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Magnetic and transport properties of $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ single crystal: The key role of intrinsic inhomogeneity

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Abstract

The magnetic and transport measurements of the mixed-valence manganite $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ have been supplemented by magnetic resonance study. Experimental data support the model of two magnetic phases coexisting in the crystal volume. Above $T_C = 119$ K, up to $1.6T_C$ ferromagnetic (FM) clusters of minority phase exist in a paramagnetic matrix of majority phase. Below T_C a magnetic state represents the coexistence of two different FM phases. These phases are observed as a spatially separated due to the frustration of the FM and antiferromagnetic (AFM) exchange interactions on the phase boundaries. Phase separation state comprised of two different magnetic phases differing in the conductivity has been used to account for the peculiarities of the transport, magnetotransport, magnetic and magnetic resonance properties found in the crystal.
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1. Introduction

The manganites $R_{1-x}R'_xMnO_3$ (R = La, Nd, Pr, etc., and R′ = Ca, Sr, Ba, Pb) attract a great interest since they show a variety of intriguing phenomena due to a crossover from localized to itinerant electronic behavior of 3d e_g electrons in the presence of localized t_{2g} electrons on the manganese ions [1]. The transition from localized to charge delocalized state is effectively controlled by an isovalent chemical substitution on the A-site of R ions with different ionic radii [2]. The introduction of different size ions leads to a change of Mn–O–Mn bond lengths and angles. That, in turn, changes the relation between the competing antiferromagnetic (AFM) superexchange and ferromagnetic (FM) double-exchange interactions, resulting in the change of the magnetic state of the system. Besides the average size of the A-site cation $\langle r_A \rangle$, the size differences between the different cations located in the A-site must be taken into consideration. The introduction of the different impurities induces the local distortions which are randomly distributed in the sample volume [3]. For example, such disorder may lead to the micrometer-scale magnetic phase separation in the manganites [4]. Finally, we should take into consideration that an electronic state of R ions occupying the A-site also influences the physical properties of the manganites. In the present study, we discuss the peculiarities of the transport and magnetic properties of the lanthanum manganite doped with Eu ions.

2. Experimental details

The single crystals $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ were grown by a method of spontaneous crystallization from solution in a melt. The composition of the samples was confirmed using the X-ray fluorescence analysis. The powder X-ray diffraction pattern shows that the crystal has a single phased perovskite-type structure without any impurity

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phase. All diffraction lines are assigned to the structure with a space group P4/m, the cell parameters are $a = b = 3.8800(6)$ Å, $c = 3.8705(4)$ Å. The transport and magnetic measurements were carried out in PPMS6000 (Quantum Design) from 350 down to 2 K in the magnetic field up to 50 kOe. The magnetic resonance measurements were performed by spectrometers operating in $\nu = 9 - 80$ GHz frequency range with external magnetic fields of 0–80 kOe.

3. Results and discussion

Fig. 1 shows the temperature dependence of the resistivity ρ and magnetoresistance (MR) $\Delta\rho/\rho(0)$ of the crystal. The sample does not reveal a metal-insulator transition, but CMR phenomenon is observed in all temperature range below $T^* \cong 235$ K, $\Delta\rho/\rho(0)$ reaches its maximal value of 96% in the magnetic field of 50 kOe at $T_f \cong 80$ K.

In high-temperature region the temperature dependence of ρ follows a model of a small polaron hopping. This model predicts that $\rho = \rho_0 T \exp(E_g/k_B T)$, where ρ_0 is a temperature independent coefficient, E_g is an activation energy ($E_g/k_B = 1905$ K in our case). Note, that ρ starts deviating from the small polaron type of behavior at the temperatures where the noticeable MR effect appears. It has been suggested [4] that the anomalous behavior found in the transport measurement at temperatures which are well above magnetic ordering temperature is caused by the appearance of FM conducting clusters in a volume of the PM phase.

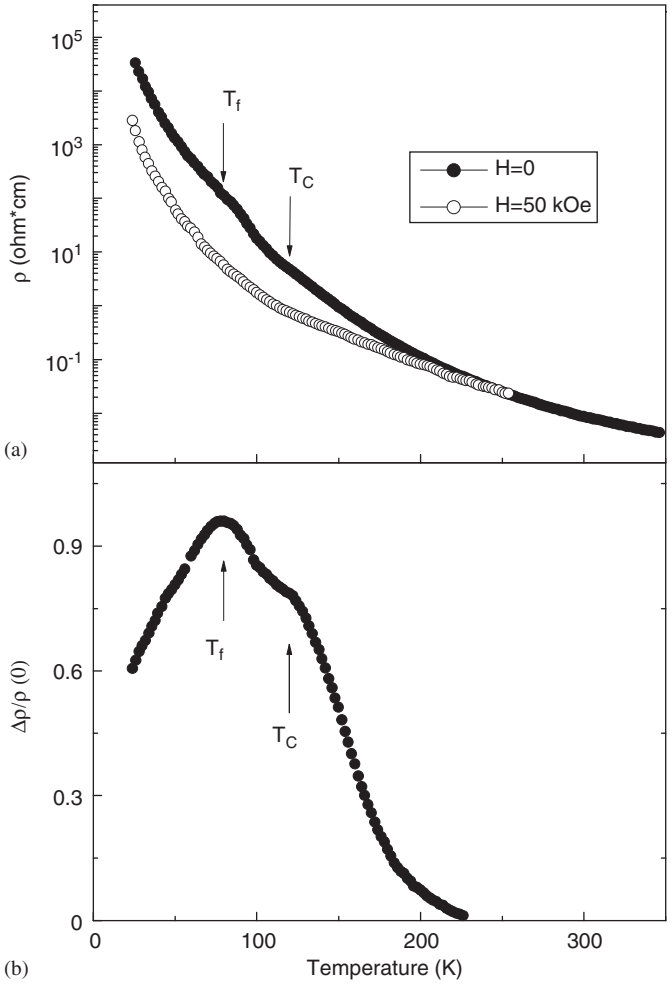

Fig. 1. (a) Temperature dependence of the resistivity ρ and (b) magnetoresistance $\Delta\rho/\rho(0)$.

Another mechanism of the conductivity dominates in the sample below T_f. At $T < T_f$ the experimental results are reasonably well fitted to Mott's variable-range hopping model. Within this model $\rho(T) = \rho_0 \exp[(T_0/T)^{1/4}]$, where ρ_0 is preexponential factor and T_0 is related to density of states at the Fermi level ($T_0 = 1.8 \times 10^7$ K in our case). Such behavior of ρ is typical for the topologically inhomogeneous medium.

The behavior of ρ and $\Delta\rho/\rho(0)$ in the temperature interval from $T_C = 119$ K to T_f are consistent with those in literature [5]. It is suggested, that, on cooling sample through T_C, the transition from PM insulating state to FM insulating state passes through an intermediate more conductive FM vibronic (FMV) state. By analogy, we identify the interval $T_f < T < T_C$ with a region where FMV state appears in the majority phase of the crystal.

At high temperature, the magnetic susceptibilityχ of the crystal follows the Curie–Weiss law, but χ^{-1} lies substantially above the Curie–Weiss limit as T_C is approached from high temperature. Such behavior suggests the spin clustering effect [3]. This conclusion is consistent with assumption that the peculiarities of the transport properties below T^* are related to the appearance of the conducting FM clusters.

Fig. 2 shows the temperature dependences of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization M in the field of 50 Oe. The difference between the FC and ZFC M increases with the decrease of temperature. An observed thermomagnetic irreversibility and λ-shape trace of the ZFC curve suggest the possibility of spin-glass-like state in the samples. The spin-glass-like behavior of M is possible, for example, when FM regions of the minority phase are embedded in FM background of the majority phase, and these different FM phases are coupled at a phase boundary by the exchange interactions which differ in sign and value from the intra-phase interactions. We have every reason to believe that such state is realized in the manganites with A-site cationic disorder [4,6]. The inset in Fig. 2 shows that the sample remains unsaturated down to $T = 2$ K. That is consistent with the assumption of the inhomogeneity of the sample.

At analysis of the experimental magnetic resonance spectra we applied a fitting procedure by Lorentzian lines. The spectra could be fitted satisfactorily, if we assumed the presence of two absorption lines. Fig. 3 shows the temperature dependencies of the resonance fields H_r^1, H_r^2 (a) for both lines in the spectra. Ratio of the integrated intensities A_2/A_1 of the lines versus temperature is

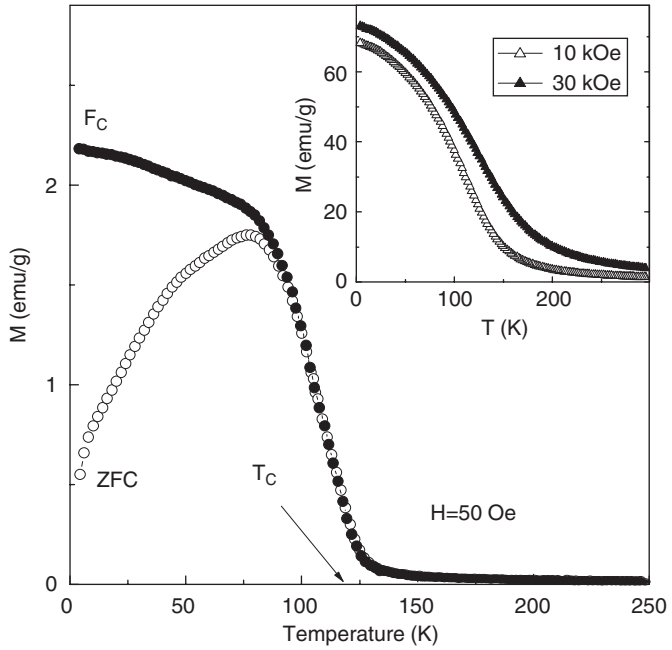

Fig. 2. FC and ZFC dc magnetization measured as a function of temperature at $H = 50$ Oe. Inset: the temperature dependencies at applied fields of 10 and 30 kOe.

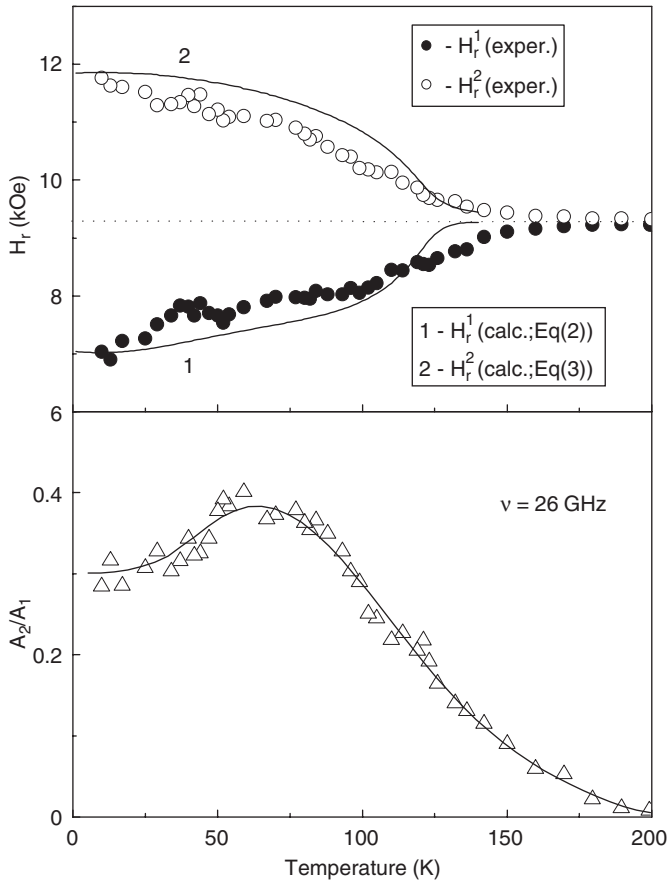

Fig. 3. (a) Temperature dependencies of the resonance fields H_r^1, H_r^2 for absorption lines in the spectra; symbols denote the experimental data; solid lines 1 and 2 represent dependencies given by Eqs. (2) and (3), respectively; (b) ratio of the integrated intensities A_2/A_1 of two lines versus temperature.

presented in Fig. 3(b). We suppose that the observed lines in the spectra are related to the absorptions in two different phases coexisting in the sample volume, and A_2/A_1 reflects an evolution of the two-phase state.

We found out, that resonance data are consistent with the transport and magnetization measurements. When $T > 220$ K the sample is in the homogeneous PM state, and a single line is only observed in the spectrum. At $T \simeq 220$ K the FM clusters of the minority phase appear in the volume of the majority PM phase, and the additional line corresponding to the FM resonance absorption arises in the spectrum at a higher magnetic fields relative to PM line. With the further decrease of the temperature, the intensity of this line A_2 increases, that is related to the increasing of the volume fraction of the FM phase and its magnetization. On cooling through T_C the FM order forms in the volume of the majority phase. Below T_C two FM phases coexist in the sample. It is interesting that A_2/A_1 is frequency dependent, it increases with the increasing of the microwave frequency ν. We can interpret that as the change of the volume fractions of the coexisting phases with magnetic field.

We have used a simple model, which reproduces the main features of the experimental spectra. It is further assumed that the sample has a shape of a thin plate and the applied magnetic field is taken to be in the plane of the plate. The disconnected regions of the minority FM phase having volume of V_2 are embedded in the volume V_1 of the majority FM phase. The majority and minority phases with the magnetizations M_1 and M_2, respectively, are coupled through the interface. The total free energy of the system per unit volume can be written as

$$E = \frac{1}{1+x}\{-\bar{M}_1\bar{H} + K_{A1}\} + \frac{x}{1+x}\{-\bar{M}_2\bar{H} + K_{A2}\} - J_{\mathrm{ef}}\bar{M}_1\bar{M}_2, \quad (1)$$

where $x = V_2/V_1$; K_{A1} and K_{A2} terms include the energies of the magnetocrystalline anisotropies and the demagnetization energies. The coupling between phases is described by the coupling parameter J_{ef}, which is a function of the area of the boundaries separating the different phases. We have considered only strong demagnetizing field for the majority phase, which is originated from the plate-like shape of the sample, and we have neglected the demagnetizing effect related to magnetic inhomogeneity for both phases and the magnetocrystalline anisotropy. With all these considerations, solving linearized equations of motion we have obtained the dispersion relation for two absorption peaks in the spectra:

$$(\nu_1/\gamma)^2 \approx (H_r^1 + (1+x)J_{\mathrm{ef}}M_2) \times (H_r^1 + (1+x)J_{\mathrm{ef}}M_2 + 4\pi M_1), \quad (2)$$

$$(\nu_2/\gamma) \approx H_r^2 + \left(\frac{1+x}{x}\right)J_{\mathrm{ef}}M_1, \quad (3)$$

where γ is a gyromagnetic ratio, H_r^1 and H_r^2 are the resonance fields for absorption lines from the majority and

minority phases, respectively. The equations were derived under the assumption that $\bar{M}_1 \| \bar{M}_2$, i.e. at $H > H_{sat}$, where H_{sat} is the saturation field. Computing these equations we have obtained the dependencies of H_r^1 and H_r^2 on temperature, Fig. 3, and v. In the computation we have approximated $\bar{M}_1$ and $\bar{M}_2$ by the Brillouin functions, and used a simple condition that $J_{ef} = Cx^{2/3}$, which is valid for a spherical shape of the regions of the minority phase. The experimentally measured ratio A_2/A_1 has been used instead of x value. To obtain the dependencies which reproduce the experimental behavior of the H_r^1 and H_r^2, we had to assign negative value to J_{ef} ($C = -2.1$), that corresponds with the AFM exchange coupling between the coexisting phases.

4. Conclusion

In this work, we have investigated the physical properties of the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ crystal. The transport, magnetization and magnetic resonance measurements confirm the coexistence of the two magnetic phases in the crystal. From a high temperature down to $T^* \simeq 235$ K the sample is in the homogeneous PM state with the polaron type of the conductivity. At T^* the FM clusters having higher conductivity than the PM matrix appear in the sample volume. At $T_C = 119$ K the FM order forms in the majority phase, and below T_C the coexistence of the two different FM phases takes place in the sample. In respect of magnetic properties, these phases are observed as a spatially separated due to the frustration of the FM and AFM exchange interactions on the phase boundaries.

Acknowledgments

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