(H)$ plot [Fig. 3(a)].

The important feature of the PS in our sample is a possibility to control the phase composition by magnetic field. To fix the obtained phase composition one needs just to decrease the field below H_c. Here, in the range of stability, the new phase composition depends on neither time nor magnetic field variations. In principle, in our sample one can obtain and stabilize any prescribed phase composition.

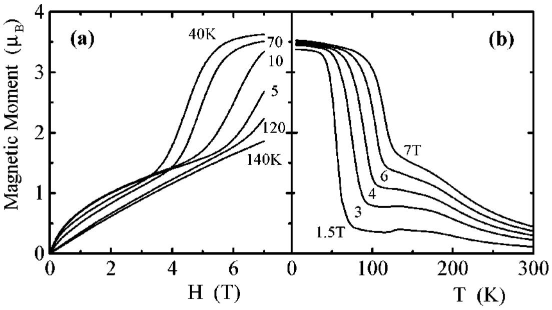

FIG. 3. (a) Magnetization of the $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}Mn^{18}O_3$ sample as a function of the external field at different temperatures. All the plots were obtained when the field was swept from $H = 0$ after ZFC to the prescribed temperature. (b) Magnetization of the sample as a function of temperature at various fields. All the plots were obtained in a warming up process after FC ($H = 7$ T) and decreasing field to the prescribed value at 5 K.

As described above, a magnetic field progressively destroys a virgin (mainly AFM) ground state in the ZFC sample and transforms it into the FM state. A reverse situation is observed in the FC sample demonstrating a field independent FM state at low T, which can be transformed gradually into the AFM state at a warming up process. Figure 3(b) shows the $M(T)$ plots for the FC (at $H = 7$ T) sample warmed up in various fields. The part of the plot with a steep decrease of M corresponds to the PS range, which is supported by our ZFNMR data. It should be noted that the specific features of PS in the ZFC sample, namely, time relaxation of M and a possibility to fix the intermediate phase composition (by the temperature decrease in this case) are observed for the FC sample as well.

Figures 4(a) and 4(b) show the ground-state magnetic phase diagrams of our sample constructed from the La NMR and magnetization data measured over wide field and tem-

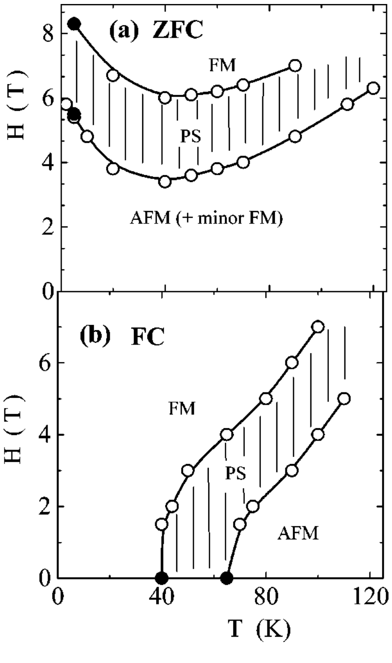

FIG. 4. Magnetic phase diagrams of $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}Mn^{18}O_3$ sample after the ZFC (a) and FC (b) procedures constructed from the results of magnetization (open circles) and NMR (filled circles) measurements.

perature ranges. The data in Figs. 4(a) and Fig. 4(b) refer to the ZFC and FC samples [Figs. 3(a) and 3(b)], accordingly. For the ZFC case the main part of the sample is in a virgin AFM phase below H_c. In the shaded area an irreversible PS state is observed where the AFM and FM phases strongly compete. Above this area the magnetic state is nearly saturated FM. For the FC case a virgin FM state is observed below T_c, which is transformed into the PS state in the shaded area. At higher temperatures the FM phase is completely destroyed and the sample is in the AFM state. The nature of the AFM phase which rather easily converts into the FM metallic phase by magnetic field seems to be $x=1/2$-type CO phase as has been proposed in Ref. 9. (The AFM state of $LaMnO_3$ is completely insensitive to magnetic field Ref. 17.) It seems interesting that the minimum of $H_c(T)$ corresponds to the minimum of $T_c(H)\sim 40$ K, which, in turn, agrees with the Curie temperature for Pr magnetic ordering in our sample.[12] The recent magnetothermal study of $Pr_{0.7}Ca_{0.3}MnO_3$ (Ref. 18) has given an evidence that the coupling of the ordered Pr and Mn spins is essential for better insight into the very high sensitivity of the insulator-metal transition in the Pr-containing doped manganites to various external parameters.

Finally, we discuss a very asymmetric line shape of the ZFNMR spectrum in our FC sample. This spectrum [see inset in Fig. 1(b)] is evidently composed of at least two peaks which means two types of La sites in the sample. A similar asymmetry of La and Mn ZFNMR spectra in manganites was reported earlier[6–8,19] and was attributed to either La sites with various covalence to the nearest Mn ions[19] or to the presence of two FM phases with various doping[6,8] or with different orbital ordering.[20] Unfortunately, neither of these models explains a strong influence of the external magnetic field on the line asymmetry. It is seen from Fig. 1(b), that the asymmetry practically disappears in a rather small magnetic field. The authors of Ref. 19 assigned this effect to the suppression of the AFM-CO state by magnetic field. But in our case the effect is observed in the saturated FM phase which is not sensitive to magnetic field. To our mind the nature of these additional La sites is still an open question.

IV. CONCLUSION

In summary, the joint La NMR and magnetization study of $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ manganite sample enriched in ^{18}O has revealed a specific phase separation behavior controlled by magnetic field and temperature. The ground-state phase diagrams have been obtained for both virgin magnetic states (nearly AFM after ZFC and FM after FC). Some details of the phase separation behavior demonstrate the possible influence of the coupling between the ordered Pr and Mn spins on the insulator-metal transition.

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