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MAGNETISM

Magnetic Properties of a Layered Cobaltite $Sr_{1-x}Y_xCoO_{3-\delta}$ ($x = 0.1$)

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Abstract—The structure, the magnetic and magnetotransport properties of perovskite $Sr_{0.9}Y_{0.1}CoO_{2.63}$ have been studied. The sample is shown to have a two-phase structure. The main phase has a tetragonally distorted unit cell and is described by space group *I*4/*mmm*. The broadening of the reflections with indices corresponding to doubling unit cell parameter *c* indicates the absence of the rigorous translation symmetry along axis *c*. The existence of the broadened superstructure reflection observed in the diffraction pattern at small angles at temperature lower than 400 K is explained by the existence of the monoclinic phase whose content is significantly lower than that of the tetragonal phase, but is dominant in the $Sr_{0.8}Y_{0.2}CoO_{3-\delta}$ composition. The spontaneous magnetization appears as the monoclinic phase forms. The magnetic structure is mainly *G*-type antiferromagnetic with magnetic moments $1.5\mu_B$ in the layers of CoO_6 octahedra and $2\mu_B$ in the anion-deficit $CoO_{4+\gamma}$ layers. The conduction of the $Sr_{0.9}Y_{0.1}CoO_{2.63}$ composition has a semiconducting character. The magnetoresistance is 57% in a field of 14 T at a temperature of 5 K and strongly decreases with the temperature increase.

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1. INTRODUCTION

Complex cobalt oxides with the perovskite structure attract interest, because of various spin states of Co^{3+} ion, the existence of the relation between their magnetic and transport properties [1] and the giant magnetoresistance effect [2]. The character of magnetic interactions in cobaltites is dependent on the spin state of Co^{3+} ions that can be in the low-spin (t_{2g}^6, $S = 0$), intermediate spin state ($t_{2g}^5e_g, S = 1$) and high spin states ($t_{2g}^4e_g^2$, $S = 2$). In the base $LaCoO_3$ compound, Co^{3+} ions are in the low-spin state at temperatures lower than 30 K [1]. The increase in temperature higher 30 K leads to an increase in the magnetization that is maximal at 110 K. At temperatures higher than 500 K, a gradual semiconductor–metal transition and the magnetization increases with temperature. These transitions are accompanied by a change in the Co^{3+} ion spin state. In [3], ferromagnetism with T_C was detected at the surface of crystallites in powders and inside epitaxial films of $LaCoO_3$.

The substitution of Sr ions for La ions in the $La_{1-x}Sr_xCoO_3$ leads to the ferromagnetism with the Curie temperature to 305 K ($SrCoO_3$) [4]. Base compound $SrCoO_{3-y}$ can have different structural distortions in the dependence on the synthesis conditions and the oxygen content: orthorhombic distortions at $\gamma = 0.5$, tetragonal ones at $\gamma \approx 0.15$, and the compound close to the stoichiometric in oxygen is characterized by a cubic unit cell with space group $Pm\bar{3}m$ [4]. A decrease in the oxygen content leads to the transition from the ferromagnetic state with $T_C \approx 305$ K ($\gamma \approx 0$) to the antiferromagnetic with $T_N \approx 537$ K ($\gamma \approx 0.5$) [5]. In [6], it was shown that insignificant substitution of rare-earth ions for Sr ions (~5%) can stabilize the cubic phase of $Sr_{0.95}Y_{0.05}CoO_{3-\gamma}$ during its synthesis in air, while the cubic phase of $SrCoO_{3-\gamma}$ is only obtained at high oxygen pressure [4]. The $Sr_{0.95}Y_{0.05}CoO_{3-\gamma}$ compounds can also be tetragonal $a_p \times a_p \times 2a_p$ (a_p is the primitive unit cell parameter), space group *P*4/*mmm*, depending on the oxygen content.

Recently anion-deficit layered cobaltites $Sr_3YCo_4O_{10.5+\delta}$-reduced formula $Sr_{0.75}Y_{0.25}CoO_{3-\gamma}$, in which rare-earth ions replace strontium ions and can be ordered were synthesized [7]. These compounds are predominantly antiferromagnetic with the Néel temperature higher than room temperature [7]. A

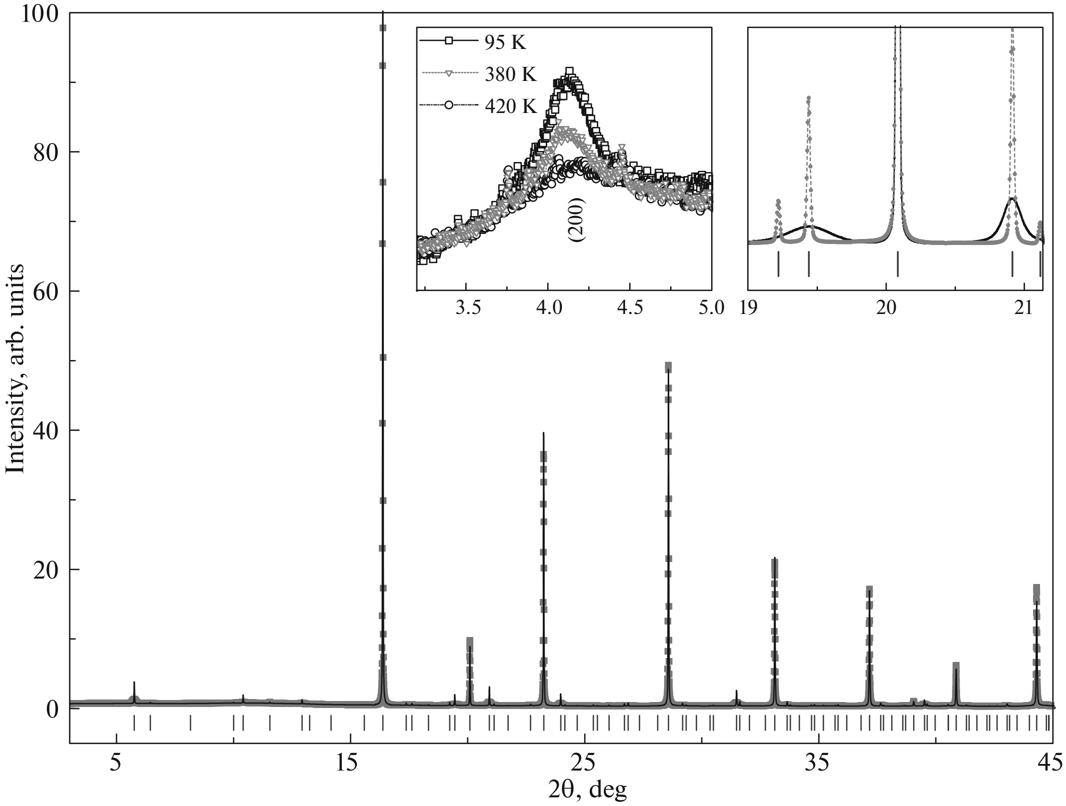

Fig. 1. X-ray diffraction pattern of the $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ measured at 100 K. The bars indicate the Bragg reflections; the black curve and the grey curve show the measured and calculated profiles of the X-ray diffraction pattern. The insets show the broadening of peaks at angles of 19°–21° and the superstructure reflection (200) measured at 95, 380, and 420 K.

relatively small ferromagnetic component appears simultaneously with magnetic ordering [7]. The crystal structure of layered cobaltites $Sr_3LnCo_4O_{10.5+\delta}$ consists of alternating anion-deficit layers $CoO_{4+\delta}$ and layers consisting of CoO_6 octahedra contacting by apexes [7].

The $Sr_3LnCo_4O_{10.5+\delta}$ compounds have a high temperatures of magnetic ordering that can be to 360 K [8]. Below the magnetic ordering temperature, a spontaneous magnetization achieving the maximum value at room temperature manifests itself [8]. In addition, according to [8], the magnetic ordering is accompanied by the formation of a superstructure of the type $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$, and the crystal structure is described by monoclinic group $A2/m$. It was shown that the magnetic structure of $Sr_3YCo_4O_{10.5}$ is mainly G-type antiferromagnetic with T_N close to 350 K.

The $Sr_3LnCo_4O_{10.5+\delta}$ compounds undergo the first-order antiferromagnet–ferromagnet transition [9] similar to that observed in a series of layered cobaltites $LnBaCo_2O_{5.5}$ [10]. The ferromagnetic component disappears in the case of insignificant substitution of Ca^{2+} ions for Sr^{2+} ions or Fe ions for Co ions [7, 11]. The origin of the ferromagnetic component is explained by orbital ordering [12], ferrimagnetism caused by the presence of nonequivalent positions of Co^{3+} ions in anion-deficit layers [13], the formation of ferromagnetic regular spin clusters in oxygen-rich CoO_6 layers [14] or a noncollinear magnetic structure in anion-deficit $CoO_{4-\gamma}$ layers [7, 9].

In [12], layered cobaltite $Sr_3YCo_4O_{10.5}$ was studied by X-ray spectroscopy; the studies showed the existence of ordering of $3d$-orbitals of cobalt ions below the Néel point. Thus, the ferromagnetic component of this compound was explained by ordering of $3d$-orbital of Co^{3+} ions being in the intermediate spin state in layers enriched with oxygen ions. However, the ordering of $3d$-orbitals of cobalt ions can be related to anion-deficit layers. In the connection of various point of view on the nature of the ferromagnetic component in layered cobaltites $Sr_{3-x}Ln_xCo_4O_{10.5+\delta}$, we studied the structure, the magnetic and magnetotransport properties of cobaltite $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ in which the yttrium and oxygen contents are intermediate between $SrCoO_{2.5}$ and $Sr_3YCo_4O_{10.5+\delta}$.

2. EXPERIMENTAL

The polycrystalline $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ sample was prepared by usual ceramic technology in air. The ini-

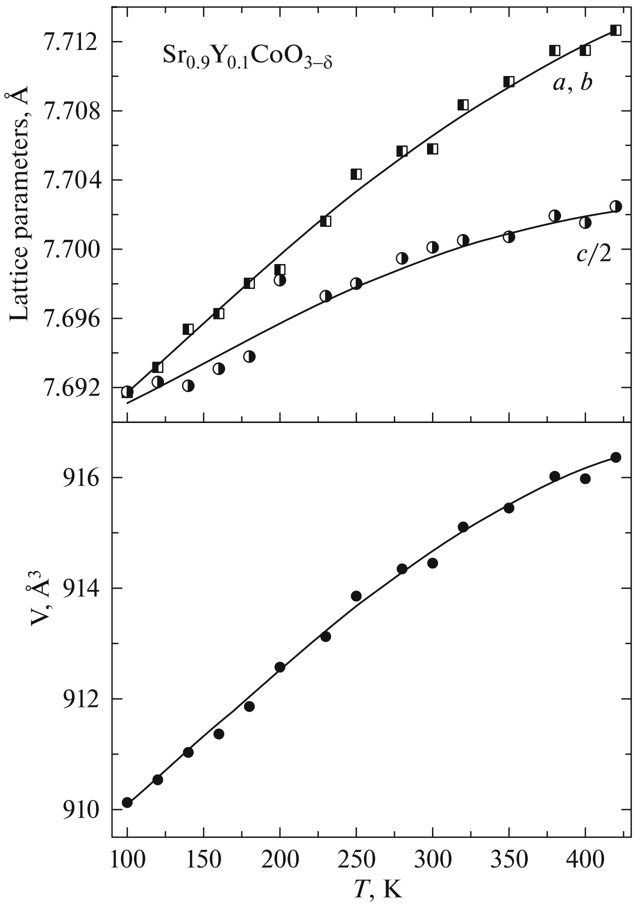

Fig. 2. Temperature dependences of unit cell parameters and volume of the $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ composition.

tial high-purity Y_2O_3, Co_3O_4, and $SrCO_3$ reagents were taken in the stoichiometric proportion and carefully mixed in a "RETSCH" PM-100 planetary ball mill for 30 min at a rate of 250 rpm. Oxide Y_2O_3 was previously annealed at a temperature of 1000°C to remove moisture. The samples were synthesized for two stages. The preliminary burning was carried out at a temperature of 1000°C. The final synthesis was carried out at a temperature of 1185°C for 8 h. Then, the sample was cooled to a temperature of 300°C for 12 h. The X-ray diffraction studies ($95 \text{ K} \leq T \leq 420 \text{ K}$) were performed on a Synchrotron Radiation Source of the research Center at Paul Scherrer Institute (Willigen, Switzerland). The neutron diffraction studies in the temperature range 10–420 K were performed on a high-resolution D2B diffractometer at the Institut Laue Langevin (Grenoble, France). The crystal and magnetic structures were refined by the Rietveld method using the FullProf program package [15]. The magnetic and magnetotransport measurements were carried out at a setup for measurements of physical properties (Cryogenic Ltd.) in magnetic fields to 14 T in the temperature range 5–315 K. The electrical conductivity was measured by the four-probe method with indium contacts deposited using ultrasound.

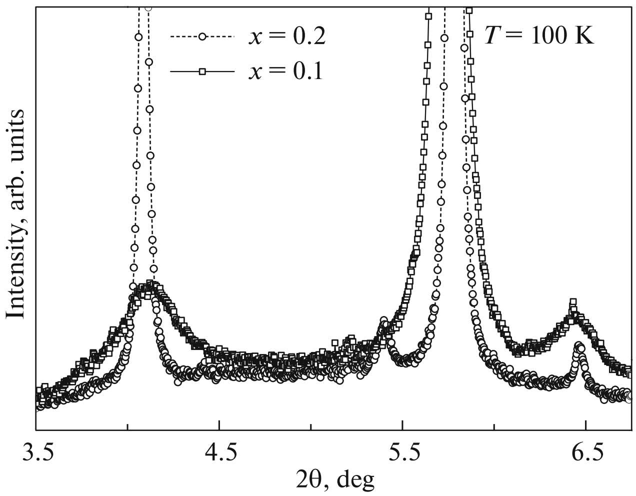

Fig. 3. X-ray diffraction patterns of the $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ and $Sr_{0.8}Y_{0.2}CoO_{3-\gamma}$ samples measured at a temperature of 100 K at angles 3.5°–6.5°.

3. RESULTS AND DISCUSSION

The X-ray diffraction studies of the $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ compounds were carried out in the temperature range 95–420 K. Figure 1 shows the X-ray diffraction pattern measured at a temperature of 100 K and also the result of its processing in the FullProf program in two-phase model. The main structural phase in $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ was calculated in the tetragonal space group $I4/mmm$ with a unit cell of the $2a_p \times 2a_p \times 4a_p$ (a_p is the primitive cubic cell parameter). We did not observe phase transitions in this phase in the temperature range under study. The X-ray diffraction patterns (95–420 K) demonstrate a significant broadening of reflections with indices 103, 202, 206, etc., related to doubling of the unit cell parameter along axis c (Fig. 1, inset). Such broadening of the reflections is most likely due to the absence of the rigorous translation symmetry along axis c. In addition, the diffraction pattern has a strongly broadened superstructure reflection at small angles (4°–4.5°) that was observed up to a temperature of 400 K (Fig. 1, inset). The existence of this superstructure reflection is most likely related to the existence of the monoclinically distorted phase, since it is described in the framework of the superstructure inherent in space group $A2/m$.

Figure 2 shows the temperature dependences of the unit cell parameters and volume of $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ compositions. From Fig. 2, it is seen the thermal expansion along axis a is larger than axis c. The unit cell parameters and volume monotonically increase with temperature. No crystal structure and spin transitions were detected.

As the yttrium ion content increases to $x = 0.2$, the X-ray diagrams demonstrate the appearance of additional reflections 111 and $\bar{1}11$ that disappear at a temperature higher than 350 K. These reflections can be described in the framework of space group $A2/m$ and the cell of the $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ type (Fig. 3). The appearance of these reflections seems likely to be related to a spin transition of Co ions or orbital ordering in CoO_6 layers, as it was shown before for the $Sr_{3.12}Er_{0.88}Co_4O_{10.5}$ at temperatures lower than 360 K [8]. The increase in the temperature above 350 K leads to a first-order phase transition that is accompanied by a crystal-structural transition in the framework of space group $A2/m$ to a cell of the $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$. The neutron diffraction studies were carried out at temperatures of 10, 260, and 400 K. Figure 4 shows the results of calculation of the crystal and magnetic structures of the main phase in $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ at 10 and 400 K that was carried out in the framework of space group $I4/mmm$ and a cell of the $2a_p \times 2a_p \times 4a_p$. According to the obtained data, the crystal structure consists of layers of CoO_6 octahedra and anion-deficit $CoO_{4+\gamma}$ alternating along axis c, that was shown before for other layered cobaltites $Sr_{0.75}Y_{0.25}CoO_{3-\gamma}$ [7]. At 400 K, there is no monoclinically distorted phase.

The oxygen content in the sample refined from the neutron diffraction data is close to 2.63, which means that the cobalt ion is in trivalent state. The analysis of the neutron diffraction data measured at a temperature of 10 K showed that the main magnetic contribution exists in reflections 110, 112, 202, and 211, where the indices belong to the $2a_p \times 2a_p \times 4a_p$ type cell (Fig. 4). It follows that the base magnetic structure can be described by the G-type antiferromagnetic ordering with a $2a_p \times 2a_p \times 4a_p$-type cell with two different magnetic positions in the layers of CoO_6 octahedra and in anion-deficit layers. The increase in the 110 reflection intensity with a decrease in temperature indicates different values of the magnetic moments of Co ions the layers of CoO_6 octahedra and in the anion-deficit $CoO_{4+\gamma}$ layers. The refinement of the magnetic structure in the model in which the magnetic moment directions coincides with the crystal-structural axis c enables a more correct description of the contribution to all magnetic reflections as compared to the model, in which the magnetic moments of both sublattices are directed collinearly along the crystal-structural aces axes a and b. The magnetic moments in the anion-deficit layers and in the layers of CoO_6 octahedra at a temperature of 10 K are $2\mu_B$ and $1.5\mu_B$, respectively. At a temperature of 400 K, we did not observe any magnetic contribution. Table 1 gives the main calculated crystal-structural and magnetic parameters.

Table 1. Parameters of the crystal and the magnetic structures of the $Sr_{0.9}Y_{0.1}CoO_{2.63}$ composition refined by the Rietveld method. Space group $I4/mmm$

Temperature, K	10	260	400
a, b, Å	7.6907(3)	7.7017	7.7022
c, Å	15.3830(1)	15.4126	15.4394
V, Å^3	909.86(14)	914.174	915.926
Sr1/Y1	0, 0, z		
z	0.86471	0.86432	0.86571
B_{iso}, Å^2	1.45(34)	1.87(50)	2.27(03)
Sr2/Y2	0, 0.5, z		
z	0.86844	0.86772	0.86673
B_{iso}, Å^2	1.13(10)	1.37(94)	1.79(56)
Sr3/Y3	0, 0, z		
z	0.37409	0.37438	0.375
B_{iso}, Å^2	0.27(84)	0.64(27)	0.75(6)
Co1	x, y, 0		
x	0.24172	0.24154	0.24439
y	0.24172	0.24154	0.24439
Magnetic moment μ_z, μ_B	1.517	1.199	
B_{iso}, Å^2	0.63(33)	0.89(61)	1.02(38)
Co2	0.25, 0.75, 0.25		
Magnetic moment μ_z, μ_B	1.964	1.534	
B_{iso}, Å^2	0.29(61)	0.68(32)	1.37(02)
O1	0, y, z		
y	0.2481	0.24817	0.24883
z	0.2545	0.25471	0.25428
B_{iso}, Å^2	1.22(56)	1.62(82)	1.91(94)
O2	x, y, z		
x, y	0.23086	0.23119	0.22927
z 0.11635	0.11615	0.11599	
B_{iso}, Å^2	2.14(99)	2.50(20)	2.72(38)
O3	0, y, 0		
y	0.75(48)	0.75399	0.75536
B_{iso}, Å^2	0.17(01)	0.41(05)	0.16(30)
O4	x, 0.5, 0		
x	0.21197	0.21065	0.21238
B_{iso}, Å^2	2.78(52)	3.15(56)	3.50(41)
R_p/R_{wp} (%)	4.66/6.37	4.24/5.77	4.01/5.33
R_{Bragg} (%)	9.53	9.93	11.4
Magnetic R-factor	13.1	11.9	
χ^2	13.5	11.1	9.5

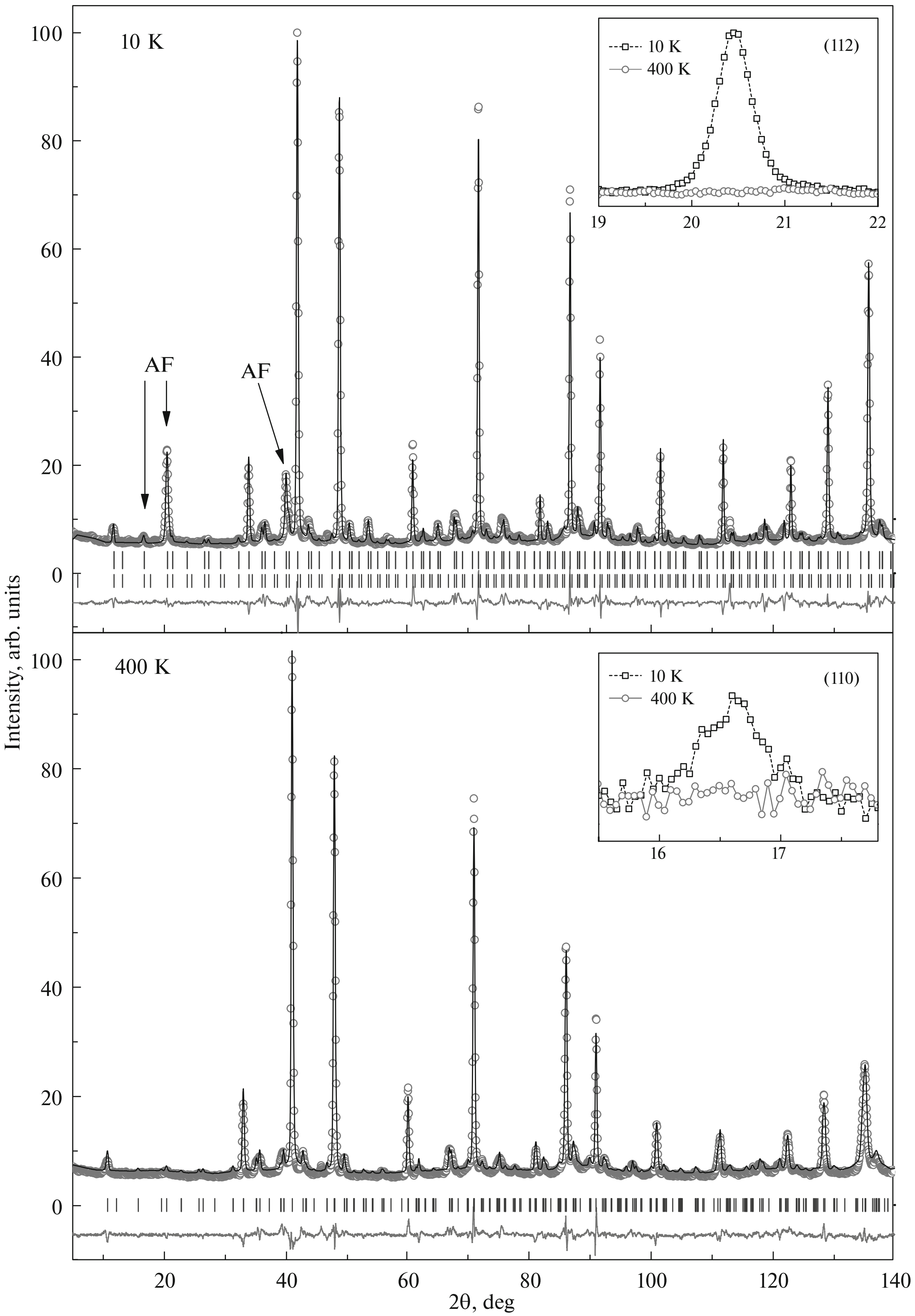

Fig. 4. Profiles of the neutron diffraction patterns of the $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ sample measured at temperatures 10 and 400 K. The bars indicate the Bragg reflections and also (black line) measured and (grey line) calculated profiles of the neutron diffraction patterns.

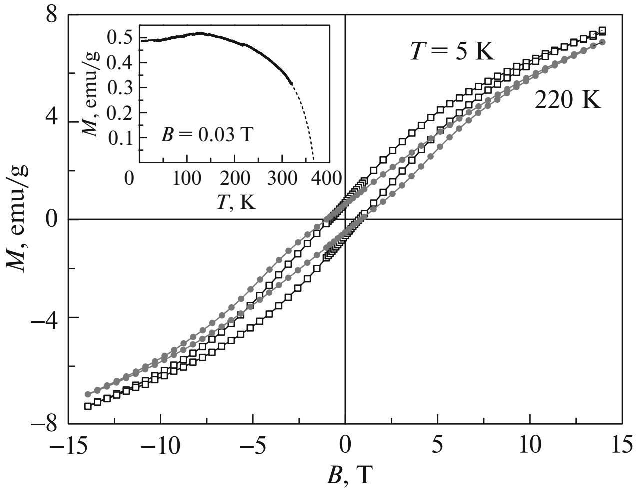

Fig. 5. Field dependences of the magnetization of the $Sr_{0.9}Y_{0.1}CoO_{2.63}$ composition. The inset shows the temperature dependence of the magnetization.

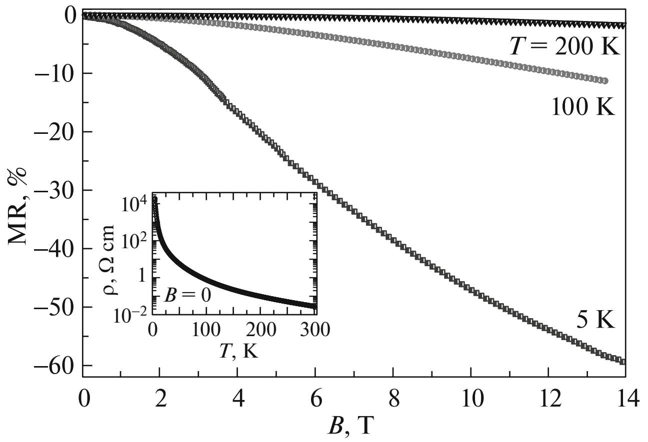

Fig. 6. Field dependence of the magnetoresistance of the $Sr_{0.9}Y_{0.1}CoO_{2.63}$ composition at temperatures 5, 100, and 200 K; the inset shows the temperature dependence of the resistivity without applied magnetic field.

The temperature dependence of the magnetization of the $Sr_{0.9}Y_{0.1}CoO_{2.63}$ compound is shown in the inset in Fig. 5. The measurements were performed on cooling in field $B = 0.03$ T (FC). According to the data of the magnetic measurements, the rough estimation gives the Néel temperature about $T_N \approx 380$ K. As the temperature decreases from 320 to 5 K, the magnetization first increases, attaining the maximum value 0.5 emu/g at $T \approx 130$ K and, then, slightly decreases.

Figure 5 shows the field dependences of the magnetization of the $Sr_{0.9}Y_{0.1}CoO_{2.63}$ compound. At a liquid-helium temperature, the coercive force is 0.75 T and it slightly changed, as well as the magnetization, as the temperature increases to 220 K. The remanent magnetization is ~$0.022\mu_B$ per cobalt ion (0.65 emu/g) at a temperature of 5 K and, then, slightly decreases to $0.017\mu_B$ per cobalt ion (0.5 emu/g) at a temperature of 220 K. The magnetization was not saturated in fields to 14 T. The magnetizations at 5 and 220 K in a field of 14 T are almost the same.

The measurement of the electrotransport properties of the $Sr_{0.9}Y_{0.1}CoO_{2.63}$ compound showed that the temperature dependence of the conductivity has a semiconducting character (Fig. 6, the inset). The resistivity increases from ~0.02 Ω cm at 300 K to 20 kΩ cm at a liquid-helium temperature. We did not observe any anomalies in the temperature dependence of the resistivity. The negative magnetoresistive effect defined as $\mathrm{MR} = (\rho(0) - (\rho(H)/\rho(0) \times 100\%$ is 57% at a temperature of 5 K in magnetic field $B = 14$ T (Fig. 6). The magnetoresistance significantly decreases to 1.6% in field 14 T as the temperature increases to 220 K.

The obtained data show that the crystal structure of the $Sr_{1-x}Y_xCoO_{2.63+\gamma}$ system is changed from the tetragonal $P4/mmm$ ($a_p \times a_p \times 2a_p$) to monoclinic $A2/m$ via the intermediate tetragonal $I4/mmm$ phase ($2a_p \times 2a_p \times 4a_p$), in which the rigorous translation symmetry along axis *c* is absent. Simultaneous disappearance of the monoclinic phase and the spontaneous magnetization is the demonstration of the fact that the crystal structure type determines the formation of the ferromagnetic component.

4. CONCLUSIONS

The X-ray diffraction and the neutron diffraction studies and the measurements and also the measurements of the magnetic and magnetotransport properties have been performed to determine the properties of the $Sr_{0.9}Y_{0.1}CoO_{2.63}$ perovskite. The found oxygen content corresponds to the fact that cobalt ion is in the trivalent state. The sample structure is two-phase. The main phase is described by the tetragonal space group $I4/mmm$ with the superstructure cell $2a_p \times 2a_p \times 4a_p$ due to the existence of alternating CoO_6 and $CoO_{4+\gamma}$ layers. The reflections caused by doubling the lattice parameter along axis *c* are strongly spread, which demonstrates the absence of the rigorous translation symmetry along axis *c*. At temperatures lower than 400 K, the diffraction patterns have a strongly spread-out peak that is indexed in monoclinic space group $A2/m$ ($2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$). The existence of the spontaneous magnetization with T_C significantly higher than room temperature is related to the monoclinic phase that appears simultaneously with the spontaneous magnetization. The magnetic structure of the antiferromagnet is the *G*-type structure. The magnetic moments of Co^{3+} in CoO_6 and $CoO_{4+\delta}$ are $1.5\mu_B$ and $2\mu_B$, respectively. The electrical conduction has a semiconducting character. The magnetoresistance is high at low temperatures; however, it substantially decreases as temperature increases despite a weak change in the magnetization.

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REFERENCES

1. N. B. Ivanova, S. G. Ovchinnikov, M. M. Korshunov, I. M. Eremin, and N. V. Kazak, Phys. Usp. **52**, 789 (2009).
2. A. Maignan, C. Martin, D. Pelloquin, N. Nguyen, and B. Raveau, J. Solid State Chem. **142**, 247 (1999).
3. D. Fuchs, C. Pinta, T. Schwarz, P. Schweiss, P. Nagel, S. Schuppler, R. Schneider, M. Merz, G. Roth, and H. V. Löhneysen, Phys. Rev. B **75**, 144402 (2007).
4. Y. Long, Y. Kaneko, Sh. Ishiwata, Y. Taguchi, and Y. Tokura, J. Phys.: Condens. Matter **23**, 245601 (2011).
5. A. Muñoz, C. de la Calle, J. A. Alonso, P. M. Botta, V. Pardo, D. Baldomir, and J. Rivas, Phys. Rev. B **78**, 054404 (2008).
6. M. James, D. Cassidy, K. F. Wilson, J. Horvat, and R. L. Withers, Solid State Sci. **6**, 655 (2004).
7. I. O. Troyanchuk, D. V. Karpinsky, V. M. Dobryanskii, A. N. Chobot, and A. P. Sazonov, J. Exp. Theor. Phys. **108**, 428 (2009).
8. S. Ishiwata, W. Kobayashi, I. Terasaki, K. Kato, and M. Takata, Phys. Rev. B **75**, 220406 (2007).
9. I. O. Troyanchuk, M. V. Bushinsky, V. M. Dobryanskii, and N. V. Pushkarev, JETP Lett. **94**, 849 (2011).
10. I. O. Troyanchuk, N. V. Kasper, D. D. Khalyavin, H. Szymczak, R. Szymczak, and M. Baran, Phys. Rev. Lett. **80**, 3380 (1998).
11. I. Terasaki, S. Shibasaki, S. Yoshida, and W. Kobayashi, Materials **3**, 786 (2010).
12. H. Nakao, T. Murata, D. Bizen, Y. Murakami, K. Ohoyama, K. Yamada, S. Ishiwata, W. Kobayashi, and I. Terasaki, J. Phys. Soc. Jpn. **80**, 023711 (2011).
13. D. D. Khalyavin, L. C. Chapon, E. Suard, J. E. Parker, S. P. Thompson, A. A. Yaremchenko, and V. V. Kharton, Phys. Rev. B **83**, 140403 (2011).
14. J. L. Bettis, H. Xiang, and M.-H. Whangbo, Chem. Mater. **24**, 3117 (2012).
15. T. Roisnel and J. Rodríquez-Carvajal, Mater. Sci. Forum **378–381**, 118 (2001).

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