NMR in local fields at ^{139}La nuclei in ferromagnetic manganites with a metal–semiconductor transition

M. K. Gubkin, A. V. Zalesskiĭ, V. G. Krivenko, T. M. Perekalina, T. A. Khimich, and V. A. Chubarenko
Institute of Crystallography, Russian Academy of Sciences, 117333 Moscow, Russia

(Submitted 31 May 1994)
Pis'ma Zh. Eksp. Teor. Fiz. **60**, No. 1, 56–59 (10 July 1994)

A spin-echo method has been used to measure the temperature dependence of the local magnetic fields at ^{139}La nuclei in several manganites in the region of ferromagnetism and a metallic conductivity. The observed fields, on the order of 30 kOe, depend only weakly on the temperature. They remain high right up to the Curie point. It is suggested that the local fields at the ^{139}La nuclei stem from spin-polarized current carriers which mediate a double exchange. An explanation is proposed for the unusual temperature dependence of the local field and that of the amplitude of the spin echo. The explanation is based on the argument that the samples are of a magnetically multiphase nature near the Curie point.

The perovskite manganites based on $LaMnO_3$ have long been recognized as compounds in which there is a close relationship between electrical and magnetic properties (Ref. 1, for example). Stoichiometric $LaMnO_3$ is a semiconductor and an antiferromagnet. In compositions in which some of the Mn^{3+} cations are replaced by Mn^{4+}, however, a metallic conductivity is seen, and a ferromagnetism arises. The Mn^{4+} cations can be introduced in the structure of $LaMnO_3$ either by replacing some of the La^{3+} ions by lower-valence cations (Ca, Sr, Ba, Pb, or Na) or by introducing superstoichiometric oxygen ($LaMnO_{3+\delta}$). The Curie point T_c of these manganites generally falls in the temperature region of the metal–semiconductor transition.

In most papers, the ferromagnetism of the manganites has been explained on the basis of Zener's model[2] of a double exchange between Mn^{3+} and Mn^{4+} ions. Mechanisms other than double exchange have also been proposed. In particular, there are the mechanism due to specific features of the interactions in a system of Jahn–Teller ions[3] and the RKKY interaction.[4] The question of the nature of the ferromagnetism of these manganites and its relationship with the electrical conductivity has not been resolved unambiguously.

Valuable information on the nature of exchange interactions in manganites might be provided by NMR, which can provide information on the local magnetic fields H_l at ^{139}La or ^{55}Mn nuclei. The NMR method has advantages over macroscopic measurements in that it is of a local nature and in that it can be used in the absence of an external field. If the sample consists of more than one phase, an investigator can work from the temperature dependence of the resonant frequency to follow the changes in the magnetization of an individual phase, and from the intensity of the resonance conclusions can be drawn about the relative concentration of this phase.

 0021-3640/94/010057-04$10.00

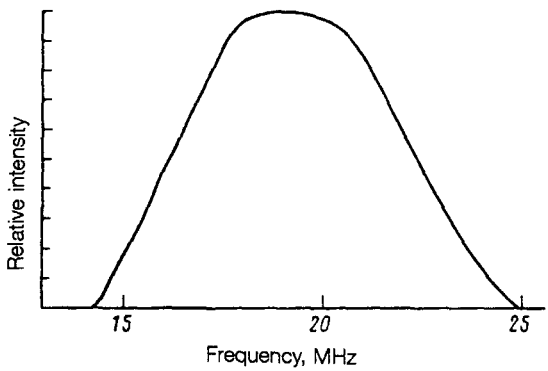

FIG. 1. Spin-echo spectrum of ^{139}La in $La_{0.9}Na_{0.1}MnO_3$ at 77 K.

The NMR at ^{55}Mn nuclei was studied for the compositions $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Pb_xMnO_3$ in Refs. 5 and 6, respectively. The spin-echo spectrum was observed at temperatures of 1.4 and 77 K in the frequency range 310–430 MHz, which corresponds to $H_L = 290–400$ kOe. The temperature dependence of H_L was not studied. With regard to the NMR at ^{139}La nuclei, there is only a single brief communication,[7] in which the resonant peak at 385 MHz at 78 K for the composition $La_{0.7}Sr_{0.3}MnO_3$ was erroneously (see the discussion below) assigned to ^{139}La nuclei. The existence of an anomalously high field $H_L = 640$ kOe at ^{139}La nuclei corresponding to this frequency has not subsequently been either confirmed or refuted, to the best of our knowledge.

In this letter we are reporting the use of the standard pulsed spin-echo technique in a zero field to study the NMR spectrum of ^{139}La nuclei in manganites with the compositions $La_{0.9}Na_{0.1}MnO_3$ (sample I), $La_{0.9}Na_{0.1}Mn_{0.9}Cu_{0.1}O_3$ (II), and $LaMnO_{3+\delta}$ (III). Since these test samples have a metallic electrical conductivity, we used powders fixed in paraffin for the NMR measurements. Samples I and II were ground crystals and a ceramic, respectively; their electrical and magnetic properties had been studied previously in Ref. 8 (information on the preparation of the samples and their characterization is reported in the same paper). Sample III was prepared by the standard ceramic procedure; it was identified as $LaMnO_{3.15}$ by x-ray diffractometry.

We observed the spin-echo spectrum of ^{139}La in all samples in the frequency range 11–26 MHz. Accordingly, the assignment of the peak at 385 MHz, in the "manganese" range, to ^{139}La nuclei is erroneous. The spectrum is a wide, bell-shaped line, as shown in Fig. 1 for sample I. For samples II and III the spectrum has a similar shape, but is shifted 1 and 2 MHz, respectively, toward lower frequencies. The spin echo was observed at low levels of the rf power, as is characteristic of ferromagnets with a high gain coefficient, due to a large value of the rf magnetic susceptibility. The spectrum corresponds to the case in which the Zeeman energy (due in our case to the internal field H_L) is significantly greater than the energy of the quadrupole interaction. In first-order perturbation theory the quadrupole interaction should lead to a splitting of an NMR line into $2\times I$ components (for ^{139}La, with a spin $I = 7/2$, the splitting should result in seven lines). Theoretically, the spectrum should consist of a central line at the frequency $\nu_L = \gamma H_L/2\pi$ (for ^{139}La, we would have $\gamma/2\pi = 0.60144$ MHz/kOe), corresponding to the transition with

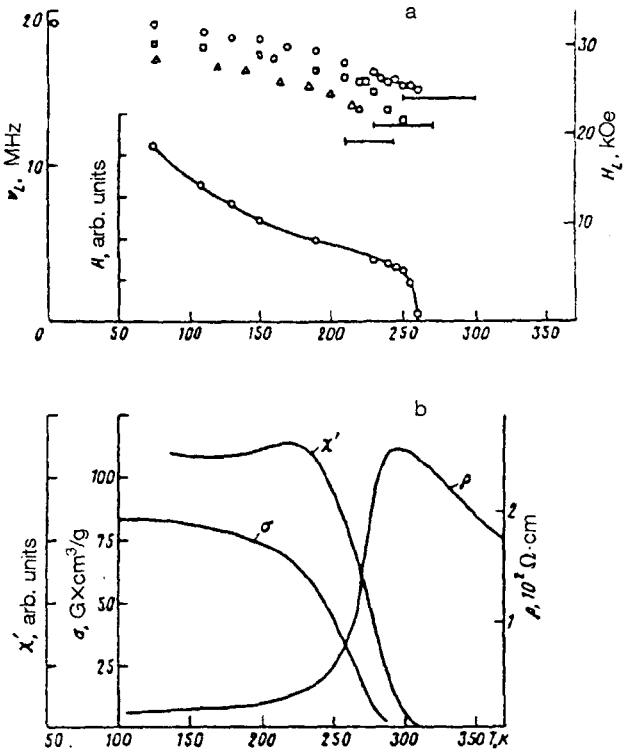

FIG. 2. a: Temperature dependence of the frequency ν_L ; of the local field H_L for ^{139}La nuclei for samples I (○), II (□), and III (△); and of the spin-echo intensity A for sample I. The line segments show the temperature intervals in which the ferromagnetism and the metal–semiconductor transition disappear. b: Temperature dependence of the specific spontaneous magnetization σ, of the rf susceptibility χ', and of the resistivity ρ for sample I.

$m = 1/2 \leftrightarrow -1/2$, flanked by six other lines, positioned symmetrically in pairs, with decreasing intensity, at equal-frequency separations from ν_L . Because of the pronounced broadening, quadrupole components are not seen in our spectrum. The broadening, as in the case of the NMR of ^{55}Mn (Ref. 6), is due to the variation in H_L and in the gain coefficient due to the large contribution of nuclei in domain walls.

The local fields H_L(La), found from the position of the maximum for samples I, II, and III at 77 K, are 31.6, 29.6, and 28.1 kOe, respectively (the error is ± 0.04 kOe in all cases). These values amount to about 8–9% of $H_L \approx 350$ kOe at the ^{55}Mn nuclei, as found in Ref. 5 for the related composition $La_{0.7}Ca_{0.3}MnO_3$. A study of the temperature dependence of H_L(La) yielded an unexpected result (Fig. 2a): For all samples, the field H_L(La) does not vanish, as it should in the limit $T \rightarrow T_c$, at the temperatures at which the ferromagnetism disappears, according to the magnetic measurements. This field instead remains high, at about 80% of its maximum value as $T \rightarrow 0$. If we approximate H_L(La) by a Brillouin function, the temperature T_c should lie significantly above the range 320–370 K, which follows from the magnetic measurements. The disappearance of the ferromag-

netism is illustrated by Fig. 2b, which reproduces curves of $\sigma(T)$ and $\rho(T)$ for sample II from Ref. 8. This figure also shows the change in the relative magnitude of the real part of the rf susceptibility χ' (at 10 MHz) for the same sample. We see that the ferromagnetism disappears in the same temperature interval (250–300 K) in which the metal–semiconductor transition is observed. With regard to the temperature dependence of the spin-echo intensity, we note that this intensity decays sharply toward T_c, against the background of the natural hyperbolic decay due to the Curie–Weiss law for the nuclear magnetic moment.

We thus see that the temperature dependence of $H_L(\mathrm{La})$ does not reproduce the $\sigma(T)$ curve, and that the high local field (≈ 30 kOe) could hardly be a consequence of dipole fields alone (in magnetic oxides with an approximately cubic structure, this value would usually be no more than a few kiloersteds). Both of these factors strongly imply that the local field at the ^{139}La nuclei is due not so much to the magnetic moments of the manganese as to spin-polarized carriers which mediate a double exchange. In other words, we have $H_L(\mathrm{La}) \propto \langle s \rangle$, where $\langle s \rangle$ is the average magnetization of the collectivized 3d electrons of manganese. According to certain models of double exchange in manganites (e.g., Ref. 9), free carriers (which mediate a metallic conductivity) in the ferromagnetic region have an essentially total spin polarization. We therefore have $\langle s \rangle \approx (1-x)\mu_B$ per structural unit, where x is the fraction of Mn^{4+} ions, and μ_B is the Bohr magneton. We see why the decrease in $H_L(\mathrm{La})$ with increasing temperature is slower than that on the $\sigma(T)$ curve when we consider the suggestion[10] that a magnetically multiphase state exists in the manganites. As T_c is approached, the volume fraction of nonferromagnetic regions increases. This tendency is reflected on the $\sigma(T)$ curve. In these regions, however, the carriers are mostly localized and do not create a local field at ^{139} La nuclei. Nonferromagnetic regions do not contribute to the NMR, and their growth near T_c affects only the decrease in the spin-echo amplitude. We note in conclusion that in order to achieve the $H_L(\mathrm{La}) = 0.1 H_L(\mathrm{Mn})$ which we measured, it would be necessary to satisfy (at least) the condition $\langle s \rangle > 0.1 \langle S \rangle$, where $\langle S \rangle$is the average magnetization due to localized moments. Since we have $\langle S \rangle \approx 3\mu_B$ per structural unit, we have $\langle s \rangle \approx (0.27\text{–}0.23)\langle S \rangle$in our case ($x = 0.2\text{–}0.3$), and this condition clearly holds.

[1] S. Krupicka, *Physik der Ferrite und der verwandten magnetischen Oxide* (Prague, 1973).
[2] C. Zener, Phys. Rev. **82**, 403 (1951).
[3] I. O. Troyanchuk, Zh. Eksp. Teor. Fiz. **102**, 251 (1992) [Sov. Phys. JETP **75**, 132 (1992)].
[4] T. M. Perekalina *et al.*, Fiz. Tverd. Tela (Leningrad) **32**, 1242 (1990) [Sov. Phys. Solid State **32**, 731 (1990)].
[5] G. Matsumoto, J. Phys. Soc. Jpn. **29**, 615 (1970).
[6] L. K. Leung and A. H. Morrish, Phys. Rev. B **15**, 2485 (1977).
[7] G. Matsumoto and S. Iida, J. Phys. Soc. Jpn. **21**, 2734 (1966).
[8] M. K. Gubkin *et al.*, Fiz. Teved. Tela (Leningrad) **35**, 1443 (1993) [Physics of the Solid State **35**, 728 (1993)].
[9] J. Mazzaferro *et al.*, J. Phys. Chem. Solids **46**, 1339 (1985).
[10] É. L. Nagaev, *Physics of Magnetic Semiconductors* [in Russian] (Nauka, Moscow, 1979).

Translated by D. Parsons