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An NMR study of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$ ($x = 0$ and 0.03)

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An NMR study of polycrystalline $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$ ($x = 0$ and 0.03) 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), a ^{55}Mn double exchange line at 375 MHz (35.5 T) and a weak Mn^{3+} signal between 400 and 550 MHz. Measurements in an applied field show a step-like increase in the double exchange line intensity, which corresponds to an increase in the amount of the ferromagnetic metallic phase. This coincides with a step-like feature in the bulk magnetization measurements. The effect is similar to that in the previous field dependent ^{55}Mn NMR measurements of $Pr_{0.67}Ca_{0.33}MnO_3$. At the demagnetized and remanent state, a variation of spin–spin relaxation time, T_2, across the ^{55}Mn line, due to the Suhl–Nakamura interaction is observed, which suggests that the ferromagnetic metallic double exchange regions, at liquid helium temperatures, are at least 4 nm in size.

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1. Introduction

The perovskite manganites of general formula $Ln_{1-x}Ca_xMnO_3$ (Ln = lanthanide) are of great interest due to their large variety of structural and magnetic

properties [1], including colossal magnetoresistance (CMR). For Pr and Ca in the region of $x \approx 0.5$, charge ordering (CO) and orbital ordering (OO) takes place among the Mn^{3+} and Mn^{4+} cations, which is accompanied by antiferromagnetic (AFM) ordering of CE type. For $Pr_{0.5}Ca_{0.5}MnO_3$ compound a magnetic field as high as 20 T is required to collapse the CO state [2]. A method of introducing CMR in such systems is to substitute the Mn sites with foreign cations. In such a way the collapse of the charge and orbital ordering of the Mn^{3+} and Mn^{4+} ions can be controlled. One particular example of interest is $Pr_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$, where M = Ga, Cr, Ru, Al...[3]. It was observed for Ga doping that for x of 0.03 the magnetization and resistivity curves at low temperatures show a series of jumps as a function of applied field [4] and the effect is found to be sensitive to thermal cycling [5]. In addition, the temperature of the OO/CO transition is smaller than that of $Pr_{0.5}Ca_{0.5}MnO_3$ ($T_{OO/CO} = 250$ K). The inverse susceptibility curves exhibit two hysteretic regimes. One of them corresponds to the temperature region $30 < T < 100$ K and is connected to a structural transformation from the distorted OO/CO phase to the less distorted ferromagnetic phase. The other regime, which corresponds to the temperature region $100 < T < 230$ K, reflects the structural transition associated to OO/CO [5].

In order to shed some light on the microscopic nature of the magnetic field induced transitions an NMR study has been undertaken in the present work. Polycrystalline samples of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$ ($x = 0$ and 0.03) were measured using the spin-echo spectrometer [6] at 3 K. NMR spectroscopy probes the microscopic properties through measurements of the hyperfine fields and nuclear relaxation times. From these quantities, information on the ionic and magnetic state of the atom and its near neighborhood can be derived. From the resonant condition: $\omega = 2\pi\nu = \gamma|B_e|$, where ν is the resonant frequency, the effective field at the nucleus, B_e, is obtained. In the magnetically ordered state, this field is mostly of hyperfine origin and is usually termed the hyperfine field (HFF). Nuclear relaxation parameters include the spin–lattice, T_1, and spin–spin, T_2, relaxation times, which are usually determined by carrying out the recovery time and the spin echo versus pulse spacing measurements, respectively.

2. Results and discussions

The ^{55}Mn NMR spectra of $Pr_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ samples are presented in Fig. 1. It shows that the absolute intensity of the NMR signal of the Ga doped sample is four orders of magnitude greater than that of the undoped sample. The Ga doped sample exhibits a single line centered at 375 MHz, with corresponding hyperfine field of 35.5 T. As the line has a similar position to that in metallic manganites it reveals the existence of a double exchange (DE) controlled state in the compound. This corresponds to ferromagnetic metallic (FMM) clusters and an averaged Mn ionic state due to the DE driven electron (hole)

hopping within them [7]. The Ga doped sample also exhibits a weak Mn^{3+} signal that extends from 400 to 550 MHz and presents a broad range of hyperfine fields that may be due to the anisotropy of the hyperfine field of the Mn^{3+} ion [8]. The manganese NMR signal of $Pr_{0.5}Ca_{0.5}MnO_3$ shows very weak signals at 251 MHz and 293 MHz due to Mn^{4+} ions in antiferromagnetic and ferromagnetic regions (ferromagnetic zig-zag chains antiferromagnetically coupled), respectively.

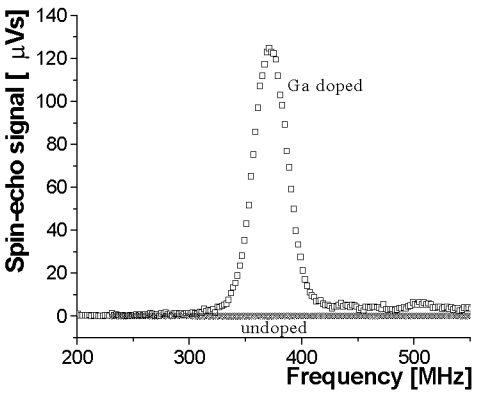

Fig. 1. ^{55}Mn NMR spectra of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$, with $x = 0$ (×) and $x = 0.03$ (□), at 3 K.

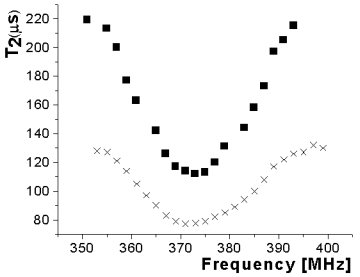

Fig. 2. Spin–spin relaxation time, T_2, of $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ against frequency at 3 K, in demagnetized (■) and magnetized (×) state.

The spectra of $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ obtained for large pulse separation show a minimum at the center of the resonant line, which is due to a variation of relaxation time, T_2, across the resonant line. A plot of T_2 versus frequency, Fig. 2 (■), shows that it differs by a factor of two between the wings and the center of the resonance line and reaches its lowest value of 110 μs at the line center. Such an effect is caused by the exchange of virtual magnons between nuclear spins due to the Suhl–Nakamura (SN) interaction [7, 9]. As the central part of the resonance line corresponds to manganese atoms inside the DE clusters, it means that the magnetic state of manganese neighbors is identical to that of the probe

atom allowing for an effective exchange of virtual magnons between nuclear spins. The presence of a minimum of T_2 at the line center means that the size of the interior of DE clusters is comparable or larger than the effective range of the Suhl–Nakamura interaction. The radius of the effective SN interaction is defined as $b = a(B_{\mathrm{exch}}/B_{\mathrm{anis}})^{1/2}$ [10], where B_{exch}, B_{anis}, and a are the exchange field, the magnetic induction of the anisotropy field, and the Mn–Mn distance (of 3.8 Å), respectively. Following previous works in determining the radius of SN interaction [11], one obtains the value of b of 4 nm and this allows us to conclude that the DE clusters in the compound studied are of the size of 4 nm or larger.

Field dependent measurements of the DE line in $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$, Fig. 3, show that the line shifts to lower frequencies with increasing field and the magnitude of the slope is close to the gyromagnetic ratio of ^{55}Mn. A negative slope is due to the fact that the manganese hyperfine field is of the Fermi contact origin and is antiparallel to the Mn magnetic moment (and to the applied field). Figure 4 is a plot of the field dependence of the intensity of the DE line corrected for the enhancement factor and nuclear spin–spin relaxation, combined with magnetization curves. The plot shows that the "virgin" curve (denoted by ■) reveals an increase in intensity with increasing field. As the field was raised from 2 T to 3 T, the inten-

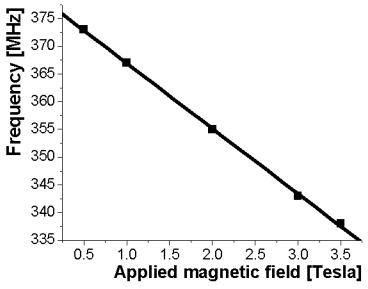

Fig. 3. Resonant frequency of the DE line in $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ versus applied field.

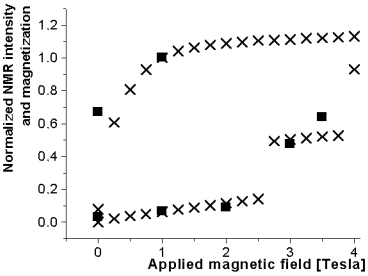

Fig. 4. A plot of the absolute intensity of the spin echo at different field points (■), combined with magnetization measurements (×). Both plots are normalized to the corresponding values at 1 T (magnetized from 6 T).

sity of the spin echo had jumped by an order of magnitude. This is similar to the step-like feature observed in magnetization measurements (×), at 2.5 K [5], which is attributed to a martensitic-like transition as discussed extensively in Ref. [12]. The jump in the absolute intensity of the DE NMR line reveals an increase in 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 T 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.

One should note that this feature is similar to that observed in the previous NMR study of the magnetic state of $Pr_{0.67}Ca_{0.33}MnO_3$ [8]. At the "virgin" state, the $Pr_{0.67}Ca_{0.33}MnO_3$ sample is an antiferromagnetic insulator [13] with a Mn^{4+} signal and traces of Mn^{3+} and DE resonances, Fig. 5. Applying a field up to 5 T gives rise to an increased population of Mn ions in the DE controlled regions ([13] and Fig. 2 therein). When the field is increased to 7 T the spectrum collapses to a DE line, which corresponds to a field-induced insulator-to-metal transition. The DE line remains after decreasing the field to zero and the field dependence of the resonant frequency corresponds to a full gyromagnetic ratio of ^{55}Mn, as in the other metallic ferromagnetic manganites.

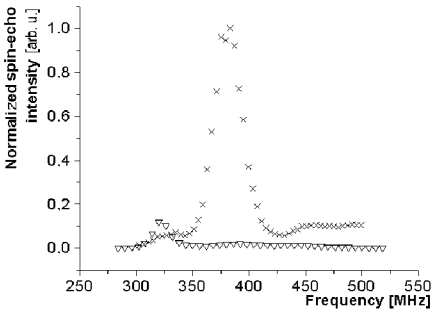

Fig. 5. NMR spectra of the demagnetized (∇) and remanent (×) state of $Pr_{0.67}Ca_{0.33}MnO_3$. The spectrum of the demagnetized state was normalized to that of the remanent state.

The spin–spin relaxation time at the center of the Mn resonance line of $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ at remanence is 78 μs, Fig. 2 (represented by ×), which is smaller than that for the "virgin" state. The value of T_2 at the wings is almost twice that of the minimum, which is similar to that in the "virgin" state and shows that the size of DE regions is comparable or larger than the effective radius of the Suhl–Nakamura interaction; that is, at least 4 nm, similarly to that in the "virgin" state. A smaller absolute value of T_2 in the magnetized state can be related to a possible influence of magnetic fluctuation from the adjacent DE regions due to their much closer distances in the remanent state.

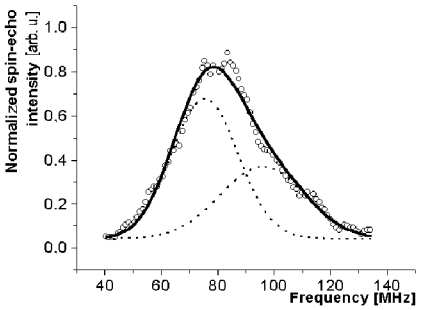

Fig. 6. Low frequency part of the NMR spectrum corresponding to Ga resonances. Dotted lines correspond to the fitted Gaussian lines for ^{69}Ga and ^{71}Ga isotopes (see text). Solid line is the sum of ^{69}Ga and ^{71}Ga lines.

Figure 6 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 10.21 MHz/T (60.4%) and 12.98 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 line widths corresponding to the relative gyromagnetic ratio, provides a value of gallium's hyperfine field, which is 5.3 T. Ga^{3+} ions, which occupy B (Mn) sites do not carry a magnetic moment and therefore this value can be regarded as a transferred hyperfine field from magnetic manganese neighbors.

3. Conclusions

NMR study of the manganese perovskites, $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$ provided the following information:

- Ga doping induces ferromagnetic metallic regions,
- 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 step-like behavior which mimics the bulk magnetization curve,
- The amount of the FMM phase is an order of magnitude larger in the remanent state than in the "virgin" state,
- Promotion of the FMM phase by the applied field is similar to that in $Pr_{0.67}Ca_{0.33}MnO_3$ where a magnetic field induced insulator-to-metal transition was observed,
- A Suhl–Nakamura effect in the spin–spin relaxation time T_2 is observed for the Mn resonance line at both the demagnetized and remanent state and reveals that the size of FMM regions is at least 4 nm,
- A transferred HFF from Mn magnetic neighbors of 5.3 T is present at Ga nuclei and can serve as an estimate for the transferred HFF at the Mn site.

Acknowledgments

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