Low-Temperature Resistivity of Polycrystalline 
(La_{0.5}Eu_{0.5})_{0.7}Pb_{0.3}MnO_{3} in a Magnetic Fields

K A Shaykhutdinov¹²³, S I Popkov¹, S V Semenov¹², D A Balaev¹², A A Dubrovskiy¹, K A Sablina¹, and N V Volkov¹²

¹ Kirensky Institute of Physics, Russian Academy of Sciences, Siberian Branch, Krasnoyarsk, 660036, Russia
² Siberian Federal University, Krasnoyarsk, 660041, Russia
E-mail: dir@iph.krasn.ru

Abstract. The effect of grain boundaries on magnetoresistance (MR) of manganites have been investigated by the comparative analysis of the properties of single-crystal and polycrystalline (La_{0.5}Eu_{0.5})_{0.7}Pb_{0.3}MnO_{3}. While MR of the single crystal is maximum near the Curie temperature and vanishes in the low-temperature region, the polycrystalline (La_{0.5}Eu_{0.5})_{0.7}Pb_{0.3}MnO_{3} sample exhibits high MR in the low-temperature region. In order to clarify the origin of the low-temperature MR, the transport and magnetic properties of the polycrystalline (La_{0.5}Eu_{0.5})_{0.7}Pb_{0.3}MnO_{3} in magnetic fields have been supplemented by study of magnetic properties and specific heat measurements. The results obtained could be attributed to spin-dependent tunneling between ferromagnetic grains through insulating antiferromagnetic grain boundaries.

1. Introduction

It is known that the compounds of lanthanum manganites R_{1-x}A_{x}MnO_{3}, where R is the trivalent rare-earth ions, such as La³⁺ and Pr³⁺, and A is the bivalent ions (Ca²⁺, Sr²⁺, Ba²⁺, or Pb²⁺) in the form of single crystals, thin films, and polycrystals exhibit the colossal magnetoresistance effect [1-5], which makes these materials promising candidates for practical application. The occurrence of the low-temperature resistance minimum and hysteresis in the R(H) dependences is not clear. In a number of studies [1-7], the low-temperature behavior of electrical resistance was explained by spin-dependent tunneling of charge carriers via dielectric spacers separating ferromagnetic grains.

In view of the aforesaid, experimental study of the low-temperature behavior of electrical resistance of manganites is an urgent problem. To solve it, we propose the following approach. Manganite single crystals are taken as a basis. Their magnetotransport characteristics are thoroughly investigated. Then, the initial single crystals are grinded, pressed, and annealed, in order to prepare polycrystalline samples in which crystallites posses of the properties of the initial single crystals and all the possible effects occur at the intergrain boundaries formed during the synthesis.

As an initial single crystal, we chose a previously synthesized and investigated sample with the (La_{0.5}Eu_{0.5})_{0.7}Pb_{0.3}MnO_{3} composition. Previously [8], we had studied single-crystal (La_{1-x}Eu_{x})_{0.7}Pb_{0.3}MnO_{3} samples with x = 0, 0.2, 0.4, and 0.6. In the area of the inhomogeneous state, the colossal magnetoresistance effect is observed for all the samples. In the crystals with x = 0 - 0.5 both above and below the temperature of the magnetic phase transition the paramagnetic phase with polaron conductivity and the ferromagnetic phase with metal conductivity coexist. At T < Tc, the sample with x = 0.6 is in the inhomogeneous state which represents the coexistence of two different ferromagnetic phases with different conductivity. The sample with x = 0.6 does not posses of maximum electrical resistance at the temperature of the metal/dielectric transition; its resistance smoothly increases up to the helium temperatures. Correspondingly, the sample with x = 0.5 with the maximum MR effect value, which is practically important, is at the edge of the substitution series. Also, it possesses of the maximum electrical resistance near the metal/dielectric transition. This is the sample we chose as an initial single crystal.
2. Experimental details

A single-crystal sample of the \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) composition was grown by spontaneous crystallization. PbO and PbF\(_2\) compounds worked as solvents and, simultaneously, provided the required quantity of Pb atoms in the crystals. The single crystals were cubes 3×3×3 mm\(^3\) in size with the black shiny surface and sharp edges. The measurements were performed on well-polished plate-like samples 3×3×0.1 mm\(^3\) in size. The X-ray diffraction study showed the presence of the only perovskite-like phase in the crystal.

In order to prepare polycrystalline \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) samples, the initial single crystals were grinded in an agathic mortar and pressed in pills. The pills were annealed in a furnace at a temperature of 600°C for 3 hours. The obtained samples had sufficient mechanical strength to bear the magnetotransport measurements. Scanning electron microscopy (SEM) study of the annealed samples revealed an average crystallite size of about 1-2 μm. High-resolution transmission electron microscopy of the grains showed the presence of about 5-nm-thick surface layer whose structure differs from the structure of the internal volume of the grains. Thus, the surface layer formed during the synthesis serves as an intergrain boundary.

The transport and magnetic measurements were performed with a PPMS–6000 facility in the temperature range from 1.9 to 300 K in magnetic fields from 0 to 9 T. Temperature dependences of electrical resistance \(R(H)\) for the single-crystal and polycrystalline \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) samples were taken using a standard four-probe method. For the correct description of absolute values of electrical resistance, in both cases the samples 3×3×0.1 mm\(^3\) in size were used.

3. Results and discussion

The \(R(T)\) dependences of \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) for different applied magnetic fields for the single-crystal and polycrystalline samples are given in Figs. 1a and 1b, respectively. The inserts in the figures present the temperature dependences of electrical resistance for some values of the magnetic field. It is noteworthy the \(R(T)\) dependences of the single-crystal and polycrystalline samples are different, as many authors mentioned [9]. First of all, there is a shift of the metal/dielectric transition towards lower temperatures for the polycrystal and the difference in absolute values of electrical resistance related to the presence of the intercrystallite boundaries in the polycrystal. In addition, below ~50 K the polycrystalline sample reveals minimum resistance; after that, resistance starts increasing and at helium temperatures reaches the values comparable with those for the metal/dielectric transition. The MR effect values in the range 2 – 100 K are practically the same, which is not observed for the single crystal.

Figure 2 demonstrates the \(R(H)\) dependences for the polycrystalline \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) sample in a wide temperature range including the temperature of the metal/dielectric transition and the low-temperature region. The \(R(H)\) dependences for the single-crystal \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) sample are not presented here; note, however, that they are typical of single crystals of lanthanum manganites [9] and have no features in the low-temperature region. The main peculiarities of the \(R(H)\) curves (Fig. 2) are the following. First, at the magnetic field \(H \approx 3\) kOe in the temperature range 2 – 120 K the \(R(H)\) dependence changes its character; then, resistance uniformly decreases up to 9 T with no saturation magnetization observed. Second, in the temperature range 2 – 30 K, i.e., below the temperature of the minimum electrical resistance, the \(R(H)\) curves reveal hysteresis with a width decreasing with an increase in temperature. The direction of the...
magnetic field sweep is pointed by arrows in Fig. 2. Above the temperature of the minimum electrical resistance, no hysteresis features are observed.

Figure 3 shows the temperature (a) and field (b) dependences of magnetization of the \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) samples. One can see from the \(M(T)\) curves that Curie temperature \(T_C\) is nearly the same (~215 K) for two samples; however, the absolute values and magnetization behaviors are different (Fig. 3a). For the \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) single crystal, magnetization is \(M(2\text{K}, H = 15\text{ kOe}) = 60\) emu/g, while for the polycrystalline sample it is \(M(2\text{K}, H = 15\text{ kOe}) = 47\) emu/g, i.e. lower by 22%. It is seen from the field dependence of magnetization \(M(H)\) that at \(T = 1.9\) K (Fig. 2b) magnetization of the single-crystal \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) sample saturates in a field of about 5 kOe, while magnetization of the polycrystal in fields higher than 5 kOe linearly grows.

We should pay attention that in the \(M(T)\) curve at \(T = 40\) K (Fig. 3a) there exists a feature corresponding to the magnetic phase transition. This feature is clearly seen in the temperature dependence of a derivative \(dM/dT\) (insert in Fig. 3a).

The results of the measurements of low-temperature heat capacity \(C_p(T)\) for two samples are shown in Fig. 4. At \(T = 40\) K, the \(C_p(T)\) curve for the polycrystalline sample has a feature which is related to the second-order phase transition.

4. Conclusions

The data of the magnetic (Fig. 3) and heat capacity (Fig. 4) measurements allow one to conclude that during the synthesis of the polycrystalline \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) sample the second phase forms. This phase is characterized by the magnetic order with the temperature of the magnetic phase transition \(T = 40\) K and, in our opinion, can be antiferromagnetic. The transmission electron microscopy data suggest that the second phase, whose properties are different from those of the grain core, is the material of the surface layer of the crystallites with a thickness of about ~5 nm. Thus, one can conclude that in the polycrystalline \((\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3\) sample a network of tunnel contacts ferromagnet-antiferromagnet-ferromagnet (FM-AF-FM) forms. The possibility of the formation of such a network was pointed in [10] where the authors suggested that in the surface layer of manganite grains, due to depletion in oxygen, the magnetic moments is aligned antiferromagnetically; thus, the FM-AF-FM network is created. In [11], the authors calculated the dependences of conductivity of such a structure on the external magnetic field.

Consider the qualitative form of the \(R(H)\) dependences of the polycrystalline
(La_{0.5}Eu_{0.5})_{0.7}Pb_{0.3}MnO_3 sample (Fig. 2). Note that the temperature of the minimum electrical resistance (Fig.1) weakly increases from 39.5 K at \( H = 0 \) T to 45 K at \( H = 9 \) T, i.e., correlates well with the temperature of the magnetic phase transition. In addition, it is seen from Fig. 2 that the hysteresis features are observed in the R(H) curves only below the temperature of the minimum electrical resistance. Also, after the considerable drop of electrical resistance in weak fields (up to 3 kOe) the resistance smoothly decreases. The primary drop of electrical resistance is related to the orientation of the ferromagnetic grains, which is clearly seen in the \( M(\text{T}) \) dependences (Fig. 3), whereas further decrease in R cannot be explained considering only the magnetization processes. In this case, it is reasonable to suggest that, indeed, in the polycrystalline \( (\text{La}_{0.5}\text{Eu}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3 \) sample the network of tunnel contacts forms. In this network, the surface grain layer depleted in oxygen works as an AF spacer [10] and the spin-dependent tunneling occurs via dielectric with the magnetic order, which can be exchanged-coupled with the ferromagnetic grains. The aforesaid can explain the hysteresis features in the R(H) curves and the smooth decrease in electrical resistance in fields up to 9 T.

Acknowledgments
The work was partially supported by grant of RFBR N 08-02-00259a.

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