Microscopically homogeneous magnetic structure of $La_{1-x}Sr_xMnO_3$ beyond the range of $0<x<0.1$ observed by La NMR

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A ^{139}La NMR study was carried out on melt-grown samples of $La_{1-x}Sr_xMnO_3$ ($0\leqslant x\leqslant 0.15$). The microscopic magnetic structure of the parent $LaMnO_3$ was identified as a homogeneous antiferromagnet at low temperatures. Substituted compounds with $x\geqslant 0.1$ demonstrate the homogeneous ferromagnetic phase. Only a lightly doped sample with $x=0.05$ shows the coexistence of NMR lines from ferromagnetic and antiferromagnetic phases. [S0163-1829(99)15901-0]

The lanthanum manganite $LaMnO_3$ is an antiferromagnetically correlated insulator (Mott insulator) at all temperatures. It is a parent material for a wide range of the manganites families which are so popular now. Stoichiometric $LaMnO_3$ below the Néel temperature $T_N\approx 140$ K exhibits a layerlike antiferromagnetic order; i.e., the ferromagnetically coupled spins within *ac* planes (space group P_{nma}) are antiferromagnetically coupled along *b*.[1] The low-temperature magnetic structure for real $LaMnO_3$ samples has been variously reported as spin-canted antiferromagnetic (AFM), ferromagnetic (FM), or a domain mixture of the two. This discrepancy is a result of the strong dependence of magnetic properties on the very small variations of the La/Mn ratio and of the oxygen content.

Upon substitution of Sr^{2+} for La^{3+}, holes are induced at the Fermi level. As a result, the Mn spins first tilt until the system becomes a FM metal at high doping. The most detailed electronic and magnetic phase diagram for $La_{1-x}Sr_xMnO_3$ based on macroscopic magnetic and transport measurements was published in Ref. 2. It shows a canted AFM insulator for $x<0.1$, FM insulator for $0.1\leqslant x<0.17$, and FM metal at $x\geqslant 0.2$. The colossal magnetoresistance is typical for the latter part of the diagram which has attracted the main experimental (see Ref. 3, and references therein) and theoretical[4] interest. The low doping part of the phase diagram received much less attention.

As to the microscopic magnetic structure (especially in the insulating part of the diagram) there has been no complete agreement until now. Recent neutron[5] and NMR (Refs. 6 and 7) studies came to very different conclusions about the doping range for coexistence of AFM and FM phases in manganites. It should be noted that the question about the real microscopic magnetic structure of this materials seems to be of principal importance in a long discussion between two theoretical models. One of the models was proposed by de Gennes[8] and predicts for undoped and lightly doped $LaMnO_3$ a homogeneous canted AFM phase at low temperatures. This canted structure allows us to explain the presence of FM peaks in neutron experiments.[1] The alternative model is based on the coexistence of FM and AFM phases and was proposed by Wollan and Koehler.[1] Recently the latter model was developed by Nagaev[9] who considered this phase coexistence as intrinsic feature of the material with its origin to an electronic phase separation similar to high-T_c superconductors.[10]

NMR of ^{139}La with its reasonable gyromagnetic ratio ($\gamma=6.0146$ MHz/T), moderate quadrupole moment ($Q=0.22\times 10^{-24}$ cm^{-2}) and 99.9% natural abundance represents a nice local tool sensitive to both microscopic magnetic and quadrupolar interactions in the material. Keeping in mind the very high quality of the melt-grown crystals of $La_{1-x}Sr_xMnO_3$ prepared recently,[2] we have undertaken a detailed ^{139}La NMR study of these samples, addressing mainly their microscopic magnetic structure at low substitutions.

Crystals of $La_{1-x}Sr_xMnO_3$ ($x=0$, 0.05, 0.10, 0.15) were melt grown by a floating zone technique as described in detail in Ref. 2. A powder x-ray diffraction pattern showed all the samples were single phase. Analyses of chemical composition were carried out using an electron probe microanalyser, redox titration, and thermogravimetry. Crystals were also characterized by resistivity and magnetization measurements as described in Ref. 2.

^{139}La NMR spectra were measured both in zero field (point by point frequency sweep, 5–30 MHz) and in a field-sweep mode (0–8.5 T) at fixed frequencies with a phase-coherent spin-echo spectrometer. For the NMR experiment, crystals were powdered and two types of samples were prepared. The first one was just a powder which was oriented along the easy direction in an external magnetic field during the NMR experiment. The second sample was randomly oriented and fixed in paraffin.

^{139}La NMR at zero external field H_0 was measured for randomly oriented powders at 4.2 K. The spectrum for

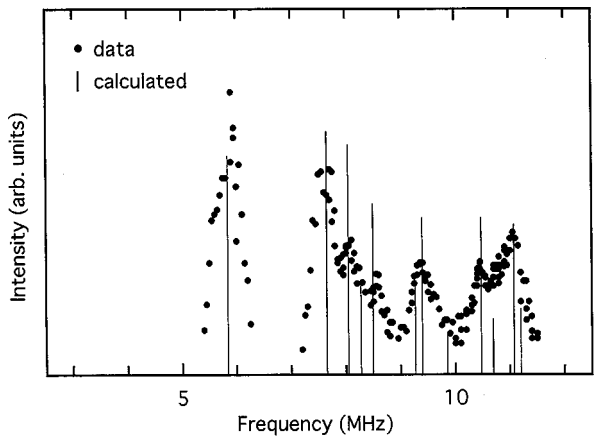

FIG. 1. Zero field La-NMR spectrum of randomly oriented $LaMnO_3$ sample at 4.2 K. Thin vertical lines show the calculated transitions with parameters given in the text.

$x=0$ sample is shown in Fig. 1. It consists of many peaks and the thin vertical lines show the calculated positions for various transitions with the following set of parameters: quadrupole frequency $\nu_Q=3.8$ MHz, asymmetry parameter $\eta=0.92$, internal field $H_{\rm int}=3.5$ kOe along b. The low value of $H_{\rm int}$ [compared with 30 kOe, observed in off-stoichiometric $LaMnO_{3+\delta}$ (Ref. 11)] implies an AFM state at low temperature. The estimated dipolar contribution to $H_{\rm int}$ is rather small (0.7 kOe) as a result of cancellation in a site of nearly cubic symmetry. A large value of $\eta=0.92$ for a very symmetric La surrounding is rather surprising and probably means that the main part of the internal field is a result of a transferred hyperfine interaction. The details of electric field gradient analyses as well as zero field La NMR results for samples with $0<x\leqslant 0.4$ will be published elsewhere.

Figure 2 shows field-sweep ^{139}La NMR spectra of an oriented ($b\|H_0$) $x=0$ sample for several frequencies ν_R. For $I=\frac{7}{2}$ and $H_0\gg H_{\rm int}$, ν_Q seven transition are expected and thin vertical lines indicate their calculated positions with the same parameters as obtained from the zero field spectrum. The spectra for samples with $x>0$ shown in Fig. 3 differ drastically from that for undoped $LaMnO_3$. Even very light doping, $x=0.05$, NMR spectrum broadens and shifts to smaller fields. The component of the AFM line is still observable for this sample but disappears completely at higher dopings. The shift of the FM component to lower fields with increasing doping is in a good agreement with the $H_{\rm int}(x)$ dependence measured at zero field La NMR in the same samples.[12]

The spectra obtained demonstrate the homogeneous microscopic magnetic states—AFM in $LaMnO_3$ and FM in $La_{1-x}Sr_xMnO_3$ ($x\geqslant 0.1$). It is most evident in Fig. 3 where we show the field-sweep NMR spectra in the wide field range. It's seen that even traces of alternative NMR lines (FM for $x=0$ and AFM for $x\geqslant 0.1$) are not observable. It should be noted that for the single phase spectra ($x=0$, 0.1, 0.15) we used specially experimental parameters favorable for the alternative line (FM for $x=0$ and AFM for $x=0.1$, 0.15). This means that the admixture of the alternative phase is beyond the sensitivity of our experiment. We estimate an upper limit for the AFM component in FM $x=0.1$, 0.15 samples as about 2%. The $x=0.05$ sample was the only one where a coexistence of two NMR lines was observed and the spectrum in Fig. 3 reflects the real relative intensity of these lines (about 25% of AFM component).

From recent neutron data on melt-grown samples of $La_{1-x}Sr_xMnO_3$ ($x=0.04$, 0.125, 0.17) (Ref. 5) the low-temperature magnetic structures for these compounds are as follows. The material with $x=0.04$ is a canted AFM with a small admixture of FM phase. By contrast, the $x=0.125$ sample exhibits a large FM moment with small admixture of an AFM component. The sample with higher doping ($x=0.17$) shows only an FM component. Our NMR results for the substituted compounds are in qualitative agreement with those neutron data. We also observed a coexistence of AFM and FM states, but our $x=0.05$ sample is mainly FM (about 75% of FM components) and for $x=0.1$ we found no traces of AFM components. Keeping in mind that the samples used in Ref. 5 were not completely identical to ours this small quantitative discrepancy looks quite acceptable.

Recently the results of a La-NMR study in ceramic samples of La manganites (including the parent $LaMnO_3$) were published.[6,7] As for undoped $LaMnO_3$ those data differ completely from ours. In all the samples (including nominally undoped $LaMnO_3$) a very broad La-NMR line (about 10 MHz) without clear structure was detected below T_N. The authors interpreted their results as evidence of intrinsi-

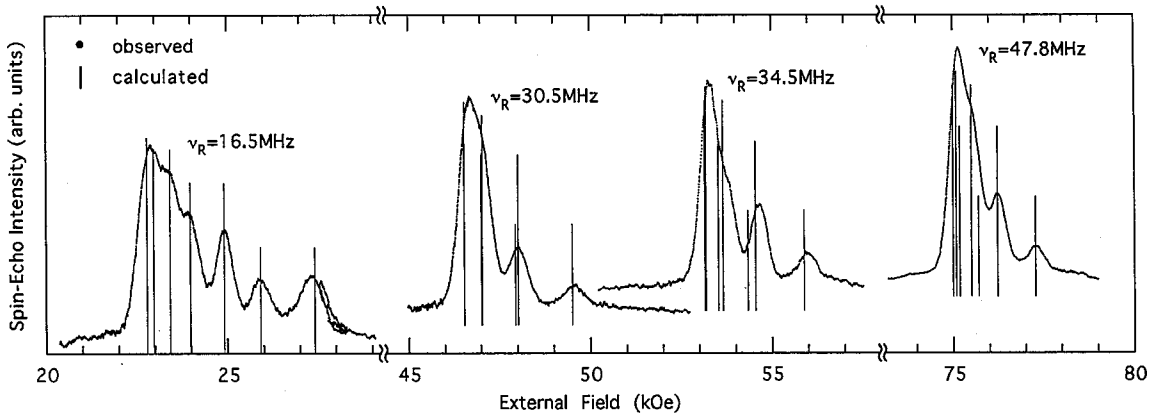

FIG. 2. Field-sweep La-NMR spectra of oriented ($b\|H_0$) $LaMnO_3$ sample at various frequences at 4.2 K. Thin vertical lines show the calculated transitions with the same parameters as in Fig. 1.

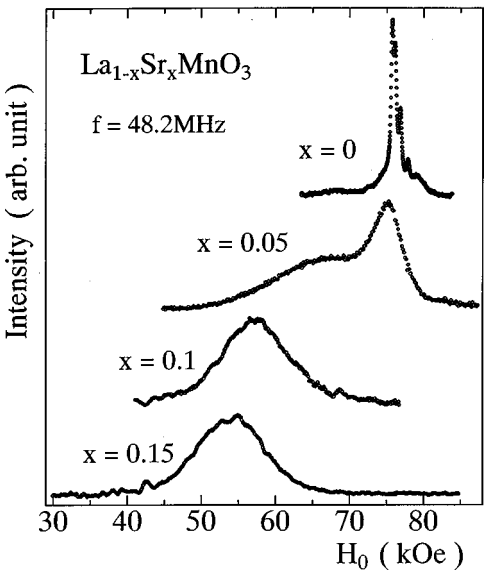

FIG. 3. Field-sweep La-NMR spectra of oriented ($b \| H_0$) $La_{1-x}Sr_xMnO_3$ samples at 48.2 MHz ($T=5$ K for $x=0$ and 20 K for others).

cally inhomogeneous magnetic order on a microscopic scale in the entire range $0 \leqslant x < 0.25$ (which develops at low temperature into the intimate mixture of FM and AFM correlated domains) and as an indication for the presence of magnetic polarons.

Our data do not confirm this conclusion demonstrating an existence of pure AFM ($LaMnO_3$) as well as pure FM ($x \geqslant 0.1$) samples. We suppose that the experimental results and the main physical conclusion of Refs. 6 and 7 are relevant rather to certain ceramic samples than to the material itself. The ferromagnetic transition at 115 K found in their nominally undoped $LaMnO_3$ sample disagrees evidently with the published magnetic diagrams of this material.[2,13,14] It should be also noticed that the low-temperature La-NMR spectrum of nominally undoped $LaMnO_3$ ceramic sample (see Fig. 9 in Ref. 6) being converted in a field domain is rather similar to our spectrum for $La_{0.95}Sr_{0.05}MnO_3$ which has 7(2)% of Mn^{4+} ions due to redox titration.[2] These disagreements support our suspicions about oxygen and/or cation off stoichiometry of the samples used in Refs. 6 and 7. This is quite possible since the ceramic samples suffer from the presence of grain boundaries where the modifications of the microscopic magnetic structure likely take place. In fact, the resistive and magnetotransport properties of our crystals differ considerably from those of ceramic samples, as shown in Ref. 2.

Following Ref. 5 we would like to emphasize the very sharp changeover of the AFM and FM components despite a linear variation of the hole density. Due to our NMR data this changeover looks probably even more sharp with its central point close to $x=0.05$. To our mind it would be interesting to study in detail the macroscopic and/or microscopic magnetic structure of the high quality $La_{1-x}Sr_xMnO_3$ crystals in a range of substitution $0<x<0.1$ to shed light on a more complicated phase diagram that believed earlier.

In conclusion, we have shown from ^{139}La-NMR data that the magnetic structure of $La_{1-x}Sr_xMnO_3$ compounds measured on high quality melt-grown crystals is microscopically homogeneous beyond the range of $0<x<0.1$. The parent $LaMnO_3$ has an AFM structure, the Sr-substituted compounds are FM, the admixture of alternative phase being negligible. The very sharp changeover of the AFM and FM components was observed around $x=0.05$.

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[1] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).
[2] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14 103 (1995).
[3] Y. Tokura, A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and N. Furukawa, J. Phys. Soc. Jpn. **63**, 3931 (1994).
[4] A. J. Millis, R. Mueller, and B. I. Shraiman, Phys. Rev. B **54**, 5405 (1996).
[5] H. Kawano, R. Kajimoto, M. Kubota, and H. Yoshizawa, Phys. Rev. B **53**, 2202 (1996).
[6] G. Allodi, R. De Renzi, G. Guidi, E. Licci, and M. Pieper, Phys. Rev. B **56**, 6036 (1997).
[7] G. Allodi, R. De Renzi, and G. Guidi, Phys. Rev. B **57**, 1024 (1998).
[8] P.-G. de Gennes, Phys. Rev. **118**, 141 (1960).
[9] E. L. Nagaev, Phys. Status Solidi B **186**, 9 (1994).
[10] P. C. Hammel, A. P. Reyes, S. W. Cheong, Z. Fisk, and J. E. Schriber, Phys. Rev. Lett. **71**, 440 (1993).
[11] M. Gubkin, A. Zalessky, V. Krivenko, T. Perekalina, T. Khimich, and V. Chubarenko, JETP Lett. **60**, 57 (1994).
[12] A. Iwai, T. Suzuki, H. Takahashi, K. Kumagai, Y. Tomioka, H. Kuwahara, and Y. Tokura (unpublished).
[13] K. Hirota, N. Kaneko, A. Nishizawa, and Y. Endoh, J. Phys. Soc. Jpn. **65**, 3736 (1996).
[14] B. C. Hauback, H. F. Fjellvag, and N. Sakai, J. Solid State Chem. **124**, 43 (1996).