
**MAGNETISM
AND FERROELECTRICITY**

Two-Phase Paramagnetic–Ferromagnetic State of $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ Single-Crystal Lanthanum Manganite

N. V. Volkov, G. A. Petrakovskii, V. N. Vasil'ev, and K. A. Sablina

*Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: volk@iph.krasn.ru*

Received June 26, 2001; in final form, November 13, 2001

Abstract—Two phases, paramagnetic and ferromagnetic, were shown by the magnetic resonance method to coexist below the temperature T_C in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ single crystals exhibiting colossal magnetoresistance. The magnetic resonance spectra were studied in the frequency range 10–78 GHz. The specific features in the behavior of the spectral parameters were observed to be the strongest at the temperatures corresponding to the maximum magnetoresistance in the crystals. The concentration ratios of the paramagnetic and ferromagnetic phases in the samples were found to be sensitive to variations in temperature and external magnetic field. This behavior suggests realization of the electronic phase separation mechanism in the system under study. © 2002 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The interest of researchers in impurity-containing perovskite manganites stems primarily from the phenomenon of colossal magnetoresistance (CMR). The CMR phenomenon has application potential. At the same time, numerous experimental studies have revealed structural, magnetic, and electronic properties in manganites which are no less exciting from the physical standpoint. It was found that the materials of this family have a very rich phase diagram [1, 2] which includes regions of the antiferromagnetic, ferromagnetic nonconducting, and ferromagnetic metallic states, as well as regions with orbital and charge ordering. In many cases, these phases are microscopically inhomogeneous. This inhomogeneity has been proved experimentally by scanning tunneling microscopy [3], electron diffraction [4], neutron scattering [5], NMR [6], optical methods [7], etc. We note that the inhomogeneous state manifests itself the strongest in the concentration and temperature ranges where the CMR effect is observed. In addition to the experimental confirmation of the coexistence of phases in materials of this class, considerable progress has been reached in theoretical substantiation of the tendency to phase separation [8]. There is, however, still a long way to go for the pattern of these phenomena to be completely understood; this would require extending the search for materials with phase separation and for experimental methods of their investigation.

Because any of the phase separation scenarios presently discussed [8] assumes the coexisting phases to reside in different magnetic states, magnetic resonance could prove to be of use. It is known that even an insignificant inhomogeneity in magnetic materials notice-

ably affects the magnetic absorption spectra. While magnetic resonance spectra of manganites have been studied by various groups of authors [9–11], interest was mainly focused therein on the paramagnetic (PM) state. As for the results covering the temperature range near the magnetic phase transition, they exhibit a considerable scatter and are often interpreted from different standpoints.

Our studies of $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ crystals exhibiting the CMR phenomenon revealed an effect of dc and ac transport current on conductivity in the microwave frequency range [12, 13]. The character of the response of this system to an electric current suggests that the mechanisms of the CMR and of the electric-current effect have the same nature and can be qualitatively interpreted in terms of the phase separation model. The existence of the two-phase paramagnetic–ferromagnetic state in single-crystal $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ received supportive evidence from studies of magnetic resonance spectra [14].

We present here the data obtained in an experimental investigation of magnetic resonance in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ crystals exhibiting CMR.

2. EXPERIMENTAL

All experimental studies were performed on single-crystal $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ samples grown by spontaneous crystallization from a solution in melt. A characteristic feature of the technology employed was that PbO and PbF_2 were used as the solvent while simultaneously providing the required amount of Pb in the crystals. The composition of the batch consisting of La_2O_3 , MnO_2 , and the solvent was chosen so as to obtain a Pb concen-

tration of $x \sim 0.3$. The crystals were grown in a platinum crucible. The technological regime chosen permitted one to grow crystals with an average size of $5 \times 5 \times 5$ mm. X-ray diffraction analysis of the single crystals obtained confirmed that the structure and the lattice parameters correspond to $x \sim 0.3$. The samples prepared for the study were plates measuring $4 \times 2 \times 0.1$ mm whose face coincided with one of the principal symmetry planes of the crystal and whose plate surfaces were polished. The external magnetic field was always applied along the sample plane. The electrical resistivity ρ and the magnetoresistance $\Delta\rho/\rho_0 = (\rho(0) - \rho(H))/\rho(0) \times 100\%$ of the samples were measured by the standard four-probe method. The magnetic resonance spectra were measured with a 10-GHz spectrometer operating in the traditional arrangement with rf modulation of the magnetic field and with a spectrometer with frequency ν tunable within the range 24–80 GHz and with a pulsed magnetic field.

3. RESULTS AND DISCUSSION

The $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ single crystals grown by us had a ferromagnetic (FM) phase transition temperature $T_C \cong 360$ K. The maximum magnetoresistance in a magnetic field $H = 10$ kOe was 20% at $T \sim 330$ K (Fig. 1a).

The main feature in the magnetic resonance spectra of the crystals under study is the presence of two well-resolved absorption lines within a broad temperature interval below the Curie point T_C . The temperature behavior of the absorption line parameters for the frequency $\nu = 10$ GHz is shown in Figs. 1b and 1c. We believe that the line denoted by *F* is due to resonance from the crystal regions in the FM state. The *F* line appears only below the temperature T_C . The decrease in the resonance field H_r with decreasing temperature is associated with anisotropic interactions, namely, with increasing magnetic crystallographic anisotropy and shape anisotropy. As the temperature drops below T_C , line *P* observed in the PM state of the sample ($T > T_C$) changes its position only insignificantly and its resonance field H_r does not depend on the sample shape and the orientation of the external magnetic field in the crystal. The slight increase in H_r in the temperature range 340–350 K may be associated with a change in the g factor caused by local lattice distortions. Such distortions initiated by strong electron-phonon coupling were observed to exist in a number of impurity-containing perovskite manganites near the transition to the FM state [1]. Figure 2 shows spectra recorded at different microwave-radiation frequencies at $T = 320$ K.

That the *P* and *F* lines are due to resonance absorption in the PM and FM regions, respectively, is convincingly argued for by the behavior of their frequency vs. field relations (inset to Fig. 2). Studies performed on spherical samples reveal a comparatively low magnetic crystallographic anisotropy (the effective anisotropy field does not exceed 100 Oe even at $T = 80$ K); there-

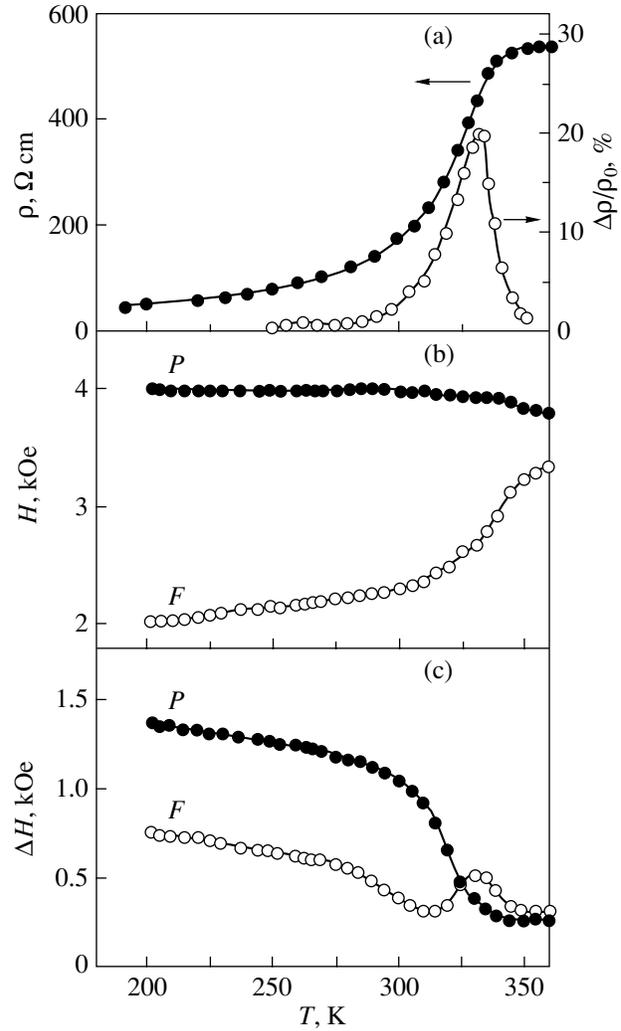


Fig. 1. Temperature dependences (a) of the electrical resistivity ρ and magnetoresistance $\Delta\rho/\rho_0$ in a magnetic field $H = 10$ kOe and of (b) the resonance field and (c) linewidth of the ferromagnetic (*F*) and paramagnetic (*P*) absorption lines in the magnetic resonance spectrum ($\nu = 10$ GHz).

fore, the frequency vs. field dependences for the absorption lines of ferromagnetic resonance should be determined primarily by shape anisotropy. For the geometry of our experiment (with the external magnetic field parallel to the sample plane), one can write

$$\frac{\omega}{\gamma} = [H_r(H_r + 4\pi M_{\text{eff}})]^{1/2}, \quad (1)$$

where $\omega = 2\pi\nu$ is the circular frequency, $\gamma = (g\mu_B/\hbar)$ is the gyromagnetic ratio, and M_{eff} is the effective magnetization, which, in the general case, is different from the true value M_0 because of the crystallographic anisotropy and possible magnetic inhomogeneity of the crystal. For the PM regions, we have a simple relation,

$$\frac{\omega}{\gamma} = H_r. \quad (2)$$

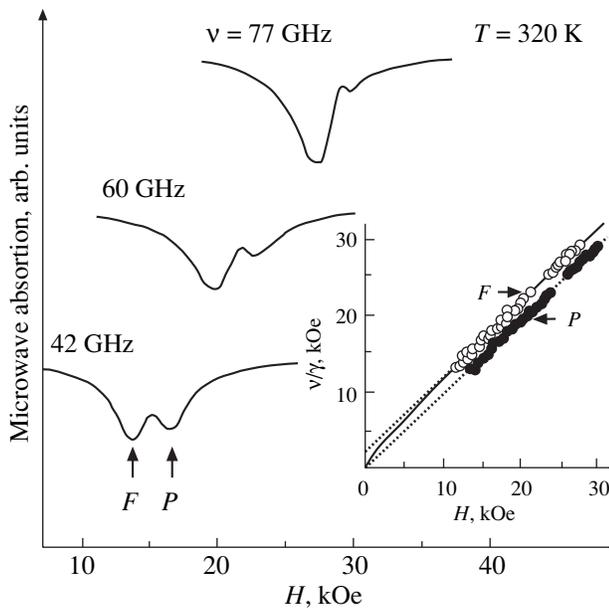


Fig. 2. Magnetic resonance absorption spectra recorded at different microwave frequencies ν at $T = 320$ K. Inset: frequency vs. field plots of the two lines observed in the magnetic resonance spectrum at $T = 320$ K; the solid line is a plot of Eq. (1), and dotted lines are linear extrapolations of the relations.

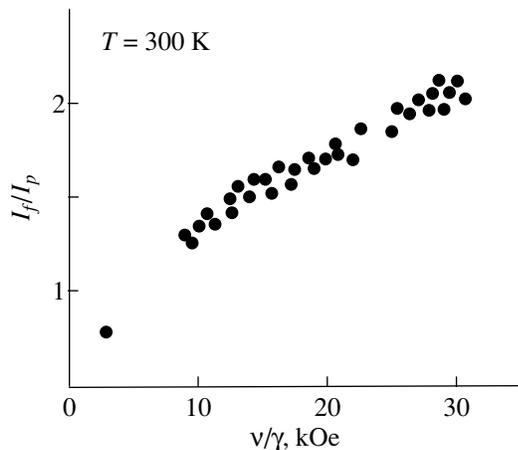


Fig. 3. Ferromagnetic-to-paramagnetic absorption line intensity ratio I_f/I_p in the magnetic resonance spectrum plotted vs. microwave radiation frequency; $T = 300$ K.

Indeed, the frequency vs. field relations for the two observed absorption lines in the spectrum are in full agreement with Eqs. (1) and (2) (inset to Fig. 2). Because the intrinsic magnetic crystallographic anisotropy is small, we succeeded in moving the FM and PM absorption line resonance fields apart by properly choosing the sample shape and geometry of the experiment, thus permitting reliable separate measurement of the lines to be made. The temperature behavior

$4\pi M_{\text{eff}}(T)$ derived from the temperature dependences of the resonance field $H_r(T)$ of the ferromagnetic resonance line with due account of Eq. (1) is almost identical to that of the magnetization $4\pi M_0(T)$ found from static measurements.

In addition to the proof of the existence of a two-phase paramagnetic–ferromagnetic state, this study produced another important result; namely, we demonstrated the possibility of controlling the phase volume ratio in a sample by means of an external magnetic field. This is illustrated by Fig. 2, which shows that an increase in the microwave radiation frequency ν and, hence, in the magnitude of the external magnetic field H brings about an increase in the intensity of the FM absorption line and a decrease in that of the PM line. Figure 3 plots the FM-to-PM line intensity ratio I_f/I_p as a function of the microwave radiation frequency at which the magnetic resonance spectra were measured. This situation can be considered to be a control of the phase volume ratio through proper variation of the external magnetic field. An increase in H gives rise to an increase in the FM phase volume and a decrease in the PM phase volume in a sample. One should note, however, that other factors, for instance, variation of the magnetization M_0 , can also contribute to the intensity of the ferromagnetic resonance absorption line. However, the frequency vs. field dependence for the FM line is fitted well by Eq. (1) with a constant value $4\pi M_{\text{eff}} \approx 2$ kOe (see inset to Fig. 2); hence, the FM regions were magnetized to saturation in the magnetic fields for which the measurements were carried out. We also analyzed the temperature behavior of the FM and PM absorption line parameters recorded at different microwave radiation frequencies. We focused our attention on the temperature dependence of the resonance line intensities. The intensity was calculated as the area under the absorption curve. Because of a partial overlap of the spectral lines, we assumed the absorption lines to have a Lorentzian shape. Figure 4 shows temperature dependences of the FM-to-PM line intensity ratio obtained when measuring magnetic resonance spectra at 10 and 78 GHz. Note the smooth course of the I_f/I_p temperature dependence, except the region of $T \sim 310$ – 350 K, where peak-shaped features are observed. The higher the frequency at which the spectra are measured, the stronger these features are. Interestingly, the peak in the I_f/I_p temperature dependences lies in the temperature region where the magnetoresistance $\Delta\rho/\rho_0$ is the largest (Fig. 1a).

The mechanisms responsible for the formation of the heterogeneous state and the role played by this state in the CMR phenomenon are fundamental problems in the study of inhomogeneous states in manganites. It is believed that the complexity of the (x, H, T) phase diagram of these materials results from the spin, charge, and orbital subsystems being strongly coupled. At some specific doping levels, the subsystem interaction energies responsible for the formation of these phases

become comparable and the inhomogeneous state with phase separation can be the ground state. The variants that are mainly discussed in the literature are as follows.

(i) Phase separation into regions with different electron densities. The inhomogeneities typically measure a few nanometers in this case, i.e., a few lattice constants [15, 16].

(ii) An alternative mechanism involves phase separation into regions with equal electron concentrations, i.e., into antiferromagnetic (or PM) regions with localized electrons and FM regions with itinerant carriers [17]. It is assumed that this phase separation can be caused by a random distribution of impurity ions in the crystal lattice, which produces a random change in the magnitude of the exchange integral. This makes the ordered (homogeneous) state unstable in the vicinity of the phase transition to the FM state. The clusters forming in this case can reach micron size. In the case of an inhomogeneous impurity distribution, this scenario does not reduce to a trivial chemical separation of a sample into phases having, for instance, different Curie temperatures T_C . At the same time, this variant cannot be disregarded in the more general context of phase separation in manganites.

The magnetic resonance method used by us here to study inhomogeneities in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ samples is of an integral character, and, therefore, the problem of the size of inhomogeneities and of the topology of the inhomogeneous state remains open. It is believed that the first scenario of electronic phase separation operates at low concentrations x , although estimates [15] do not exclude the possibility of this mechanism being also operative at higher concentrations. Nevertheless, phase separation associated with a random impurity-ion distribution appears to be a more realistic process for $x \sim 0.3$ compositions; this can be supported experimentally.

Our experimental data suggest an inference of fundamental significance, namely, that the heterophase state in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ is sensitive to the strength of an external magnetic field. This is a persuasive argument in support of the electronic phase separation mechanism, because the effect of external magnetic field cannot be expected to be strong in the case of chemical inhomogeneity. Indeed, in the latter case, the sample would actually be a multiphase system with a different T_C for each phase. Obviously enough, in such a sample, the FM and PM phases should coexist in the vicinity of the transition from the PM to the FM phase (which is also observed experimentally in our case), but the T_C point in each region should not depend on the external magnetic field. Another point of interest is that all the features in the magnetic resonance spectra of the two-phase PM-FM system are observed in the region of the peak in the temperature dependence of magnetoresistance. This suggests a relation between the phase separation and the manifestation of the CMR effect in the materials under study. It is known that the CMR finds a straightforward interpretation in terms of the percola-

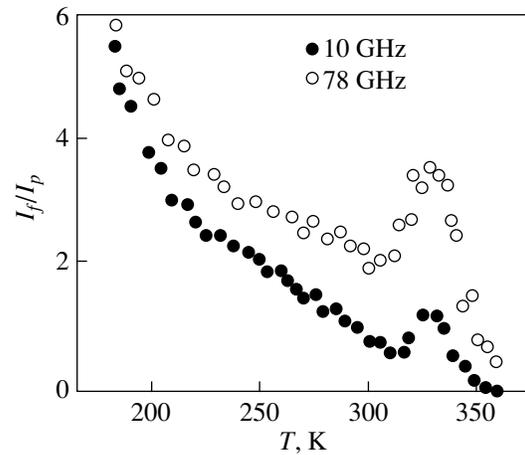


Fig. 4. Ferromagnetic-to-paramagnetic absorption line intensity ratio I_f/I_p in the magnetic resonance spectrum plotted vs. temperature. The relations are presented for the spectra measured at the microwave frequencies $\nu_1 = 10$ GHz and $\nu_2 = 78$ GHz.

tion mechanism [8]. At the same time, the origin of the peaks in the temperature dependences of the FM-to-PM absorption-line intensity ratio I_f/I_p in the magnetic resonance spectrum remains unclear. If our suggestions that the main contribution to I_f/I_p is from the magnetization M_0 of the FM phase and from the volume ratio of the FM and PM phases are correct, one could expect the relations to be smooth. It can be conjectured that in the temperature region where the features are observed, the two-phase state has a complex topology. The energies governing the ground state of the crystal are apparently in a delicate balance; this entails, as a consequence, a high sensitivity to variations in temperature and external magnetic field.

4. CONCLUSION

Thus, our experimental study of magnetic resonance spectra in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ crystals exhibiting CMR revealed the existence of two magnetic phases below T_C . The analysis of the frequency vs. field dependences of absorption spectra permitted their identification as the PM and the FM phase. Studies carried out over a broad frequency range showed the mixed phase state to be sensitive to the magnitude of an external magnetic field. This finding, as well as the specific features in the behavior of the magnetic resonance parameters observed in the CMR region, suggests that the mechanism of electronic phase separation is operative in this system.

REFERENCES

1. A. J. Millis, *Nature* **392**, 147 (1998).
2. J. P. Renard and A. Ananel, *Mater. Sci. Eng. B* **B63**, 22 (1999).

3. M. Fath, S. Freisem, A. A. Menovsky, *et al.*, *Science* **285**, 1540 (1999).
4. M. Uehara, S. Mori, C. H. Chen, and S.-W. Cheong, *Nature* **399**, 560 (1999).
5. D. Louca, T. Egami, E. L. Brosha, *et al.*, *Phys. Rev. B* **56**, 8475 (1997).
6. G. Papavassiliou, M. Fardis, M. Belesi, *et al.*, *Phys. Rev. Lett.* **84**, 761 (2000).
7. N. N. Loshkareva, Yu. P. Sukhorukov, S. V. Naumov, *et al.*, *Pis'ma Zh. Éksp. Teor. Fiz.* **68**, 89 (1998) [*JETP Lett.* **68**, 97 (1998)].
8. E. Dagotto, T. Hotta, and A. Moreo, *Phys. Rep.* **344**, 1 (2001).
9. F. Rivadulla, M. A. Lopez-Quutela, L. E. Hueso, *et al.*, *Phys. Rev. B* **60**, 11922 (1999).
10. A. Shengelay, Guo-Meng Zhao, H. Ckeller, and K. A. Muller, *Phys. Rev. B* **61**, 5888 (2000).
11. D. L. Huber, G. Alejandro, A. Caneiro, *et al.*, *Phys. Rev. B* **60**, 12155 (1999).
12. N. V. Volkov, G. A. Petrakovskii, K. A. Sablina, and S. V. Koval', *Fiz. Tverd. Tela (St. Petersburg)* **41**, 2007 (1999) [*Phys. Solid State* **41**, 1842 (1999)].
13. N. V. Volkov, G. A. Petrakovskii, and K. A. Sablina, *Fiz. Tverd. Tela (St. Petersburg)* **41**, 2187 (1999) [*Phys. Solid State* **41**, 2008 (1999)].
14. G. A. Petrakovskii, N. V. Volkov, V. N. Vasil'ev, and K. A. Sablina, *Pis'ma Zh. Éksp. Teor. Fiz.* **71**, 210 (2000) [*JETP Lett.* **71**, 144 (2000)].
15. L. P. Gor'kov, *Usp. Fiz. Nauk* **168**, 665 (1998) [*Phys. Usp.* **41**, 589 (1998)].
16. É. L. Nagaev, *Usp. Fiz. Nauk* **165**, 529 (1995) [*Phys. Usp.* **38**, 497 (1995)].
17. A. Moreo, M. Mayr, A. Feiguin, *et al.*, *Phys. Rev. Lett.* **84**, 5568 (2000).

Translated by G. Skrebtsov