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Magnetotransport and magnetic properties of manganites doped with iron and aluminum

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1. Introduction

One of the topical areas of scientific research in solid state physics is the creation and study of complex multifunctional magnetic materials, the elucidation of the mechanisms of changing their spin and electronic states. Such systems have a unique relationship between structural, magnetic and electrical properties, which consists in a significant change in the state of the spin and electronic subsystems with the application of small external influences like temperature, pressure, or superposition of an external magnetic or electric field. Manganites with mixed valence of manganese ions and perovskite structure, which are model objects in the physics of strongly correlated electron systems [1-3], possesses such properties.

In this paper, we present a study on the effect of the replacement of Mn by Fe and Al in the single crystalline samples of $La_{0.7}Ba_{0.3}(Mn_{1-x}Me_x)O_3$ ($Me=Fe^{3+}$, Al^{3+}). Our study shows that the replacement of manganese by other ions enhances magnetic randomization without appreciable changes in the magnitude of magnetoresistance effect despite the huge difference in the electrical behavior of the samples. The temperature range where GMR effect is observed becomes gradually wider with the increase of Fe-content reflecting the magnetic randomization process.

2. Experimental procedures

The single crystals of $La_{0.7}Ba_{0.3}(Mn_{1-x}Me_x)O_3$ (Me= Fe, Al) compositions were grown in platinum crucible by flux method. The starting components La_2O_3, MnO_2, $BaCO_3$, Fe_2O_3 or Al_2O_3 were taken in stoichiometric proportion and dissolved in the $BaO–BaF_2–B_2O_3$ solvent. The mixture was soaked for 24 h at 1300 ^{0}C followed by temperature decreasing down to the point where single crystals start to grow. The

single crystals with dimensions up to 5×4×4mm were grown by slow cooling of the crucible at an average rate of 18 ^{0}C/h. According to X-ray data, all the crystals have rhombohedrally distorted unit cell of perovskite structure. Chemical analysis has shown that compositions of Fe-doped samples approximately correspond to proportion of row materials; however for the heavily doped manganites the content of Fe ions was slightly less than in the initial mixture. We have not managed to obtain single crystals doped by large amount of Al ions despite the wide range of synthesis conditions. The upper limit of Al^{3+} ions entering was around $x \sim 0.15$. Resistivity measurements were made by the conventional four-probe method. The indium electric probes were formed using ultrasonic soldering. The magnetization measurements were performed with a vibrational sample magnetometer.

3. Results and discussion

According to measurements of the magnetization, the Curie point of the sample $La_{0.7}Ba_{0.3}MnO_3$ is 350 K. Magnetic moment at 5 K corresponds to parallel alignment of all the magnetic moments. A metal-insulator transition is observed slightly below the Curie point, which is expressed in a sharp decrease in the resistivity (Fig. 1) and is accompanied by a peak of the magnetoresistance reaching a maximum value of 24 % at 325 K at the field of about 0.3 T (Fig. 1). Here magnetoresistance is defined as $\{[R(H)-R(H=0)]/R(H=0)\}\times100\%$.

The replacement of Mn ions by Al ions leads to the decrease in the Curie temperature to 311 K for the sample $La_{0.7}Ba_{0.3}(Mn_{0.9}Al_{0.1})O_3$. The resistivity and magnetoresistance dependences are similar to those obtained for the $La_{0.7}Ba_{0.3}MnO_3$ sample (Fig. 1). At 100 K, the resistivity is approximately 10^{-4} Ω·cm, which is a fairly conducting state for 3d oxides.

In the case of the replacement of manganese ions by iron, the change in electrical and magnetic properties is more pronounced due to the larger sizes of substituent ions. The Curie temperature of $La_{0.7}Ba_{0.3}Mn_{0.87}Fe_{0.13}O_3$ is 208 K. With further replacement of manganese by iron ions, the Curie temperature drops noticeably and for the sample $La_{0.7}Ba_{0.3}Mn_{0.82}Fe_{0.18}O_3$ it becomes equal to 150 K. In this case, the spontaneous magnetic moment M = 1.94 μ_B/f.u. is rather less than the expected value for ferromagnetic ordering. According to the measurement of the magnetization, the long-range ferromagnetic order in the sample $La_{0.7}Ba_{0.3}Mn_{0.72}Fe_{0.28}O_3$ is fully destroyed so that this sample exhibits the magnetic properties characteristic of spin glass.

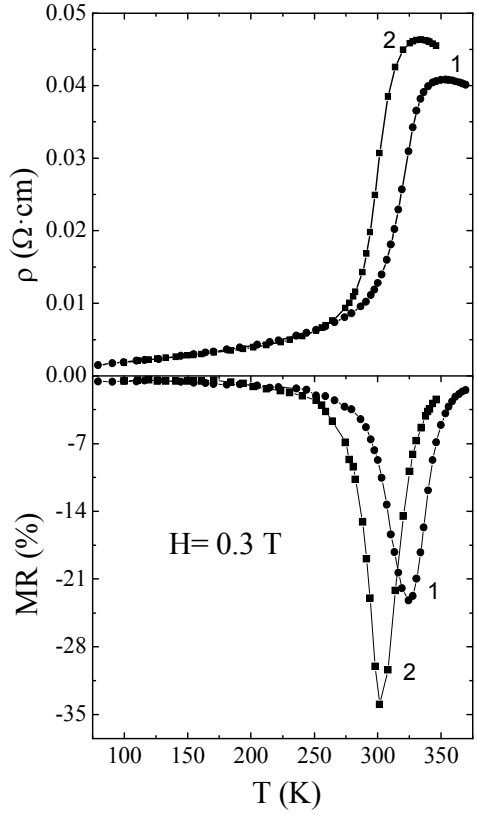

Fig. 1. The temperature dependence of resistivity (top panel) and magnetoresistance (bottom panel) for $La_{0.7}Ba_{0.3}MnO_3$ (1) and $La_{0.7}Ba_{0.3}(Mn_{0.9}Al_{0.1})O_3$ (2).

The electrical resistivity behavior correlates with magnetization data. The ferromagnetic sample with x = 0.13 exhibits a transition from high temperature insulating state to the metallic one while the magnetic long range order is developed when cooling (Fig. 2). The magnetoresistance peak has approximately the same magnitude as for the sample doped with 10% aluminum; however, the temperature width of the peak is much larger. The behavior of resistivity drastically challenges for the sample doped with 20 %Fe. This sample remains insulating in the ferromagnetic state. There is only a weak anomaly around the Curie point on the resistivity *vs*. temperature curve. The magnetoresistance effect is large both below and above the Curie point; however, around the Curie point this effect is maximal.

The x = 0.28 sample shows very large resistivity at low temperatures (Fig. 2). The magnetoresistance increases gradually as temperature decreases and reaches

25 % at 77 K. This value is comparable with the values typical for ferromagnetic single crystals near the Curie point.

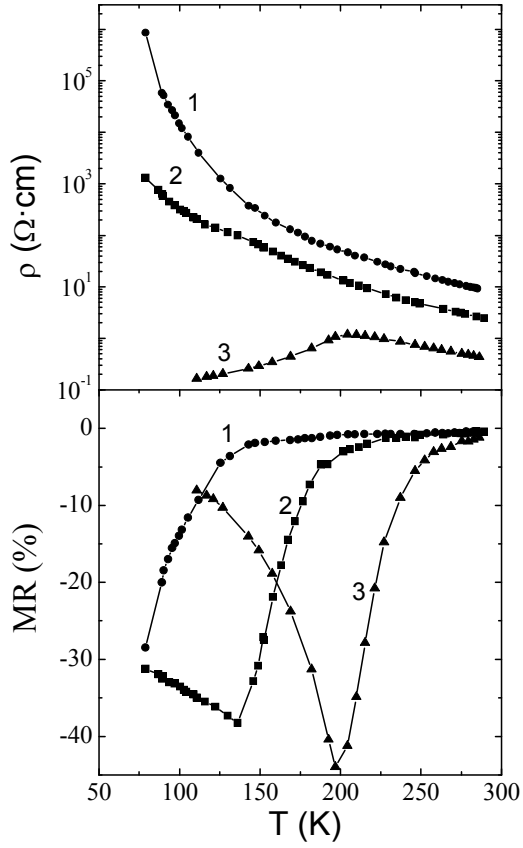

Fig. 2. The resistivity (top panel) and magnetoresistance (bottom panel) for $La_{0.7}Ba_{0.3}(Mn_{1-x}Fe_x)O_3$ (x=0.28 (1); 0.18 (2) and 0.13 (3)).

According to literature data, there are two possible mechanisms of electrical conductivity in manganites. The conductivity in the paramagnetic range is usually ascribed to a small polaron hopping between nearest and non-nearest neighbor sites. In the low temperature range where the metallic state is developed the electrical conductivity seems to be resulted from the moving of holes in the wide valence zone dominantly formed from 2p-orbitals of oxygen [8]. The metal–insulator transition may be the result of an intersection of wideт 2p-band and narrow manganese band of 3d-type [8]. The findings presented here agree with the assumption that the mechanism responsible for the realization of GMR effect close to T_C is common for both insulating and fairly conducting manganites. When the La^{3+} ions are replaced

with alkaline earth ones, the Mn^{3+} converts into Mn^{4+}. However, the Mn^{4+} is not a mobile charge carrier. As a rule, complex of alkaline earth ions and Mn^{4+} ions form an acceptor impurity state. Under the doping level above ~10–15 % from the total number of lanthanum sites, acceptor states are overlapped thus forming an impurity band. The mechanism of the conductivity depends on both the width of impurity band and the energy gap between the impurity band and wide valence band. In any case, the Mn-site substitution goes down results to the narrowing of the impurity band width because of decreasing quantity of the available sites for the charge carrier motion. By contrast, the ferromagnetic ordering favors the increasing width of the impurity band due to parallel orientation of all the magnetic moments. The metal–insulator transition occurs while impurity band and valence band overlap. It might be the result of the magnetic ordering of $La_{1-x}Sr_xMnO_3$ in the range of $0.15 \leq x \leq 0.4$ or the decrease of distance between Mn-sites in the range of $0.4 \leq x \leq 0.6$ [9]. We believe that for both insulating and conducting manganites the ferromagnetic ordering process markedly affects the binding energy of the trapped carriers. This effect does not depend strongly on concentration of carriers or magnitude of the Curie point. The magnitude of magnetoresistance depends on the effect of external magnetic field on the magnetic state. The large narrow peak of the magnetoresistance is usually observed for manganites with well defined Curie point. Magnetic inhomogeneity leads to the broadening of the temperature interval where a large magnetoresistance occurs. In the case of spin glasses there is no peak of magnetoresistance because the lower the temperature, the more effectively an external magnetic field supports the ferromagnetic order.

Acknowledgments

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Abstract

The single crystals of $La_{0.7}Ba_{0.3}(Mn_{1-x}Fe_x)O_3$ ($x \leq 0.28$) and $La_{0.7}Ba_{0.3}(Mn_{1-x}Al_x)O_3$ ($x \leq 0.15$) compositions were grown using flux method and characterized by X-ray, electrical and magnetization measurements. The replacement of Mn ions by Al ions in the $La_{0.7}Ba_{0.3}Mn_{1-x}Al_xO_3$ system leads to a decrease in the temperature to 311 K for the sample x=0.1. The Fe-doping above x=0.2 destroys a long range ferromagnetic order thus leading to a spin glass state. It is found that insulating spin glasses exhibit a large magnetoresistance in the paramagnetic region that is comparable to that for ferromagnetic crystals showing metal–insulator transition near T_C.

Abstrakt

Monokryształy $La_{0,7}Ba_{0,3}(Mn_{1-x}Fe_x)O_3$ ($x \leq 0,28$) i $La_{0,7}Ba_{0,3}(Mn_{1-x}Al_x)O_3$ ($x \leq 0,15$) wyhodowano metodą strumieniową i charakteryzowano poprzez badania rentgenowskie, pomiary elektryczne i magnetyzacyjne. Zastąpienie jonów Mn jonami Al w układzie $La_{0,7}Ba_{0,3}Mn_{1-x}Al_xO_3$ prowadzi do obniżenia temperatury do 311 K dla próbki x = 0,1. Domieszka Fe powyżej x = 0,2 niszczy ferromagnetyczny porządek dalekiego zasięgu atomów Fe, prowadząc w ten sposób do spinowego stanu typu szkła. Stwierdzono, że izolacyjny spinowy stan typu szkła wykazuje dużą rezystancję magnetyczną w obszarze paramagnetycznym, która jest porównywalna z kryształami ferromagnetycznymi i wykazują przejście metal-izolator w pobliżu TC.

Słowa kluczowe: magnetorezystancja, oddziaływanie magnetyczne, magnetyzacja