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Ferromagnetic-antiferromagnetic transition in $Pr_{0.51}Sr_{0.49}MnO_3$ manganite

M. M. Savosta and V. A. Borodin
Donetsk Institute of Physics & Technics, Academy of Sciences of Ukraine, Rozy Luxembourg 72, 83114 Donetsk, Ukraine

M. Maryško, Z. Jirák, J. Hejtmánek, and P. Novák
Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Praha 8, Czech Republic

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The temperature dependence of ^{55}Mn NMR in $Pr_{0.51}Sr_{0.49}MnO_3$ manganite was studied around the ferromagnetic-antiferromagnetic transition. The ferromagnetic phase ($T_C = 265$ K) is inhomogeneous; the corresponding NMR signal may be described as arising from two regions. Regions A_1, compared to regions A_2, possess a higher hyperfine field and a slower nuclear spin-spin relaxation, which may be attributed to the relatively higher mobility of electrons and stronger double-exchange interaction. Starting from ≈ 150 K the antiferromagnetic phase develops, nucleating from regions A_2, which no longer exist below ≈ 100 K. The volume of regions A_1 decreases markedly below 125 K, but its fraction $\approx 3\%$ survives down to low temperatures.

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The magnetic phase diagram of the half-doped manganites $R_{1-x}A_xMnO_3$ ($x \approx 0.5$) is very rich due to the presence of competing antiferromagnetic (AFM) superexchange and ferromagnetic (FM) double-exchange interactions. In addition, a strong coupling between magnetic, charge, and orbital degrees of freedom exists. The tendency to ferromagnetism increases with increasing size of the A and/or R cations—in the charge ordered $La_{1/2}Ca_{1/2}MnO_3$ system the CE-type antiferromagnetism dominates. $Pr_{1/2}Sr_{1/2}MnO_3$ is an A-type antiferromagnet with a polaronic conductivity in ferromagnetically ordered planes,[1] while $La_{1/2}Sr_{1/2}MnO_3$ is a ferromagnetic metal.[2] In these systems the AFM and FM phases often coexist; moreover, two different FM phases A_F and B_F have been observed by means of ^{55}Mn NMR in $La_{1/2}Ca_{1/2}MnO_3$ (Ref. 3) and $Pr_{0.5}Ca_{0.2}Sr_{0.3}MnO_3$ (Ref. 4) with CE-type AFM ground states. Phase A_F originates from the FM regions embedded in the AFM matrix, while phase B_F, appearing above the Néel temperature T_N, corresponds to bulk ferromagnetism. An additional complexity appears, as phase A_F was found to be spatially inhomogeneous, consisting of regions with different electron mobility and double exchange, which results in different nuclear spin dynamics and different magnitude of the hyperfine field. In a recent paper[5] we have shown that such an inhomogeneity is rather a general feature of the FM state in manganites. Of particular interest is the character of FM phase in systems with the A-type AFM ground state. Using ^{55}Mn NMR at 1.3 K in $Pr_{1/2}Sr_{1/2}MnO_3$ single crystals, Allodi *et al.*[6] studied the AFM → FM transition induced by a magnetic field. The development of the FM state with increasing temperature was not yet elucidated, however.

In this paper we present the temperature dependence of ^{55}Mn NMR in $Pr_{0.51}Sr_{0.49}MnO_3$, supplemented by magnetic measurements. In this compound we found that the FM state above T_N corresponds to an inhomogeneous phase A_F and we investigated in detail how the character of this phase changes at and around the FM → AFM transition. The results have been mentioned elsewhere.[1,5]

Single-crystal $Pr_{0.51}Sr_{0.49}MnO_3$ was prepared by the floating-zone method. Measurements of the magnetization and susceptibility were carried out using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The magnetization was measured in fields up to 5 T and the spontaneous moment was then determined by extrapolating the data to zero magnetic field.

As the crystal was highly conducting it was crushed and the resulting fine crystallites were then fixed together in paraffin. In this way the influence of the skin effect on the amplitude of the NMR signal was minimized. The NMR spectra were recorded by a two-pulse spin echo method at temperatures between 63 and 230 K using a noncoherent spectrometer with frequency sweep and boxcar detector signal averaging. The NMR spectrum was 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 τ. The intensity of the spectrum is proportional to $\exp(-2\tau/T_2)$, where T_2 is the spin-spin relaxation time.

The magnetization M measured at cooling and warming in a field 0.75 T is displayed in Fig. 1. The susceptibility was measured as well and its features are analogous to those of M (inset in Fig. 1). $Pr_{0.51}Sr_{0.49}MnO_3$ undergoes on warming a transition to bulk ferromagnetism at $T_N \sim 125$ K and then to a paramagnetic state at $T_C = 265$ K. This is also illustrated by resistivity curves in Fig. 2. Both $M(T)$ and $\rho(T)$ dependences exhibit a clear hysteresis around T_N, pointing to a first-order type of AFM → FM transition.

NMR spectra of ^{55}Mn at selected temperatures, recorded on cooling using $\tau = 3.5$ μs, are displayed in Fig. 3. At $T = 63$ K the NMR spectrum consists of a single Gaussian line at 356 MHz, in distinction to Allodi *et al.*[6] who in $Pr_{0.5}Sr_{0.5}MnO_3$ at $T = 1.3$ K observed two peaks centered at 370 and 290 MHz. We have no simple explanation for this difference; it might be connected either with a different composition or with some process taking place at temperatures below 63 K. The amplitude of the NMR signal in the present sample increases rapidly as $T \to T_N$. The reduction of this

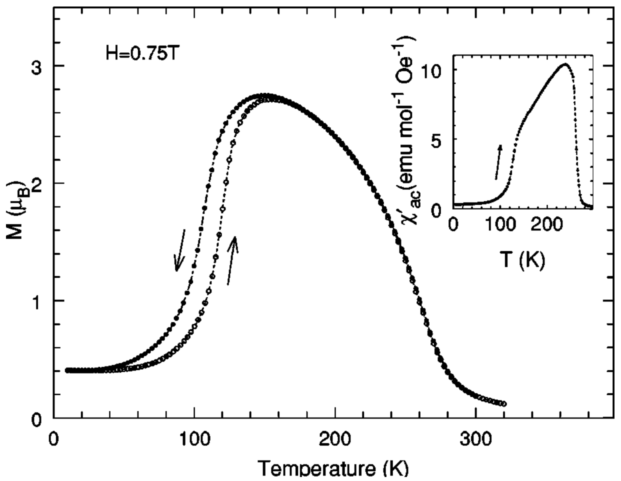

FIG. 1. $Pr_{0.51}Sr_{0.49}MnO_3$. Temperature dependence of the magnetization taken at 0.75 T on cooling and warming. In the inset the temperature dependence of the ac susceptibility on warming is shown.

amplitude in the FM state, when T increases further, is mainly connected with the shortening of T_2 which becomes comparable to the spin-echo interval τ. An additional reduction of the amplitude, proportional to $1/T$, results from the Curie law for the nuclear magnetic moment. This signal may be therefore associated with the FM phase, which is further supported by a characteristic high value ≈ 300 of the NMR enhancement factor. Around T_N the amplitude of the NMR signal exhibits a similar hysteresis as the magnetization. On the other hand, no hysteresis of either the NMR frequency or the relaxation time has been observed.

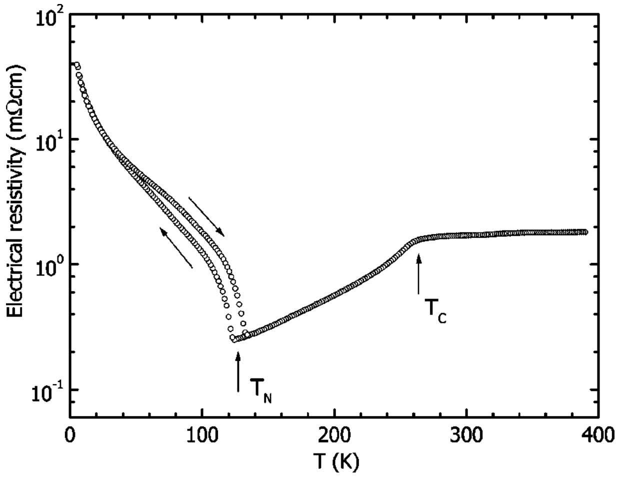

FIG. 2. Temperature dependence of the resistivity on cooling and warming.

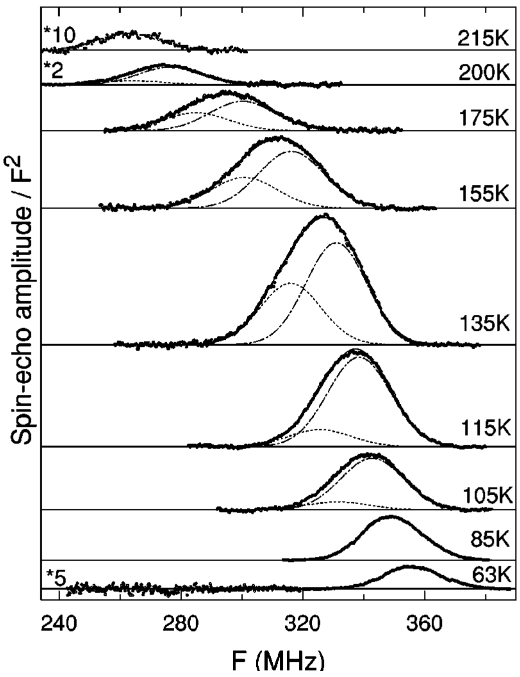

FIG. 3. NMR spectra taken on cooling at several temperatures. The spectra are decomposed in two lines (dashed curves) as described in the text.

Below 100 K the form of NMR spectrum does not depend on τ [Fig. 4(a)]; above this temperature the situation becomes more complex—the width of the spectrum first decreases with increasing τ, but then remains constant after τ surpasses a certain critical value. For $T = 135$ K the critical value τ_{crit} of τ equals 12 μs [Fig. 4(b)]. The simplest interpretation, as discussed in Ref. 5, is to assume that the NMR signal consists of two lines which possess different T_2. For sufficiently large $\tau > \tau_{crit}$ only the line possessing larger T_2 contributes and the spectra can be fitted by a single Gaussian line A_1, centered at 331 MHz, with a half-width of 23.4 MHz and $T_2 = 8.3$ μs. The contribution of faster relaxing nuclear spins can be then determined by subtracting $A_1(\tau)$ from the experimental spectrum. This contribution can also be fitted by a Gaussian line A_2 centered at 316 MHz with the same half-width as the line A_1, but shorter $T_2 = 5.0$ μs. The corresponding two-line decomposition of the $T = 135$ K spectrum is shown in Fig. 4(c), while the decomposition of NMR spectra taken at different temperatures are displayed in Fig. 3. Note that as the temperature increases, the contribution of the line A_2 to the measured signal becomes smaller due to the increasing relaxation rate and the fact that $T_2(A_2) < T_2(A_1)$. Above 210 K practically only the A_1 line contributes to the signal observed.

The two-line character of the NMR spectra suggests that the compound studied contains two different types of FM regions A_1 and A_2, which give rise to lines at higher and lower frequency, respectively. Regions A_2 are characterized by shorter T_2, i.e., by a faster dynamics of Mn nuclear spins, which implies a slower hopping of the Mn e_g electrons.[7] The temperature dependence of the resonance frequency of the A_1 and A_2 lines is similar to the one of the magnetization [Fig. 5(a)], pointing to the second-order phase transition at T_C. In almost the whole temperature interval the relaxation rate $1/T_2$ increases approximately exponentially with increasing temperature [Fig. 5(b)], which is the same behavior as in other FM manganites.[7,8] In the vicinity of T_N the relaxation exhibits a plateau, however.

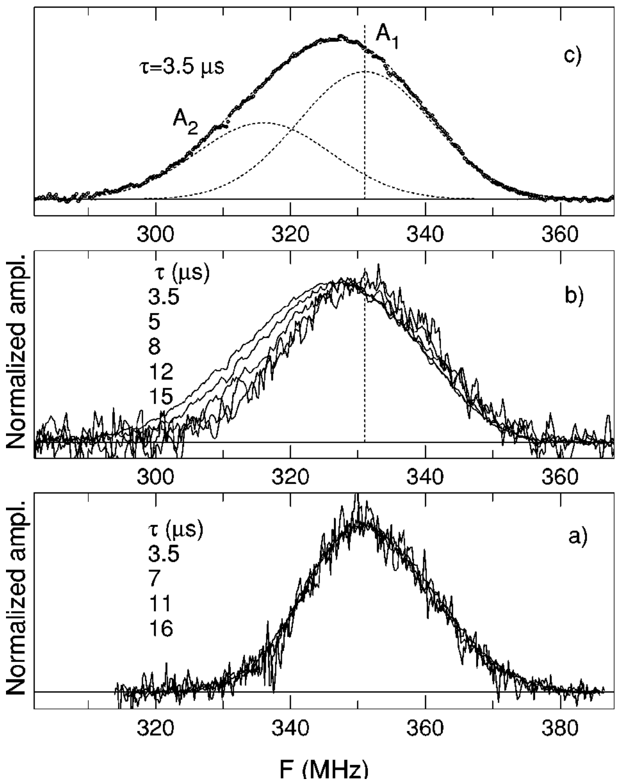

FIG. 4. NMR spectra of ^{55}Mn taken for different values of the time interval τ at 77 K (a) and 135 K (b). The amplitudes are normalized to show the evolution of the line shape. The width of the spectra at 135 K first decreases when increasing τ, then remains constant giving rise to the A_1 line. Based on this behavior, spectra are decomposed on two lines (c).

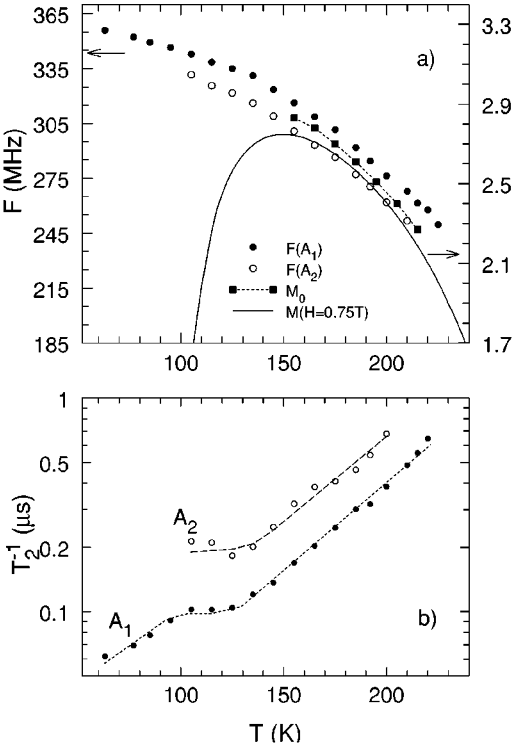

FIG. 5. Temperature dependence of resonance frequencies compared to spontaneous magnetic moment and magnetization at 0.75 T on cooling (a). Temperature dependence of the spin relaxation rate $1/T_2$ of A_1 and A_2 lines (b).

Using the decomposition of the NMR spectra described above, the relative volume of the regions A_1 and A_2 can be determined by extrapolating the corresponding NMR amplitudes to $\tau=0$. The temperature dependence of the relative volume of A_1 and A_2 obtained in this way is displayed in Fig. 6. In the same figure the relative volume of the AFM phase is also shown. This volume was obtained by assuming that the decrease of the FM signal is fully due to the growth of the AFM phase. It is seen that between 150 and 125 K the increase of the AFM volume is caused entirely by the decrease of the A_2 volume, while the volume of regions A_1 remains unchanged. The AFM phase thus nucleates in the A_2 regions—this is to be expected if the double exchange in A_2 is weaker compared to the A_1 regions, confirming thus that A_1 and A_2 have the origin suggested by us earlier.[5] Below 125 K the volume of the A_1 regions also decreases; a residual fraction $\approx 3\%$ is retained down to low temperatures, however. The A_2 regions disappear completely at about 100 K.

The results obtained show clearly that the character of local ferromagnetism in the A-type and the CE-type antiferromagnetic ground states is different. In the A-type AFM compound studied, the residual ferromagnetism at low temperatures and the bulk ferromagnetism above T_N originate from the same thermodynamic phase, in which the regions of A_1 and A_2 type are microscopically intertwinned.[9] This observation is in contrast to the NMR study of $Pr_{0.5}Ca_{0.2}Sr_{0.3}MnO_3$,[4] in which we have found that the ferromagnetic signal originates from two FM phases possessing quite different characteristics. As suggested in Ref. 4 the minority A_F phase in the CE-type systems is intrinsically linked to the charge-ordering defects (like antiphase boundaries). In the A-type compounds no charge order exists; hence, the A_F

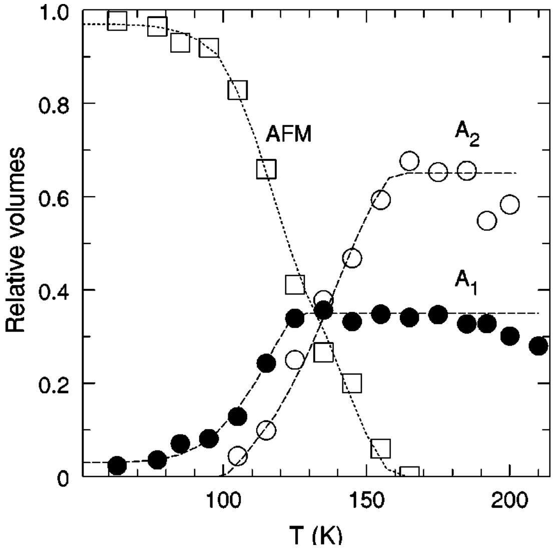

FIG. 6. Relative volumes of the A_1 and A_2 FM regions and the AFM phase as a function of the temperature. The curves serve as a guide for eyes.

ferromagnetic phase at low temperatures has probably a parasitic character—it is not intimately connected to the majority AFM phase as evidenced by the absence of the thermal hysteresis of NMR frequency and relaxation (such hysteresis was found in CE-type systems[3,4]).

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