Nuclear magnetic resonance study of insulator-metal transitions in $(Pr,Ca)MnO_3$

C. J. Oates,* Cz. Kapusta, and M. Sikora
Department of Solid State Physics, Faculty of Physics and Nuclear Techniques, AGH University of Science and Technology, 30-059 Cracow, Poland

P. C. Riedi
School of Physics and Astronomy, University of St. Andrews, St. Andrews, KY16 9SS, Scotland, United Kingdom

C. Martin, C. Yaicle, and A. Maignan
Laboratoire CRISMAT - UMR 6508, ISMRA et Universite de Caen, 6 Boulevard du Marechal JUIN, 14050 Caen Cedex, France

M. R. Ibarra
Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza-CSIC, Facultad de Ciencias, 50009 Zaragoza, Spain
(Received 17 April 2004; revised manuscript received 3 September 2004; published 21 January 2005)

An NMR study of polycrystalline $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$ ($x=0$ and 0.03) and $Pr_{0.67}Ca_{0.33}MnO_3$ at 3 K is presented. Zero-field spin-echo spectra of the Ga-doped compound consist of an overlapping ^{69,71}Ga signal at 74 MHz (hyperfine field of 5.3 T) and a ^{55}Mn double-exchange (DE) line at 375 MHz (35.5 T). Measurements in an applied field show a steplike increase in the DE line intensity, which corresponds to an increase of the amount of the ferromagnetic metallic phase. This coincides with a steplike feature in the bulk magnetization measurements. The effect is similar to that in the previous field-dependent ^{55}Mn NMR measurements of $Pr_{0.67}Ca_{0.33}MnO_3$. The insulator - metal transition for $Pr_{0.67}Ca_{0.33}MnO_3$, at ambient pressure, occurs at fields greater than 5 T; however, at 1.1 GPa, the DE line corresponding to the ferromagnetic metallic phase is already present at zero field.

DOI: 10.1103/PhysRevB.71.014430 PACS number(s): 76.60.−k, 75.47.Lx, 75.50.−y

INTRODUCTION

The perovskite manganites of general formula $Ln_{1-x}Ca_xMnO_3$(Ln=lanthanide) are of great interest due to their large colossal magnetoresistance, charge and orbital ordering, phase separation, etc.[1,2] The ferromagnetic metallic state in the manganite is explained by the double-exchange (DE) model,[3] where there is fast hopping of the electron (holes) between adjacent Mn^{3+} and Mn^{4+} cations. One of the most interesting features in perovskite manganites is the competing interactions/orders: superexchange antiferromagnetism against DE ferromagnetism, orbital and charge order against metallic state. An external influence, such as a magnetic field or applied pressure, for example, can change their electrical transport properties (e.g., from an insulator to metal) and/or magnetic properties (e.g., from the antiferromagnetic to ferromagnetic state).[4]

$Pr_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.67}Ca_{0.33}MnO_3$, which are the low bandwidth manganites of interest in this article, are very stable charge- and orbital-ordered charge-exchange (CE)-type (moments that are parallel within the plane and antiparallel between the planes) antiferromagnets (AF) at low temperature.[5,6] These compounds exhibit insulator-to-metal transitions at applied fields of 6 and 20 T, for $x=0.35$ and 0.5, respectively.[7,8] It was observed from magnetization and resistivity curves that for $x=0.5$, doping the Mn sites with nonmagnetic cations like Ga or Sn by a few percent, leads to a series of metamagnetic jumps as a function of applied field, and the effect is sensitive to thermal cycling.[9] In undoped Mn compounds, insulator-metal (I-M) transitions can also be induced by applying pressures of 0.5 and 0.8 GPa, for $x=0.3$ and 0.5, respectively.[10,11]

The $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$ ($x=0$ and 0.03) were prepared by solid-state reaction in the CRISMAT Laboratory in Caen, as described in Ref. 9. The $Pr_{0.67}Ca_{0.33}MnO_3$ sample was fabricated by the same method in Universidad de Zaragoza-CSIC.

^{55}Mn NMR studies were carried out in order to shed some light on the microscopic nature of the magnetic-field transitions in $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ and $Pr_{0.67}Ca_{0.33}MnO_3$, as well as pressure-induced transitions in $Pr_{0.67}Ca_{0.33}MnO_3$. NMR spectroscopy probes the microscopic properties through measurements of the hyperfine fields and nuclear relaxation times. From the resonant condition: $\omega=2\pi\nu=\gamma|B_e|$, where ν is the resonant frequency, and the effective field at the nucleus, B_e, is obtained. Previous ^{55}Mn NMR work on manganites, including $(Pr,Ca)MnO_3$,[12] reveal the positions of the ferromagnetic insulating (FMI) Mn^{4+} and Mn^{3+} lines lying in the region of 300–330 MHz and 400–550 MHz, respectively.[12–16] In ferromagnetic metallic (FMM) manganites, fast hopping of the electron (hole) between adjacent manganese cations gives rise to a double-exchange (DE) line, which lies around 370–390 MHz.[13,16,17] As the resonance lines are very broad, frequency swept spin-echo NMR is applied.

The organization of this paper is as follows. The experimental section on NMR "magnetometry" of Ga-doped $Pr_{0.5}Ca_{0.5}MnO_3$ and the discussion of results are presented immediately below. They are followed by the analysis of the NMR study of $Pr_{0.67}Ca_{0.33}MnO_3$ at ambient pressure and at 1.1 GPa, and a brief summary on the results is given at the end.

 ©2005 The American Physical Society

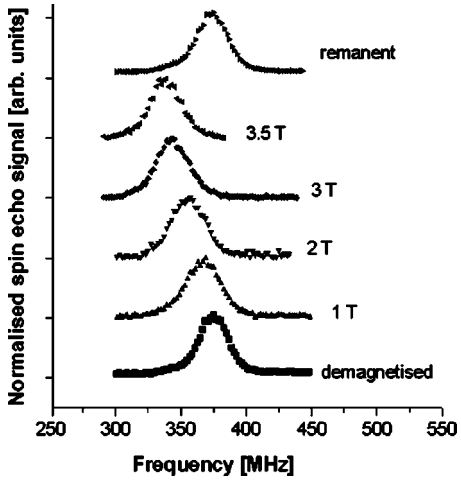

FIG. 1. Zero-field NMR and field-dependence spectra of $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$, at 3 K. The spectra at different fields are normalized to unity.

EXPERIMENTAL AND RESULTS

Magnetic-field-induced transitions in $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$ ($x=0$ and 0.03)

Polycrystalline samples of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$ ($x=0$ and 0.03), the same as those studied previously in Ref. 6, were measured using an automated spin-echo spectrometer[18] at 3 K. The ^{55}Mn NMR spectra are presented in Fig. 1. In the demagnetized state, the Ga-doped sample exhibits a single line centered at 375 MHz, with a corresponding magnitude of hyperfine field (HFF) of 35.5 T ($\gamma/2\pi$ for ^{55}Mn is 10.55 MHz/T). As the line has a similar position to that in metallic manganites it reveals the existence of a DE controlled state in the compound. This corresponds to FMM clusters and an averaged Mn ionic state due to the DE driven electron (hole) hopping within them.[13] The undoped $Pr_{0.5}Ca_{0.5}MnO_3$ sample does not show any measurable signal in the 310–450 MHz range.

Field-dependent measurements of the DE line in $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$, Fig. 1 and later in Fig. 5(b) show that the line shifts to lower frequencies with increasing field and the magnitude of the slope is very close to the gyromagnetic ratio of ^{55}Mn. A negative slope is due to the fact that the manganese hyperfine field is predominantly of Fermi-contact origin and is antiparallel to the Mn magnetic moment and to the applied field.

Figure 2 is a plot of the field dependence of the intensity of the DE line (denoted by filled squares) corrected for the NMR enhancement and nuclear spin-spin relaxation, combined with magnetization curves. The correction for the NMR enhancement is done relatively to the 1-T spectrum. Each spectrum is multiplied by the ratio of pulse length corresponding to the first echo maximum at this field and at 1 T. Moderate changes of the NMR enhancement with the applied field show a lack of typical domain-wall enhancement which indicates that the FMM regions are possibly single domainlike. The plot shows that the "virgin" curve reveals an increase in intensity with increasing field. As the field was raised from 2 to 3 T the intensity of the spin echo jumped by

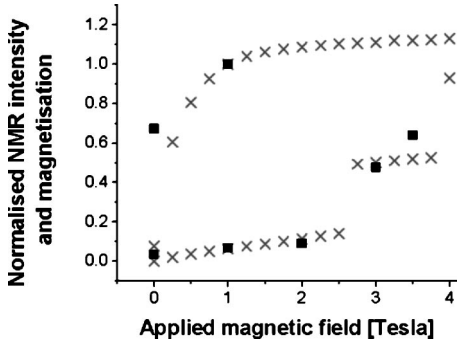

FIG. 2. A plot of the absolute intensity of the spin echo at different field points (black squares), combined with magnetization measurements (dark gray crosses). Both plots are normalized to the corresponding values at 1 T (magnetized from 6 T).

an order of magnitude. This is similar to the steplike feature observed in magnetization measurements, (gray crosses) at 2.5 K, which is attributed to a martensiticlike transition as discussed extensively.[9] The jump in the absolute intensity of the DE NMR line reveals an increase of the amount of the metallic ferromagnetic phase in the compound. The magnetic field was then raised up to 6 T, then lowered to 1 T, and finally to 0 T. The intensity of the DE line at 1 T (magnetized at 6 T) and in the remanent state, is an order of magnitude larger than that at 1 and 0 T on the virgin curve, respectively. This implies that the ferromagnetic metallic phase in the magnetized state has an order of magnitude larger content than that in the demagnetized ("virgin") state. It is worth noting that the NMR intensity in the remanent state departs from the bulk magnetization. This may be understood if we realize that two regions with antiparallel magnetization add in the NMR signal, at zero field, whereas they cancel in the magnetization.

Figure 3 shows the low-frequency part of the NMR spectrum, which is identified as originating from gallium. It corresponds to two gallium isotopes, ^{69}Ga and ^{71}Ga with gyromagnetic ratios (and natural abundances) of 10.2 MHz/T (60.4%) and 12.9 MHz/T (39.6%), respectively. Fitting with two Gaussian lines, with the intensity ratio corresponding to the ratio of natural abundances and the ratio of central frequencies and linewidths corresponding to the relative gyro-

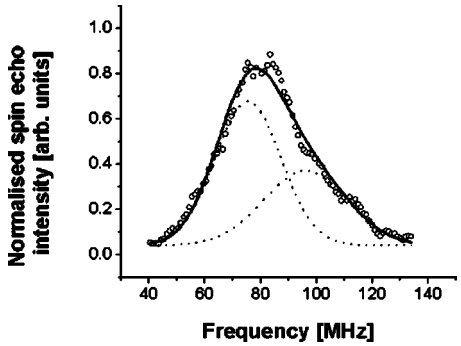

FIG. 3. Low-frequency part of the NMR spectrum corresponding to Ga resonances. The dotted lines correspond to the fitted Gaussian lines for ^{69}Ga and ^{71}Ga isotopes (see text). The solid line is the sum of the ^{69}Ga and ^{71}Ga lines.

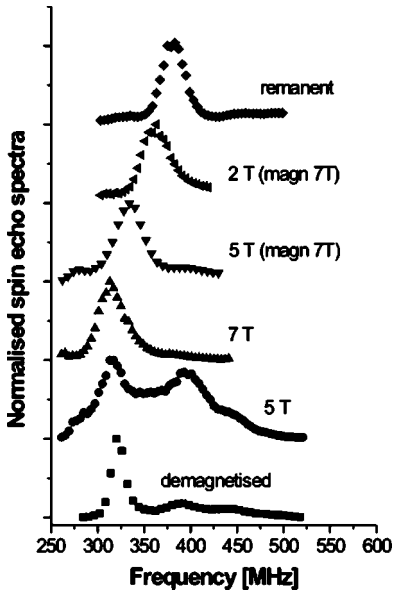

FIG. 4. Field-dependence ^{55}Mn NMR spectra of $Pr_{0.67}Ca_{0.33}MnO_3$ at 3 K and at ambient pressure. The spectra, at different fields, are normalized.

magnetic ratio, provides a value of 5.3 T for the magnitude of the HFF of Ga in $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$. Ga^{3+} ions that occupy *B* (Mn) sites do not carry a magnetic moment and therefore this value can be regarded as a transferred (supertransferred) hyperfine field from magnetic manganese neighbors. This value may seem large for a transferred field; however, previous ^{55}Mn NMR on $La(Ni_{1-x}Mg_x)_{0.5}Mn_{0.5}O_3$ by Sonobe *et al.*[19] have shown that a supertransferred hyperfine field at Mn^{4+} sites from Ni^{2+} magnetic neighbors amounts to 3.8 T.

Magnetic field and pressure-induced transitions in $Pr_{0.67}Ca_{0.33}MnO_3$

This section concerns the $Pr_{0.67}Ca_{0.33}MnO_3$ sample, which was the same sample studied in Ref. 20. As discussed earlier, in the "virgin" state, the $Pr_{0.67}Ca_{0.33}MnO_3$ sample is an antiferromagnetic insulator. Yoshizawa *et al.*[21] showed that for $Pr_{0.7}Ca_{0.3}MnO_3$, at 5 K, there exists a step increase in magnetization at around 3 T and the sample magnetically saturates at fields greater than or equal to 4 T. The spin-echo spectrum of $Pr_{0.67}Ca_{0.33}MnO_3$, at ambient pressure and at zero field, exhibits a Mn^{4+} (313 MHz) signal as well as traces of overlapping DE (381 MHz) and Mn^{3+} (420–500 MHz) resonances (Fig. 4) The FMI lines and the DE line persist at fields up to 5 T. Applying a field up to 5 T gives rise to an increased population of Mn ions in the DE controlled regions compared to the Mn^{4+} and Mn^{3+} states in the insulating regions. Also, the rate of change of the frequency of the DE line with magnetic field is much less than expected from the gyromagnetic ratio of ^{55}Mn. This suggests that the hyperfine field is nearly perpendicular to the applied field. The effect can be understood if we assume a coupling of the Mn moments in the FMI (and DE) regions to the antiferromagnetic insulating (AFI) matrix. For low magnetocrystalline anisotropy antiferromagnets, such as the manganites studied, the moments align perpendicular to the applied field because the susceptibility's perpendicular component is much larger than the parallel component. Thus, the hyperfine field is perpendicular to the applied field, which is an order of magnitude smaller, and the effective field at the nucleus is almost unchanged compared to the situation at zero field. When the field is increased to 7 T the spectrum collapses to a DE line at 313 MHz, which corresponds to a field-induced insulator—to—metal transition. The DE line persists after decreasing the field to zero and the field dependence of the resonant frequency corresponds to a full gyromagnetic ratio of ^{55}Mn [denoted by "×" in Fig. 5(b)], as in other ferromagnetic metallic manganites.

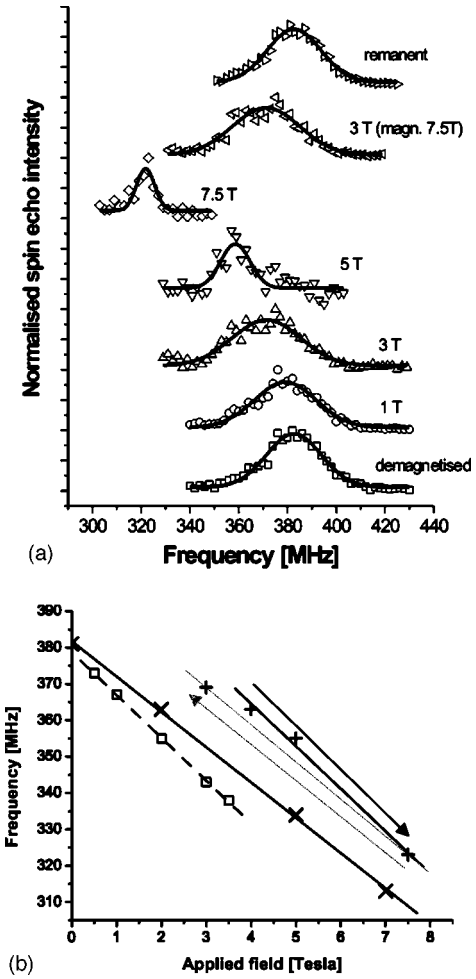

FIG. 5. (a) Field-dependence ^{55}Mn NMR spectra of $Pr_{0.67}Ca_{0.33}MnO_3$ at 3 K and at 1.1 GPa. The spectra, at different fields, are normalized. (b) Resonant frequency of the DE line in $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ and $Pr_{0.67}Ca_{0.33}MnO_3$ vs applied field, with fits to the data, as discussed in the main text. For $Pr_{0.67}Ca_{0.33}MnO_3$, the points represent ambient pressure magnetized from 7 T ("×"), 1.1 GPa from 4 to 7.5 T, and 7.5 to 3 T ("+"). (The black and gray arrows along the lines, for $Pr_{0.67}Ca_{0.33}MnO_3$ pressurized to 1.1 GPa, indicate increasing and decreasing fields, respectively.) "□" denotes the Ga-doped sample magnetized from 6 T.

The $Pr_{0.67}Ca_{0.33}MnO_3$ sample was pressurized to 1.1 GPa in a Cu/Be pressure cell, at RT, with Co powder and the ^{59}Co

NMR frequency as the pressure sensor. Figure 5(a) is a plot of the NMR spectrum at fields from zero to 7.5 T. The spectra consist of a single double-exchange line and applying fields up to 4 T shifts the DE line by as much as 5 MHz/T, as shown in Fig. 5(b) (represented by "+"). However, at 4 T, the DE line is shifted to lower frequencies by 11.7 MHz/T. On decreasing the field from 7.5 to 3 T ("+"), the DE line shifts to higher frequencies by as much as 10.2 MHz/T, which is close to the value expected from the gyromagnetic ratio of ^{55}Mn. It is plausible that 1.1 GPa is not enough to fully achieve the metallic state, as the intensity of the DE line in the demagnetized state is an order of magnitude smaller than in the remanent state after magnetizing the sample up to 7.5 T.

To summarize, an NMR study of the manganese perovskites, $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$ ($x=0$ and 0.03) provided the following information: (a) Ga doping induces ferromagnetic metallic (FMM) regions; (b) the amount of FMM phase in $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ reveals an increase with the applied magnetic field with a steplike behavior which mimics the bulk magnetization curve; (c) the amount of the FMM phase is an order of magnitude larger in the remanent state than in the "virgin" state; and (d) a transferred field from Mn magnetic neighbors of 5.3 T is present at Ga nuclei and can serve as an estimate for the transferred hyperfine field at the Mn site.

For $Pr_{0.67}Ca_{0.33}MnO_3$, at ambient pressure, a very small amount of DE controlled regions is observed at zero field. This amount increases slightly with increasing field and eventually the FMM phase percolates at a field larger than 5 T and persists in the remanent state. By comparing the NMR spectra of the demagnetized $Pr_{0.67}Ca_{0.33}MnO_3$ at ambient and 1.1 GPa, it is clear that a considerable amount of the DE controlled phase is induced at 1.1 GPa. Magnetizing the sample up to 7.5 T, with the sample pressurized at 1.1 GPa, increases this DE controlled phase by an order of magnitude.

The results provide experimental evidence for the microscopic nature of the field-induced insulator-to-metal transition in the charge-ordered manganites, which relies on the increase of the amount of the FMM phase in the applied field.

ACKNOWLEDGMENTS

The work forms part of the EU RTN SCOOTMO, Project No. HPRN-CT-2002-00293. Support from the Engineering and Physical Sciences Research Council, UK and the State Committee for Scientific Research, Poland is gratefully acknowledged.

*Email address: oates@uci.agh.edu.pl

[1] *Colossal Magnetoresistance, Charge Ordering and Related Properties of Magnetic Oxides*, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998).
[2] *Colossal Magnetoresistance Oxides*, edited by Y. Tokura (Gordon & Breach, London, 1999).
[3] C. Zener, Phys. Rev. **82**, 403 (1951).
[4] Y. Tomioka and Y. Tokura, Phys. Rev. B **66**, 104416 (2002).
[5] Z. Jirak, S. Krupicka, Z. Simsa, M. Dlouha, and S. Vratislav, J. Magn. Magn. Mater. **53**, 153 (1985).
[6] C. Yaicle, C. Martin, Z. Jirak, F. Fauth, G. Andre, E. Suard, A. Maignan, V. Hardy, R. Retoux, M. Hervieu, S. Hebert, B. Raveau, Ch. Simon, D. Saurel, A. Brulet, and F. Bouree, Phys. Rev. B **68**, 224412 (2003).
[7] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, and Y. Tokura, Phys. Rev. B **53**, R1689 (1996).
[8] M. Tokunaga, N. Miuro, Y. Tomioka, and Y. Tokura, Phys. Rev. B **57**, 5259 (1998).
[9] A. Maignan, V. Hardy, C. Martin, S. Hebert, and B. Raveau, J. Appl. Phys. **93**, 7361 (2003).
[10] C. Cui and T. A. Tyson, Appl. Phys. Lett. **83**, 2856 (2003).
[11] Y. Moritomo, H. Kuwahara, Y. Tomioka, and Y. Tokura, Phys. Rev. B **55**, 7549 (1997).
[12] G. J. Tomka, P. C. Riedi, Cz. Kapusta, G. Balakrishnan, D. McK Paul, M. R. Lees, and J. Barratt, J. Appl. Phys. **83**, 7151 (1998).
[13] G. Matsumoto, J. Phys. Soc. Jpn. **29**, 615 (1970).
[14] G. Papavassiliou, M. Pissas, M. Belesi, M. Fardis, J. Dolinsek, C. Dimitropoulos, and J. P. Ansermet, Phys. Rev. Lett. **91**, 147205 (2003).
[15] G. Allodi, M. Cestelli Guidi, R. De Renzi, and M. W. Pieper, J. Magn. Magn. Mater. **242**, 635 (2002).
[16] P. A. Algarabel, J. M. DeTeresa, J. Blasco, M. R. Ibarra, Cz. Kapusta, M. Sikora, D. Zajac, P. C. Riedi, and C. Ritter, Phys. Rev. B **67**, 134402 (2003).
[17] M. M. Savosta, P. Novak, and Z. Jirak, Phys. Rev. B **67**, 100411(R) (2003).
[18] J. Lord and P. C. Riedi, Meas. Sci. Technol. **6**, 149 (1995).
[19] M. Sonobe and K. Asai, J. Phys. Soc. Jpn. **61**, 4193 (1992).
[20] Cz. Kapusta and P. C. Riedi, J. Magn. Magn. Mater. **196**, 446 (1999).
[21] H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, Phys. Rev. B **52**, R13 145 (1995).