

## Two-Phase Character of Metallic Ferromagnetism in Manganites

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$^{55}\text{Mn}$  NMR spectra of several ferromagnetic manganites, including  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ , were measured as a function of temperature. A thorough analysis of the spin-spin relaxation and the NMR line shape revealed that in these compounds two different ferromagnetic phases coexist below  $T_C$  in a certain temperature interval which depends on the composition. The phase with lower hyperfine field has faster nuclear relaxation, its characteristic dimension is a few nm, and its volume decreases with decreasing temperature. The NMR lines of both phases are motionally narrowed, i.e., the electron holes are mobile.

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Recently several papers appeared in which it was found that the ferromagnetic (FM) phase in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  has a complex character. Muon spin relaxation [1] in the  $x = 0.33$  compound showed that at least two spatially separated FM regions exist, which possess temperature-dependent volumes and very different Mn-ion spin dynamics. The phase with more slowly fluctuating spins is relatively more insulating (though localized  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions were not found), the characteristic length scale of the regions of this phase is very small (less than 3 nm), and its volume decreases when the temperature is lowered. Two FM phases,  $M_1$  and  $M_2$ , were also observed using the Mössbauer spectroscopy in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}^{(57}\text{Co})\text{O}_3$  [2]. The volume of the phase  $M_2$  possessing a smaller hyperfine field decreases with decreasing  $T$ . This is in agreement with the above-mentioned muon results, as a smaller hyperfine field indicates weaker double-exchange interaction and thus slower motion of the electron holes. In the compound with smaller Ca content ( $x = 0.2$ ), only the  $M_1$  phase and the superparamagnetic clusters were found. Using  $^{55}\text{Mn}$  NMR, Papavassiliou *et al.* [3] investigated the FM phases for  $x = 0.25, 0.33$ , and  $0.5$ . In all three compounds two FM phases were found to coexist below  $T_C$ . One of the phases is claimed to be insulating and it disappears  $\approx 70$  K below  $T_C$ . In this paper we report a study of the FM phases in the  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  system and also in several other manganites. The study is based on a thorough analysis of the  $^{55}\text{Mn}$  NMR line shape and relaxation. Our NMR results correspond to the two-phase situation for  $T \rightarrow T_C$  and we found that this is a rather general feature of the metallic FM state in manganites.

The NMR spectra were recorded by a two-pulse spin-echo method using a noncoherent spectrometer with frequency sweep and boxcar detector signal averaging. At low temperatures, nuclei in both domains and domain walls contribute to the NMR signal. Radio frequency enhancement for nuclei in the walls is an order of magnitude larger than the one in the domains [4], which allows us

to choose the experimental conditions so that the contribution of the nuclei in the domains dominates. Moreover, at higher temperatures ( $T \gtrsim 120$  K) the relaxation of the nuclear spins in the domain walls is so fast that the spins' signal is no longer detected. In what follows the signal arising from the nuclei in the FM domains only is discussed. The polycrystalline samples  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  used in this paper were described in Ref. [5].  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  was prepared using the same technology. The Curie temperature for this sample, determined as the inflection point of the susceptibility curve, is 235 K. In addition, the single crystal  $\text{Pr}_{0.51}\text{Sr}_{0.49}\text{MnO}_3$  prepared by the floating-zone method was employed in this paper. The low-temperature state of the last compound is an A-type antiferromagnetism, though a minority FM phase (3%) is also present. On warming,  $\text{Pr}_{0.51}\text{Sr}_{0.49}\text{MnO}_3$  first undergoes a transition to bulk ferromagnetism at  $T_N \sim 125$  K, and then to a paramagnetic state at  $T_C = 265$  K [6].

$^{55}\text{Mn}$  NMR spectrum of FM, metalliclike manganites was found to consist of a single line that is caused by a motional narrowing—electron holes hop over the manganese sites with a frequency much higher than the NMR frequency, and as a result all  $^{55}\text{Mn}$  nuclei feel the same average hyperfine field [7]. The NMR spectrum is obtained by measuring the integrated intensity of the spin echo versus frequency. The spin echo appears after a two-pulse sequence consisting of exciting and refocusing radio frequency pulses separated by a time interval  $\tau$ . The intensity of the spectrum is proportional to  $\exp(-2\tau/T_2)$ , where  $T_2$  is the spin-spin relaxation time. The nuclear spin-spin relaxation in manganites is strongly temperature dependent and it may be explained by fluctuations of the hyperfine field caused by the hopping of the electron holes [4]. At lower temperatures an additional contribution to  $T_2$ , due to the Suhl-Nakamura (SN) relaxation mechanism [8], is observed. This mechanism results from the indirect spin-spin coupling mediated by virtual spin waves. SN possesses

a characteristic frequency dependence of  $T_2$  with a minimum occurring just in the center of the NMR line because the majority of nuclear spins precess at or near this frequency. Accordingly, a symmetrical double-peaked line shape is detected for sufficiently large  $\tau$ , when part of the nuclear spins relax during the pulse sequence and do not contribute to the echo signal. To illustrate this situation the set of spectra in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  taken at 105 K using different  $\tau$  and the frequency dependence of  $T_2$  is shown in Figs. 1a and 1b.

The spin waves excited by the hyperfine interaction are limited to low temperatures only. This fact, together with the increasing contribution of the hopping, leads to an equalization of the  $T_2(f)$  dependence. Finally, at high enough temperatures,  $T_2$  is frequency independent and consequently the form of the NMR spectra does not depend on  $\tau$  (Figs. 1c and 1d). The data in Figs. 1a–1d correspond to the usual pattern of a single-phase system. We have found that, in a number of FM manganites besides the SN relaxation, another frequency-dependent nuclear spin dynamics exists. Namely, a monotonic increase of  $T_2$  with increasing frequency appears, which manifests itself in a narrowing of the spectrum when the time interval  $\tau$  is increased. As an example, in Fig. 2a the NMR spectra of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  at  $T = 200$  K are displayed for several values of  $\tau$ . As seen in Fig. 2a, the width of the spectrum first decreases with increasing  $\tau$ , but then remains constant after  $\tau$  surpasses a certain critical value. The simplest interpretation, which represents this dependence fairly well, is to assume that the NMR signal consists of two lines, which possess different  $T_2$ . For sufficiently large  $\tau > 14 \mu\text{s}$  only the line possessing larger  $T_2$  contributes and the spectra can be fitted by a single Gaussian line  $A_1$ , centered at 322 MHz, with a half width of 22.4 MHz and  $T_2 = 6.86 \mu\text{s}$ . The contribution of faster relaxing nuclear spins can then be determined by subtracting  $A_1(\tau)$  from the experimental spectrum (solid curves in Fig. 2b). This

contribution can also be fitted by a Gaussian line  $A_2$  centered at 307.3 MHz with the same half width as the line  $A_1$ , but shorter  $T_2 = 4.1 \mu\text{s}$ .

In Fig. 2c the mean relaxation time  $T_2^*$  is displayed as a function of the resonance frequency [the difference  $T_2(A_1) - T_2(A_2)$  is too small to resolve clearly the two exponentials when measuring spin-echo decay at fixed frequency]. The constant value of  $T_2^*$  above 325 MHz corresponds to the relaxation of the  $A_1$  line, while the decrease of  $T_2^*$  below 325 MHz reflects the change of the relative weights of nuclei possessing shorter and longer  $T_2$ . It is interesting to note that the data in Fig. 2c indicate the existence of a small fraction of nuclei with still faster relaxation than found for the line  $A_2$ . Keeping in mind this delicate circumstance, in what follows we nevertheless use the two-line decomposition, as it represents a good approximation for most of the NMR data.

The two-line character of the NMR spectra suggests that the compound in question contains two different FM phases,  $A_1$  and  $A_2$ , which give rise to the lines at higher and

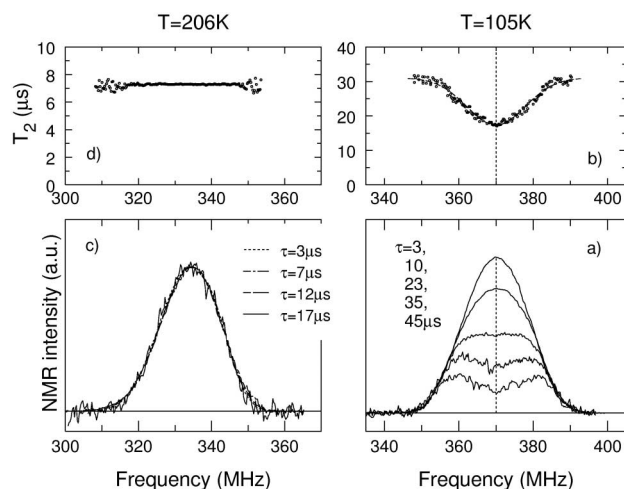


FIG. 1.  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ .  $^{55}\text{Mn}$  NMR spectra at two different temperatures and for several values of the time interval  $\tau$ . The frequency dependence of the spin-spin relaxation time  $T_2$  is shown in the upper panels.

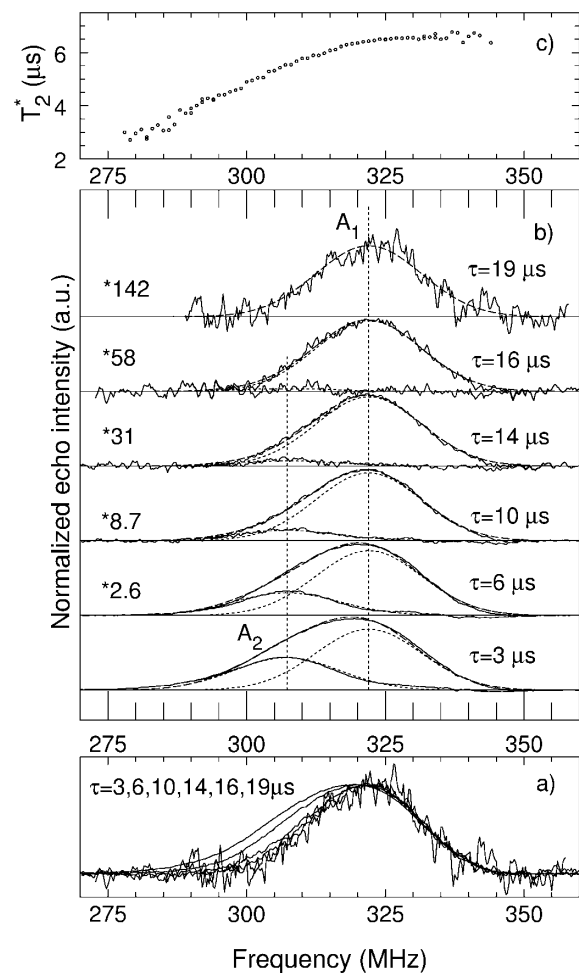


FIG. 2.  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ,  $T = 200$  K. (a) NMR spectra for several values of  $\tau$ . (b) Decomposition of the spectra on two Gaussian lines  $A_1$  and  $A_2$  (dotted curves). The solid curve, corresponding to the  $A_2$  line, resulted from the subtraction of the  $A_1$  line (dashed curve) from the experimental spectrum. (c) Frequency dependence of the mean relaxation time  $T_2^*$ .

lower frequencies, respectively. Phase  $A_2$  is characterized by shorter  $T_2$ , i.e., faster dynamics of Mn nuclear spins, which implies slower hopping of Mn electron holes [4]. We also observed that NMR enhancement for this phase is approximately 2 times smaller, indicating larger magnetic anisotropy. These NMR characteristics are in agreement with the muon and Mössbauer results [1,2] for the relatively more insulating phase.

By using the decomposition of the NMR spectra described above, the relative volume of the phases  $A_1$  and  $A_2$  can be determined by extrapolating their amplitudes to  $\tau = 0$ . The temperature dependence of the relative volume of phase  $A_1$  obtained in this way for four different manganites is displayed in Fig. 3a. The difference of NMR frequency of  $A_1$  and  $A_2$  lines is shown in Fig. 3b. In all these compounds the relaxation time  $T_2$  (not shown) decreases approximately exponentially with the temperature, as reported earlier for the (La, Na) system [4], and in the whole temperature range the ratio  $T_2(A_1)/T_2(A_2)$  is between 1.3 and 2. The integrated area of the NMR signal corrected for  $T_2$  and  $1/T$  dependence of the intensity, which follows from the Curie law for the nuclear magnetic moment, is nearly constant at all temperatures for FM samples, thus indicating that NMR probes the whole sample volume. The volumes of  $A_1$  and  $A_2$  phases are comparable, their ratio approaching 1 for  $T \rightarrow T_C$  (Fig. 3a). Close to  $T_C$  the accuracy of the NMR spectra decomposition is limited by shortening  $T_2$ —even for the shortest available  $\tau \approx 2.5\text{--}3 \mu\text{s}$  the contribution of line  $A_2$  to

the measured signal is rather small. In  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  the two-phase state exists in the whole temperature interval studied, while  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  becomes single phase below  $0.6T_C$  ( $\approx 220 \text{ K}$ ). This may indicate that larger disorder in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  produced by the difference of the  $\text{La}^{3+}$  and  $\text{Ca}^{2+}$  ionic radii favors the two-phase state. The temperature dependence of the relative volume of  $A_1$  in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  determined from NMR agrees well with both the data of muon spin relaxation and the data of Mössbauer spectroscopy (inset of Fig. 3a). Also, the substantial narrowing of the temperature interval of the two-phase coexistence for  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  compared to  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  is consistent with the single FM state observed in the  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  sample [2]. The transition from a low-temperature single-phase state to a two-phase state in  $\text{Pr}_{0.51}\text{Sr}_{0.49}\text{MnO}_3$  is accompanied by a transition to bulk ferromagnetism, giving rise to a strong increase of the FM NMR signal. The detailed results will be published elsewhere.

In principle, the frequency difference  $\Delta f$  of the  $A_1$  and  $A_2$  lines (Fig. 3b) might arise either from the different hole mobility (and consequently different double exchange) or from the different  $e_g$  electron density in the two phases in question. In the latter case it would be difficult, however, to reconcile the hole-depleted regions with the more conductive character of the  $A_1$  phase, since higher resonance frequency implies lower  $\text{Mn}^{4+}$  content [9]. We therefore attribute  $\Delta f$  to a stronger double exchange and, accordingly, to the larger spin value at finite temperatures in the phase  $A_1$  compared to the phase  $A_2$ . This explanation is supported by the tendency  $\Delta f \rightarrow 0$  when  $T \rightarrow 0$ .

We note that the SN relaxation is effective in the  $A_1$  phase, but not in the  $A_2$  phase. This is documented in Fig. 4a, where the NMR spectra in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , measured using  $\tau = 3 \mu\text{s}$  (both  $A_1$  and  $A_2$  contribute) and  $\tau = 45 \mu\text{s}$  (only  $A_1$  contributes), are shown at  $T = 140 \text{ K}$ , when the SN relaxation starts to develop. It is clearly seen (Fig. 4b) that the minimum in  $T_2$  occurs just in the center of the  $A_1$  line, indicating that only this phase is influenced by the SN relaxation. At lower temperatures the dip of  $T_2$  develops in the middle of the  $A_1$  line and it is deeper than the  $T_2$  stretch from the  $A_2$  phase (inset of Fig. 4b), thus confirming that in the center of the  $A_1$  line an additional SN relaxation mechanism is present, while it is missing in the  $A_2$  signal. The effective radius of the SN interaction for a cubic ferromagnet [10,11] is given by  $b_0 \sim a(B_e/B_a)^{1/2}$ , where  $B_e$  is the effective exchange field,  $B_a$  is the anisotropy field, and  $a \approx 3.86 \text{ \AA}$  is the lattice parameter. The estimation of  $b_0$  in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  at  $140 \text{ K}$  can be made as follows. By taking the spin-wave stiffness constant  $D_{T=140 \text{ K}} \approx 140 \text{ meV \AA}^2$  [12], we get  $B_e = D/(a^2 g \mu_B) = 81.2 \text{ T}$ .  $B_a$  can be obtained by using the expression for the enhancement factor  $\eta = B_{\text{hf}}/B_a$  [11]. The hyperfine field  $B_{\text{hf}}$  is related to the resonance frequency  $f$  by  $f = \gamma/(2\pi)B_{\text{hf}}$ , where  $\gamma/(2\pi) = 10.6 \text{ MHz/T}$  for the  $^{55}\text{Mn}$  nuclei. Values  $f = 347 \text{ MHz}$  (Fig. 4a) and  $\eta \approx 500$  for the  $A_2$  phase

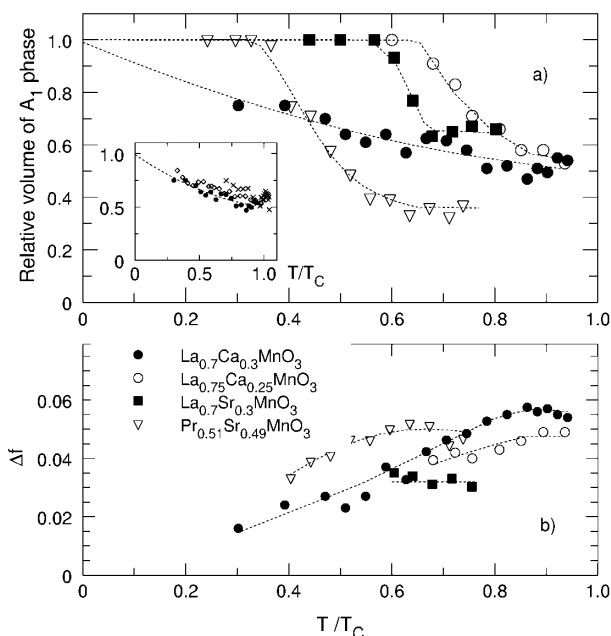


FIG. 3. Relative volume of the  $A_1$  phase defined as  $A_1/(A_1 + A_2)$  (a) and relative difference of the resonance frequencies  $\Delta f = 2[f(A_1) - f(A_2)]/[f(A_1) + f(A_2)]$  (b) as functions of the reduced temperature for four different manganites. In the inset of (a) the data of this work for  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  (●) are compared with the muon spin relaxation (×, [1]) and the Mössbauer spectroscopy (◇, [2]). The data for the (Pr, Sr) compound correspond to the FM phase only.

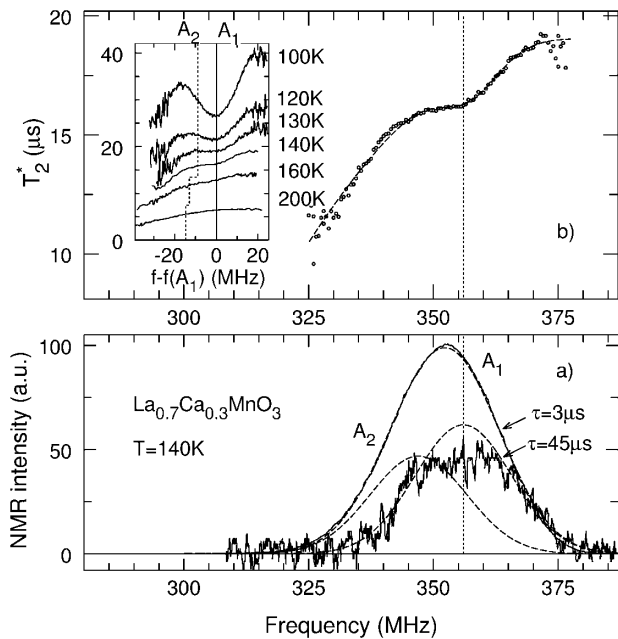


FIG. 4.  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ . (a) NMR spectra and their decomposition at  $T = 140$  K for two values of  $\tau$ . (b) Frequency dependence of the mean relaxation time  $T_2^*$ . In the inset of (b),  $T_2^*$  at several temperatures is displayed as a function of  $f - f(A_1)$ .

yield  $B_a = 0.065$  T. These values of  $B_e$ ,  $B_a$ , and  $a$  then result in the effective radius of spin-spin interaction  $b_0 \sim 35$  Å. The absence of the SN relaxation in the  $A_2$  phase indicates that this phase exists in spatially separated regions with a very small characteristic size,  $\approx b_0$ —a conclusion analogous to that obtained from the muon results [1].

The microscopic intertwining of the two phases results in a smooth shape of the NMR spectrum, and the  $A_1$ ,  $A_2$  lines can be distinguished only by using their different dynamic behavior. As an example, the  $^{55}\text{Mn}$  NMR spectra of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  at various temperatures taken at  $\tau = 3 \mu\text{s}$  are shown in Fig. 5 together with the two-line decomposition based on the analysis of the line shapes at different  $\tau$  [13]. A simple estimation shows that for clusters with the characteristic size  $\sim 10a$  the number of nuclei on the cluster surface is comparable with their number in the inner volume. As a consequence a distribution of the resonance frequencies giving rise to a smooth NMR line shape is expected in the  $A_2$  phase. It is also not surprising that part of the  $^{55}\text{Mn}$  in this phase may possess a different, shorter relaxation time, as mentioned above.

For the purpose of our paper, we remeasured the NMR of several other manganites, with an emphasis on the line shape. The two-phase character of ferromagnetism was detected in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (the results are analogous to  $x_{\text{Ca}} = 0.3$ ),  $\text{La}_{0.7}\text{Ca}_{0.15}\text{Sr}_{0.15}\text{MnO}_3$  (phases  $A_1, A_2$  coexist above temperature  $T_{\text{tp}} \approx 180$  K),  $\text{La}_{0.7}\text{Ca}_{0.15}\text{Ba}_{0.15}\text{MnO}_3$  ( $T_{\text{tp}} \approx 140$  K), and  $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$  (for  $x = 0.1, 0.15$ , and  $0.20$ ;  $T_{\text{tp}} \approx 200, 240$ , and  $160$  K). The NMR spectra consisting of  $A_1$  and  $A_2$  lines in a broad temperature interval were also observed in the minority FM phase of the

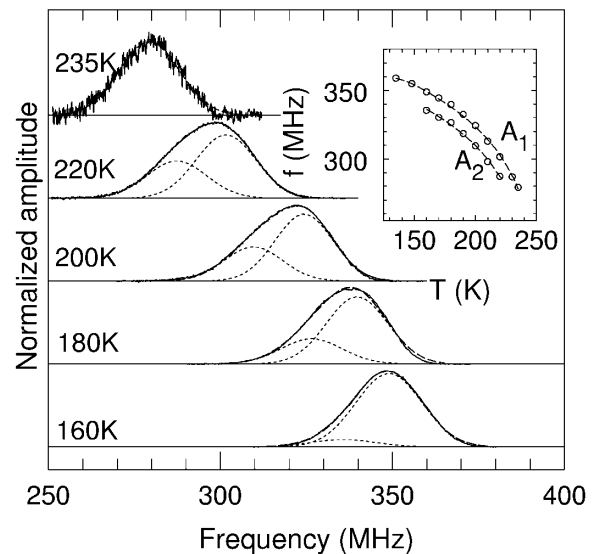


FIG. 5.  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ . NMR spectra and their decomposition for five different temperatures. In the inset the temperature dependence of the resonance frequencies of lines  $A_1$  and  $A_2$  is shown.

system  $\text{Pr}_{0.5}\text{Ca}_{0.5-x}\text{Sr}_x\text{MnO}_3$  [ $x = 0.15, 0.2, 0.3$  (see [15] for  $x = 0.3$ )] containing  $\approx 50\%$  of  $\text{Mn}^{4+}$ .

In summary, two different ferromagnetic phases were shown to coexist in a number of different manganites. In both phases the charge carriers are mobile. The less conductive phase has faster nuclear spin relaxation and its characteristic dimensions are in the nanoscale region.

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