Phase Transformations and Magnetotransport Properties of the Pr$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Mn$_x$O$_3$ System

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Abstract—The structural, magnetic, and magnetotransport properties of Pr$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Mn$_x$O$_3$ ($x < 0.65$) perovskites are studied by magnetization and electrical conductivity measurements in magnetic fields up to 14 T and by neutron diffraction. In the manganese concentration range $x < 0.5$ and $T = 300$ K, the crystal structure is described by monoclinic space group $I2/a$; at $x > 0.5$, it is described by orthorhombic space group $Imma$. When the temperature decreases, a structural transformation without changing the symmetry takes place in all compounds. This transformation is caused by an active role of the inner shells of the praseodymium ion in chemical bond formation. The substitution of manganese for cobalt breaks a long-range ferromagnetic order near $x \approx 0.25$, and a metal–dielectric transition occurs at $x \approx 0.15$. The negative magnetoresistance is found to be maximal near a critical manganese concentration, where a long-range magnetic order is broken; it reaches 95% in a field of 14 T at $T = 10$ K for $x = 0.2$. An unusual dielectric magnetic state with a small spontaneous magnetic moment and a sharp transition into a paramagnetic state at $T > 200$ K is revealed in the concentration range $0.30 \leq x \leq 0.65$ in spite of the absence of coherent magnetic neutron scattering. A model is proposed to explain the behavior of the magnetic properties in this phase.

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1. INTRODUCTION

The cobaltites of rare-earth elements with a perovskite structure have attracted close attention due to the transitions related to a change in the spin state of trivalent cobalt ions and to a correlation between their magnetic and electrottransport properties. At low temperatures, LaCoO$_3$ is a diamagnetic dielectric. As the temperature increases, researchers [1–4] detected transitions accompanied by a change in the spin state of cobalt ($T \approx 100$ K) and dielectric–metal transitions ($T \approx 550$ K). When strontium ions substitute for lanthanum in the La$_{1-x}$Sr$_x$CoO$_3$ system, a transition from a dielectric spin glass state into a ferromagnetic metallic state occurs near $x = 0.18$ [5]. The following three basic mechanisms of magnetic interactions used to explain the unusual magnetic properties of ferromagnetic metallic cobaltites were described [1–7]:

(i) a superexchange model based on the interaction of localized electrons through oxygen ions,
(ii) double exchange involving direct electron transitions between cobalt ions,
(iii) magnetism of collective electrons.

Although these mechanisms can explain certain physical properties of cobaltites, none of them is considered to be a universal model. Double exchange is assumed to be the main cause of positive exchange interactions in metallic cobaltites and manganites; however, there are many differences in the properties of these compounds. For example, manganites exhibit a first-order metal–dielectric phase transition at the Curie temperature. A shift in the temperature of this transition in an applied magnetic field results in colossal magnetoresistance, which can reach 5–6 orders of magnitude at low temperatures of magnetic ordering. Cobaltites are metals in paramagnetic and ferromagnetic phases, and the electrical conductivity at the Curie point changes relatively weakly. As a result, the negative isotropic magnetoresistance near the Curie point is low, 5–6% in a field of 10 T [8–10]. The covalent component of the chemical bond in cobaltites is significantly higher than that in manganites, and cobaltites are characterized by $2p$-hole conduction [11, 12]. In contrast to manganites, cobaltites do not exhibit intergranular tunneling magnetoresistance, which can reach 50% in a field of 1 T in manganites [13, 14]. These facts indicate a wide conduction band and weak charge polarization in cobaltites.

At a doping level $x = 0.5$, Ln$_{1-x}$Sr$_x$MnO$_3$ manganites are known to undergo charge and orbital ordering,
which radically changes the physical properties of these compounds. The charge-ordered phase is an antiferromagnetic dielectric, and an applied magnetic field can break the charge ordering. As a result, a ferromagnetic metallic state appears; this leads to a change in the resistance by 10 orders of magnitude or more. However, below room temperature, $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ ($\text{Ln} = \text{La, Nd, Sm, Eu, Gd}$) cobaltites do not undergo structural transformations and are ferromagnetic metals with a Curie point that decreases smoothly with decreasing rare-earth ion radius from $T_C = 245 \text{ K} \text{ (La)}$ to $T_C = 150 \text{ K} \text{ (Gd)}$. The sole exception from this rule is compound $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Co}_3$. A structural transformation was detected in the ferromagnetic phase of this compound at $T = 120 \text{ K}$; this transformation sharply changes the magnetic anisotropy and changes the easy axis [15–21]. Neutron diffraction studies did not reveal a change in the magnetic moment during this transformation, which remains close to $2\mu_B$ per cobalt ion at the liquid-helium temperature (as in other $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{Co}_3$-type cobaltites). In [20], we revealed a low-field positive magnetoresistance, which reached 2% in a field of 1 T at $T = 10 \text{ K}$, in the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Co}_3$ compound. This type of magnetoresistance decreases with increasing temperature, and a conventional negative isotropic magnetoresistance related to a break in a ferromagnetic order dominates near the Curie point. Based on the neutron diffraction results, the authors of [18, 21] assumed that this structural transformation is related to an active role of praseodymium ions in chemical bond formation rather than to a change in the spin or orbital state of cobaltite ions. This assumption was supported by the study of a system of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.66-x}\text{Fe}_x\text{O}_3$ solid solutions [20]. It was found that the substitution of iron ions for cobalt ions breaks a long-range magnetic order at $x = 0.44$, a dielectric cluster spin glass forms in the concentration range $0.44 < x < 0.66$, and a long-range $G$-type antiferromagnetic order inherent in $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{Fe}_3\text{O}_3$ ferrites with a perovskite structure appears at $x > 0.66$. A structural transformation similar to that in the initial compound was revealed up to $x = 0.66$ in spite of a radical change in the magnetic and electrotransport properties.

In this work, we found that the substitution of manganese ions for cobalt ions in the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Mn}_x\text{O}_3$ system causes an unusual magnetic state with a high temperature of sharp transformation into a paramagnetic phase in the absence of coherent magnetic neutron scattering. As in the case of the substitution of iron ions for cobalt ions, this structural transformation takes place over a wide concentration range of manganese ions irrespective of the type of magnetic and electric state of the composition.

2. EXPERIMENTAL

Polycrystalline $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Mn}_x\text{O}_3 \text{ (} x \leq 0.65\text{)}$ samples were prepared using a standard ceramic technique. High-purity $\text{Pr}_2\text{O}_3$, $\text{Mn}_3\text{O}_5$, and $\text{CoO}$ oxides and $\text{SrCO}_3$ carbonate were taken in a stoichiometric ratio and thoroughly mixed in a RETSCH PM 100 planetary ball mill. The samples were formed in air at a temperature that was gradually increased with the manganese content from $1250 \text{°C}$ at $x = 0$ to $1440 \text{°C}$ at $x = 0.65$. To maintain oxygen stoichiometry, the samples were slowly cooled at a rate of 30 K/h. X-ray diffraction analysis performed on a DRON-3M diffractometer revealed no traces of foreign impurities. Powder neutron diffraction patterns were taken on a high-resolution E9 (FIREPOD) diffractometer at the Berlin Neutron Scattering Center (BENSC, Berlin). The neutron diffraction data were analyzed using the Rietveld method using FullProf software package. The magnetization was measured with an MPMS-5 SQUID magnetometer in fields up to 5 T and with a Cryogenic Ltd. vibrating-sample magnetometer in magnetic fields up to 14 T. The electrical conductivity was measured by the standard four-probe method on a Cryogenic Ltd. universal measuring system in magnetic fields up to 14 T.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure

The X-ray diffraction patterns of compositions with a manganese content up to $x = 0.5$ can be indexed using rhombohedral space group $R3\overline{1}$ c or monoclinic space group $I2/a$, and the X-ray diffraction patterns of compositions with $x > 0.5$ are well indexed using orthorhombic space group $Imma$ or $Ibmm$. It is very difficult to choose among these space groups using only the powder X-ray diffraction data, since X-ray diffraction is weakly sensitive to the displacement of oxygen ions. However, the neutron diffraction studies of compositions with $x = 0.05$ and $x = 0.3$ performed at $T = 300 \text{ K}$ and $T = 2 \text{ K}$ support monoclinic symmetry at both room temperature and $T = 2 \text{ K}$. Figure 1 shows neutron diffraction patterns taken at $x = 0.3$ at $T = 300$ and 2 K and refined by the Rietveld method. The calculation with space group $I2/a$ made it possible to identify all reflections and yielded good reliability factors upon refining ion coordinates. The calculations with low-symmetry space groups $P2/n$ and $P1\overline{1}$ only weakly improved the reliability factors. A structural transformation occurs near $T = 100 \text{ K}$; as a result, the structural parameters change significantly but the symmetry does not change. Tables 1 and 2 give the ion coordinates in various phases, and Table 3 presents changes in the $\text{Co–O–Co}$ bond angles and the praseodymium–oxygen (O1) bond lengths in the $\text{CoO}_3$ octahedron. As follows from Table 3, the praseodymium–oxygen (O1) bond lengths change significantly upon the transformation. These bond lengths in the low-temperature phase become substantially closer to each other than those in the high-temperature phase. The transformation is also accom-