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Ferromagnet-antiferromagnet transition in layered perovskites of $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ type

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PAPER

Ferromagnet-antiferromagnet transition in layered perovskites of $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ typeRECEIVED
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21 November 2018I O Troyanchuk¹ , M V Bushinsky¹, N V Tereshko¹, R A Lanovsky¹, V V Sikolenko², C Ritter³, Yu S Orlov^{4,5} and S G Ovchinnikov^{4,5}¹ Scientific and Practical Center of the National Academy of Sciences of Belarus for Materials Science, Minsk, Belarus² Joint Institute for Nuclear Research, Dubna, Russia³ Institut Laue Langevin, Grenoble, France⁴ Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, Russia⁵ Siberian Federal University, 660074 Krasnoyarsk, RussiaE-mail: troyan@physics.by

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Abstract

$\text{Sr}_{1-x}\text{Y}_x\text{CoO}_{2.65}$ ($x = 0.2$) with layered perovskite structure was studied by neutron diffraction, synchrotron x-ray and magnetometry methods. It is shown that in the 90–375 K temperature range the crystal structure can be described by the monoclinic space group $A2/m$ with the superstructure $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ (with a_p corresponding to the unit cell parameter of the primitive cell) while basic diffraction peaks are well indexed in the space group $I4/mmm$ ($2a_p \times 2a_p \times 4a_p$) shows an almost standard magnetization. The basic magnetic structure is G-type antiferromagnetic with average magnetic moments of $2.7 \mu_B/\text{Co}$ and $1.7 \mu_B/\text{Co}$ in anion-deficient $\text{CoO}_{4+\gamma}$ and stoichiometric CoO_6 layers, respectively. A ferromagnetic component of about $0.27 \mu_B/\text{Co}$ is determined from the magnetization measurements at 8 K. $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$ shows an almost standard magnetization versus temperature dependence whereas $\text{Sr}_{0.75}\text{Y}_{0.25}\text{CoO}_{2.65}$ exhibits an antiferromagnet-ferromagnet transition accompanied by a structural transformation. There is practically no spontaneous magnetization in $x = 0.3$. The type of the magnetic structure and the high value of T_N suggest that the Co^{3+} ions are in both structural layers predominantly in the low-spin (LS)/high-spin (HS) state mixture. It is proposed that the ferromagnetic component is due to the orbital ordering occurring at T_N in the CoO_5 pyramids and the concomitant appearance of ferromagnetic coupling between the Co^{3+} (HS) ions located in these CoO_5 pyramids in the anion-deficient $\text{CoO}_{4+\gamma}$ layer.

1. Introduction

Magnetic materials with large magnetic anisotropy are of particular interest for practical use as permanent magnets and magnetic storage systems. Ferromagnetic structures such as nanotubes, nanowires, and ceramic materials can be used as such materials [1–3]. Cobaltites of rare-earth elements with a perovskite-like structure are of considerable interest, both from the point of view of technological applications and within the general research in the area of physics of magnetic phenomena [4, 5]. The basic compound LaCoO_3 behaves up to 30 K very similar to a diamagnetic insulator with paramagnetic defects, above 30 K a partial spin crossover of Co^{3+} ions occurs from the low-spin (LS) state to the high spin/low spin (HS/LS) state mixture which is paramagnetic [6, 7]. However the LS state is still dominant at least up to 400 K. Both magnetic and orbital ordering has not been reliably observed at any temperature. The substitution of La^{3+} with Sr^{2+} ions leads to the drop of resistivity and the appearance of long-range ferromagnetic order above 18% replacement of La^{3+} ions [8]. Subsequently, T_C and magnetization increase almost linearly from 170 K and $M_s = 1.2 \mu_B/\text{Co}$ ($x = 0.18$) up to $T_C \sim 305$ K and $M_s = 2.5 \mu_B/\text{Co}$ in practically stoichiometric metallic $\text{SrCo}^{4+}\text{O}_3$, which can be obtained only under high oxygen pressure [9]. Taking into account the magnitude of the magnetic moment it has been suggested that Co^{3+} and Co^{4+} ions are in the intermediate spin state [9]. Deviation in the stoichiometry of oxygen in cobaltites

leads to antiferromagnetic ordering with a T_N , which can be much higher than room temperature [10]. For example $\text{SrCoO}_{2.5}$ containing only Co^{3+} in HS state both in tetrahedral and octahedral surrounding is G-type antiferromagnet with $T_N = 537 \text{ K}$ [10]. The observed magnetic moments are about $3 \mu_B/\text{Co}$ for both tetrahedral and octahedral oxygen surrounding [10]. This is incompatible with the IS spin state of Co^{3+} ions ($S = 1$). So the magnetic interactions between Co^{3+} ions in the HS state are regardless of the oxygen surrounding strongly antiferromagnetic.

The $\text{Sr}_3\text{LnCo}_4\text{O}_{10.5+\delta}$ compounds are characterized by a high magnetic ordering temperature which reaches 360 K [11–13]. Spontaneous magnetization appears below the magnetic ordering temperature reaching its maximum value near room temperature [11–13]. In addition, according to [11], magnetic ordering is accompanied by the appearance of the $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ type superstructure and the crystal structure is described by the monoclinic group $A2/m$. It is shown using neutron powder diffraction methods that the magnetic structure of $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ is predominantly antiferromagnetic G-type with T_N close to 350 K [11–13].

It was shown in [11, 12, 14] that a relatively small substitution of Sr^{2+} by Y^{3+} leads to the stabilization of $\text{Sr}_{1-x}\text{Y}_x\text{CoO}_{3-\delta}$ ($0.05 < x < 0.35$) solid solutions with a layered perovskite-like structure which is associated with a strong deviation from stoichiometry in oxygen. The oxygen stoichiometric layers of CoO_6 alternate with anion-deficient $\text{CoO}_{4+\gamma}$ [11, 12]. A basic antiferromagnetic ordering of the G-type arises substantially above room temperature and is accompanied by the appearance of a small ferromagnetic component [11, 12], the origin of which is not yet clearly established. Composition $x = 0.25$ exhibits an anomalous decrease of magnetization with temperature decreasing. [11, 12]. A small substitution of Co with Fe almost completely destroys the ferromagnetic component in spite of the growth of T_N and of the magnetic moment per unit cell thus underlining the influence of structural changes [11].

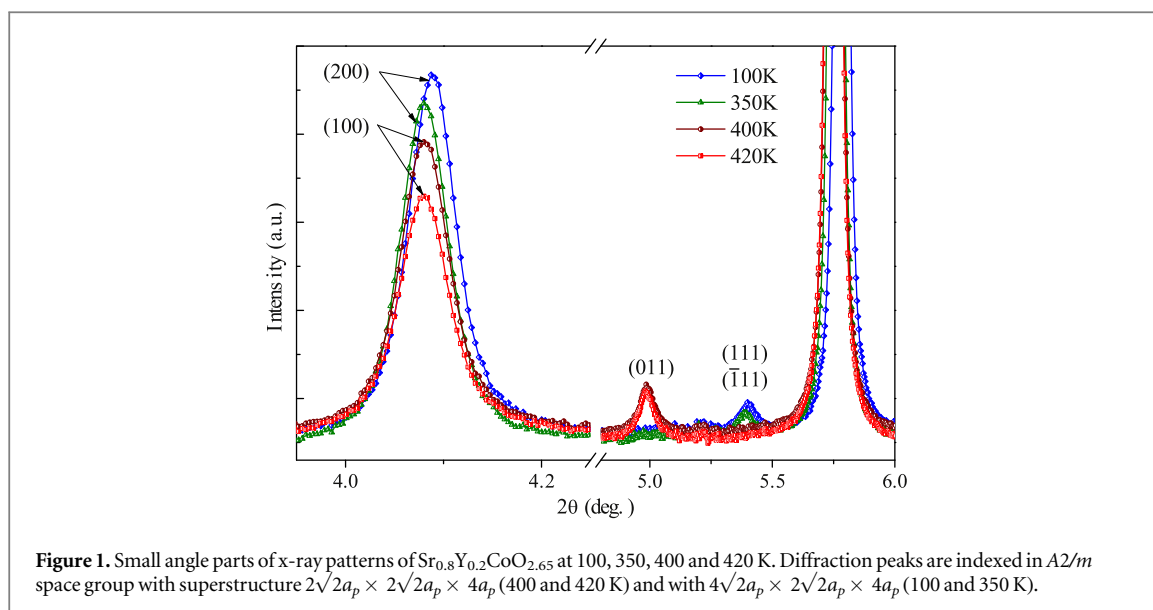
A number of scenarios for the appearance of the ferromagnetic component have been described: for example, an orbital ordering in Co^{3+} (IS) ions located in oxygen-stoichiometric CoO_6 layers is proposed as the reason for a ferrimagnetic component [13, 15], a ferrimagnetic structure in anion deficient layers due to oxygen vacancies ordering [16], ferromagnetic Co^{3+} chains in oxygen-stoichiometric CoO_6 layers [17], spin ‘bags’ in CoO_6 layers [18] and an uncompensated canted magnetic structure [19]. Whether or not the magnetic ordering is accompanied by a structural transition [13, 15] and in how far the crystal structure has an impact on the stability of the ferromagnetic component remain open questions which are still actual. Note, that the majority of the theoretical studies of the magnetic properties have been performed in frame of the space group $I4/mmm$, while the correct symmetry seems to be much lower [13]. Oxygen vacancy ordering has been observed in anion deficient layers corresponding to the general chemical formula $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ representing a very large superstructure [13]. As the origin of the ferromagnetic component is not yet clearly established we have conducted a comprehensive study of the crystal structure, magnetic and elastic properties of the composition $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$ corresponding to $\text{Sr}_{3.2}\text{Y}_{0.8}\text{Co}_4\text{O}_{10.6}$. Compounds with larger yttrium content have been studied as well in order to establish the effect of the substitution of Sr^{2+} by Y^{3+} on the magnetic properties.

2. Methods

Polycrystalline samples of compositions $\text{Sr}_{1-x}\text{Y}_x\text{CoO}_{2.65}$ ($x = 0.2; 0.25; 0.275; 0.3$ and 0.35) were obtained by conventional ceramic technology in air. The initial reagents Y_2O_3 , Co_3O_4 and SrCO_3 of high purity were taken in the stoichiometric ratio and thoroughly mixed in a planetary ball mill RETSCH PM-100 for 30 min at a speed of 250 rpm. Before weighing, the Y_2O_3 oxide was pre-annealed at 1000°C to remove moisture. The synthesis of the samples was carried out in two stages. Preliminary synthesis was carried out at a temperature of 1000°C . The final synthesis was carried out at a temperature of 1185°C for 8 h. The samples were then cooled for 7 h down to a temperature of 300°C . X-ray diffraction studies ($95 \text{ K} \leq T \leq 420 \text{ K}$) were performed at the synchrotron radiation source at the research center of the Paul Scherrer Institute (Willigen, Switzerland). Neutron diffraction studies in the temperature range from 10 to 420 K were performed on the D2B high-resolution diffractometer at the Institut Laue-Langevin (Grenoble, France). The refinement of the crystal and magnetic structures was performed by the Rietveld method using the FullProf software package [20]. Measurements of the Young’s modulus E are performed by the method of resonance oscillations in the frequency range 10^3 – 10^4 Hz. Magnetic and magnetotransport measurements were performed on a physical properties measuring unit (Cryogenic Ltd) in magnetic fields up to 14 T in the temperature range 5–315 K. Conductivity measurements were performed using a standard four-contact method with indium contacts deposited by ultrasound.

3. Results and discussion

The crystal structure of $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$ was studied using the diffraction of synchrotron x-ray radiation in the temperature range 90–400 K. Space groups $I4/mmm$, $Cmma$ and $A2/m$ were used for the refinement of the



crystal structure. The x-ray diffraction peaks were much better indexed in the monoclinic space group $A2/m$ with the superstructure $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ at 400 K and with $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ at 350 K, where a_p is the parameter of the primitive cell. The volume of the unit cell gradually increases as temperature rises indicating the stability of the ground spin state of cobalt ions. Figure 1 shows the parts of x-ray diffraction patterns at small angles at 400 and 350 K. The change in the diffraction spectra indicates that between 400 and 350 K a crystal-structural phase transformation occurs with a doubling of the unit cell along the a axis as it has been proposed before [13].

Figure 2 shows parts of the neutron diffraction patterns at small angles recorded at 10 and 400 K. At 400 K, no magnetic contribution to the neutron scattering was observed. With decreasing temperature, a number of additional peaks appeared, some of which can be indexed within the framework of the tetragonal space group $I4/mmm$ with superstructure $2a_p \times 2a_p \times 4a_p$. These peaks are marked by arrows with the designation AF. Very weak diffraction peaks that can be indexed within the space group $Cmma$ or $A2/m$ are marked with asterisks. The crystal and magnetic structures were calculated within the more simple tetragonal space group $I4/mmm$ ($2a_p \times 2a_p \times 4a_p$), since the peaks which cannot be indexed in $I4/mmm$ group have very small intensity. According to the refinement the magnetic structure is of the antiferromagnetic G type with magnetic moments of $1.7 \mu_B/\text{Co}$ in the stoichiometric layers of CoO_6 and of $2.7 \mu_B/\text{Co}$ in the anion-deficient layers (table 1). The inset to figure 2 shows the temperature dependence of the magnetic contribution in the diffraction peak 112 ($I4/mmm$) situating the Neel point at about 375 K. Judging by the fact that the intensity of the reflexes marked with an asterisk depends strongly on temperature, the magnetic cell could be much larger than the one considered using the description in $I4/mmm$. However, the intensity of the three reflexes marked with an asterisk is very small. Therefore, the presented approximation describes fairly well the basic magnetic structure. According to the refined oxygen content, cobalt ions are dominantly in the trivalent state because the chemical formula is $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$.

Figure 3 shows the temperature dependences of the Young's modulus for $x = 0.2$ and $x = 0.25$. One can see that the well pronounced minimum of Young's modulus of $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$ coincides with the Neel point T_N . This indicates that the crystal structure phase transformation takes place at the temperature of magnetic ordering. The compound $\text{Sr}_{0.75}\text{Y}_{0.25}\text{CoO}_{2.65}$ exhibits two minima of Young's modulus: below and above room temperature. The first minimum observed at 350 K corresponds to the temperature of the magnetic ordering. The second minimum at a lower temperature is associated with the antiferromagnet-ferromagnet phase transition, which occurs at a temperature of 220 K.

Field and temperature dependencies of the magnetization for $\text{Sr}_{1-x}\text{Y}_x\text{CoO}_{2.65}$ are shown in figures 4 and 5. From the field dependence of the magnetization of the $x = 0.2$ composition, it is difficult to determine precisely the spontaneous magnetization, since no saturation of the magnetization is observed in fields up to 14 T below the magnetic ordering temperature (figure 4). However, one can estimate that the spontaneous magnetization for $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$ is close to 8 emu g^{-1} or $0.27 \mu_B/\text{Co}$. Magnetization versus field dependencies at low temperature are almost linear for $x = 0.25$; 0.275 and 0.35 as one can see from figure 4. The magnitudes of spontaneous magnetization are very small in contrast to $x = 0.2$ compound.

The temperature dependence of the magnetization for $x = 0.2$ has almost standard form, but at 270 K there is an inflection point (figure 5). The sample with $x = 0.25$ shows a well pronounced antiferromagnet-

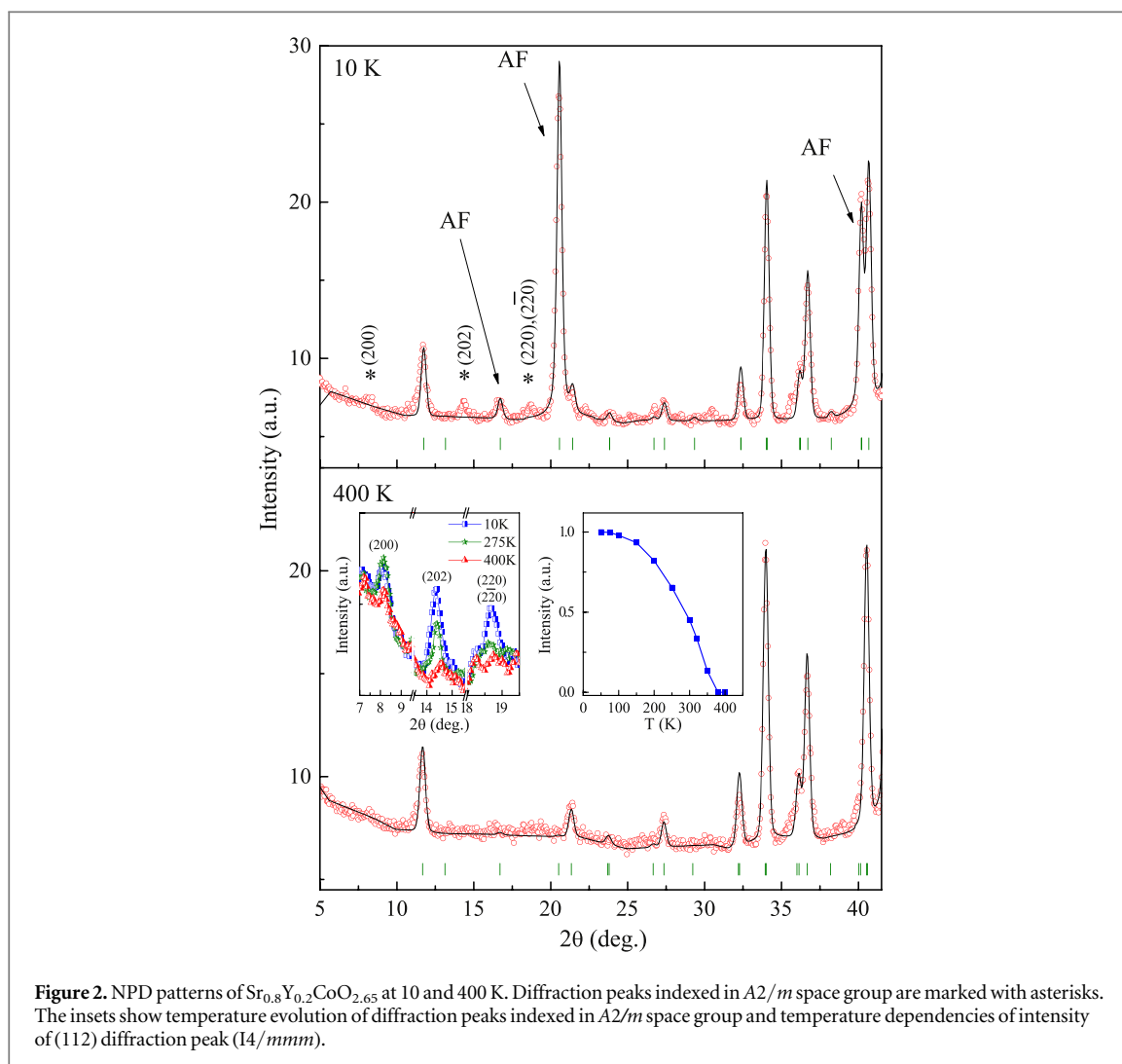


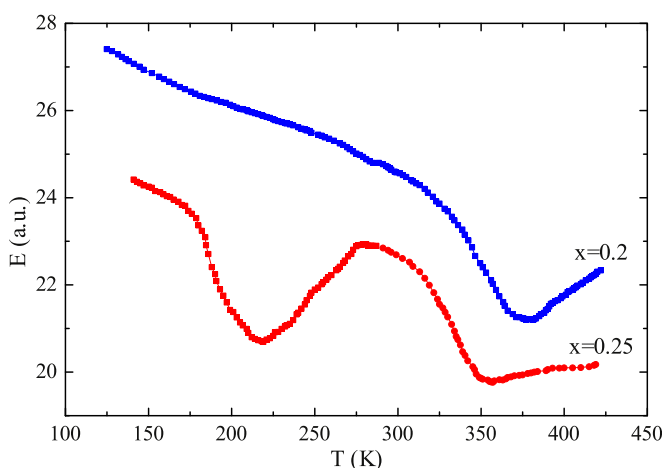
Figure 2. NPD patterns of $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$ at 10 and 400 K. Diffraction peaks indexed in $A2/m$ space group are marked with asterisks. The insets show temperature evolution of diffraction peaks indexed in $A2/m$ space group and temperature dependencies of intensity of (112) diffraction peak ($I4/mmm$).

ferromagnet transition slightly below room temperature (figure 5). The large hysteresis of the temperature dependence of the magnetization and the metamagnetic behaviour (figures 4 and 5) show that this transition is of first order. Magnetic fields transform the compensated antiferromagnetic phase into a new antiferromagnetic phase having a ferromagnetic component. The antiferromagnet-ferromagnet phase transition is accompanied by a well pronounced minimum of Young's modulus thus indicating a concomitant structural transition (figure 3). The maximum of the magnetization for $x = 0.275$ shifts to room temperature (figure 5). It shows again a sizable temperature hysteresis. There is no noticeable spontaneous magnetization in $\text{Sr}_{0.7}\text{Y}_{0.3}\text{CoO}_{2.65}$ below room temperature. A very small spontaneous magnetization might result from a tiny structural (chemical) inhomogeneity. The Neel point decreases with increasing of yttrium content. Apparently it is associated with the decrease of the unit cell volume leading to stabilization of the LS cobalt state.

Recently, we investigated the effect of cation and anion ordering on the crystal structure and magnetic properties of substituted rare-earth cobalt oxides $\text{Gd}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-\delta}$ [21]. The solid solutions considered can be in an ordered and disordered state. The disordered sample $\text{Gd}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-\delta}$ is a cubic perovskite phase with a uniform random distribution of $\text{Sr}^{2+}/\text{Gd}^{3+}$ ions and anionic vacancies in the corresponding positions of the crystal lattice. The formation of an ordered phase of a reduced symmetry is due to a partial ordering of $\text{Sr}^{2+}/\text{Gd}^{3+}$ cations and anion vacancies. The ordered perovskite has a layered tetragonal structure consisting of layers located along the c -axis in the sequence $[\text{Sr}_{0.5}\text{O}_{0.5}]$ - $[\text{Co}_{0.5}\text{O}]$ - $[\text{Gd}_{0.1}\text{Sr}_{0.4}\text{O}_{0.5-0.4\delta}]$ - $[\text{Co}_{0.5}\text{O}_{1-0.6\delta}]$. An important circumstance is that the anion-deficient layered cobaltites of the type $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ and ordered $\text{Gd}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-\delta}$ excluding the paramagnetic contribution from gadolinium ions Gd^{3+} have similar magnetic properties [19, 21, 22]. In addition, the magnetic and thermodynamic values of the ordered samples $\text{Gd}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-\delta}$ have pronounced anomalies [21, 22], therefore we consider that analogous to layered cobaltites of the $\text{Sr}_3\text{YCo}_4\text{O}_{10.5-\delta}$ type with different oxygen content [19] in the ordered compounds $\text{Gd}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-\delta}$ there is a first-order phase transition from the high-temperature 'ferromagnetic' state to the low-temperature antiferromagnetic state.

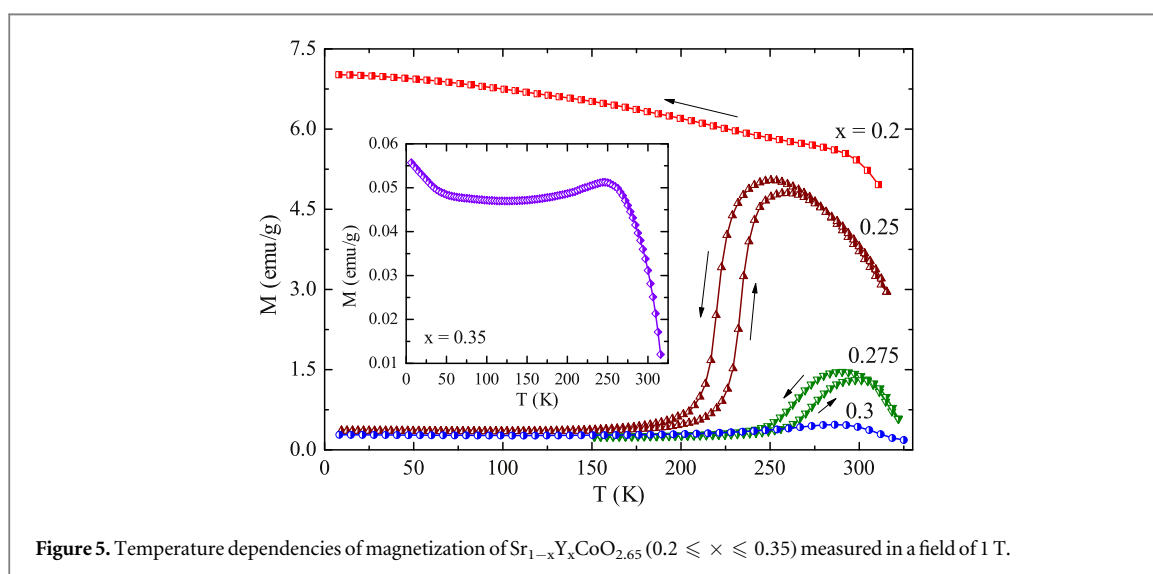
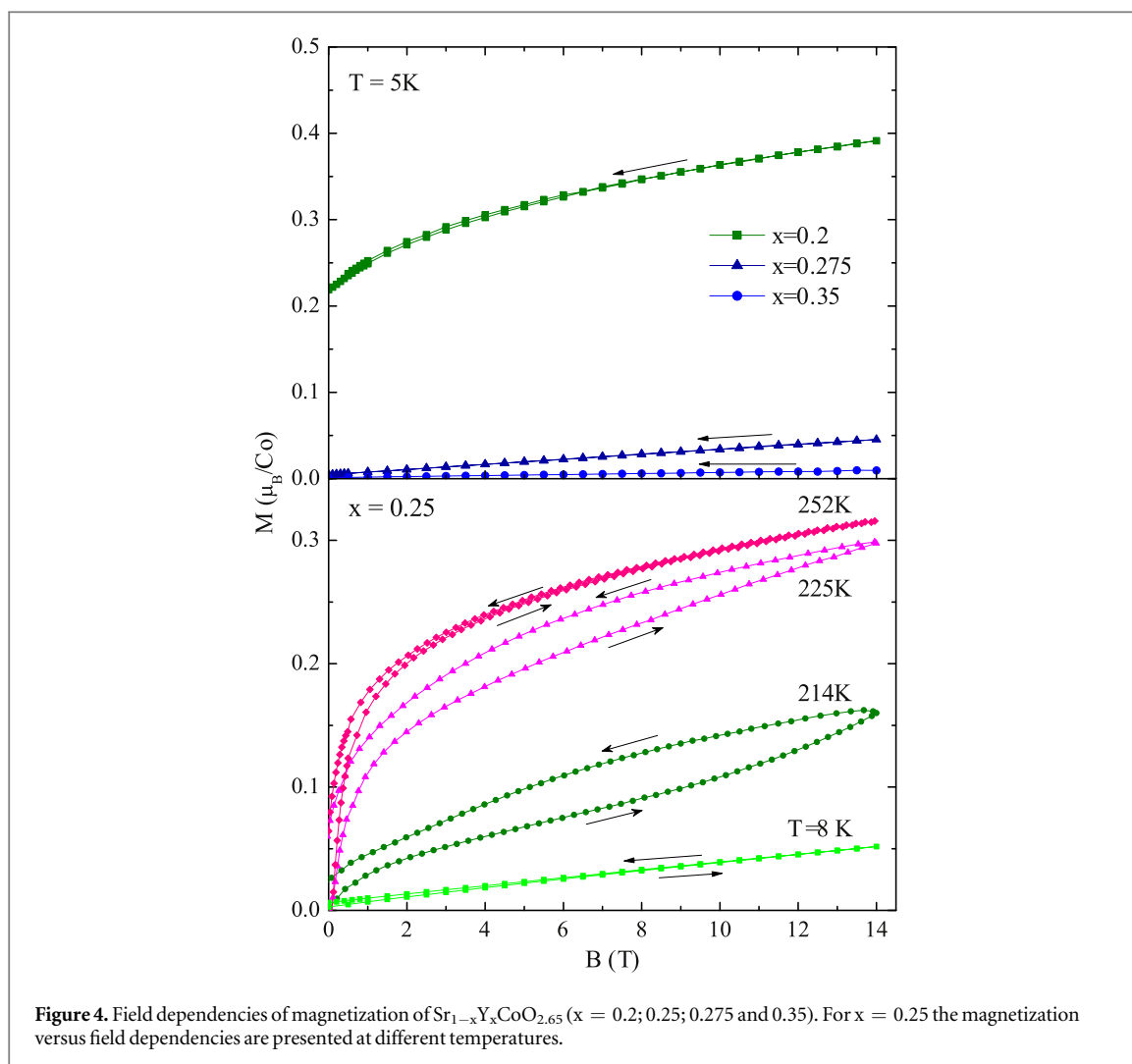
Table 1. Crystal and magnetic structure parameters of $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$ at 10 and 400 K refined in $I4/mmm$ space group.

Temperature (K)	10	400
a, b (Å)	7.6550	7.6603
c (Å)	15.3030	15.3812
V (Å ³)	986.751	902.585
Sr1/Y1		0, 0, z
z	0.852 25	0.853 21
Sr2/Y2		0, 0.5, z
z	0.869 22	0.869 23
Sr3/Y3		0, 0, z
z	0.377 80	0.377 09
Co1		x, y, 0
x	0.248 73	0.250 67
y	0.248 73	0.250 67
Co2		0.25, 0.75, 0.25
O1		0, y, z
y	0.246 04	0.245 89
z	0.259 37	0.257 89
O2		x, y, z
x, y	0.218 09	0.219 55
z	0.116 84	0.116 94
O3		0, y, 0
y	0.879 80	0.87 896
O4		x, 0.5, 0
x	0.226 25	0.221 25
R_p/R_{wp} (%)	5.13/6.61	4.51/5.97
R_{Bragg} (%)	8.15	11.5
Magnetic R-factor	10.2	
χ^2	13.1	10.3
Magnetic moment in layers	± 1.7	
CoO ₆ , μ_z (μ_B)		
Magnetic moment in layers	± 2.7	
CoO _{4+γ} , μ_z (μ_B)		

**Figure 3.** Temperature dependencies of Young's modulus of $\text{Sr}_{1-x}\text{Y}_x\text{CoO}_{2.65}$ ($x = 0.2$ and 0.25).

The electrical resistivity of compounds $x = 0.25$ in the temperature range 50–315 K shows a semiconductor-like behavior. Resistivity at 50 K is relatively large $\rho = 10^4$ Ohm-cm (figure 6). A noticeable magnetoresistive effect in the temperature range 50–300 K and magnetic fields up to 14 T was not observed.

To explain the magnetic properties, it is necessary to know the spin state of the cobalt ions in both structural layers. We assume that all Co^{3+} ions are in the LS/HS state mixture. This assertion is supported by the following facts: The basic antiferromagnetic structure is of the G-type. This means that the magnetic moments of all nearest neighbors are directed oppositely to each other in both layers. The observed Neel point is high, reaching



up to 400 K. This indicates that antiferromagnetic interactions are strong. For Co^{3+} ions in the IS state magnetic interactions lead to a low Curie point. For example, ferromagnetic epitaxial thin films of LaCoO_3 show a maximal T_C of around 90 K regardless of the sign of volume change of the unit cell due to strains arising from the mismatch between lattices of film and substrate [23]. Note that $\text{SrCoO}_{2.5}$ with Co^{3+} ions in the HS state shows G-type antiferromagnetic ordering at temperature around 540 K [10]. Strong antiferromagnetic interaction

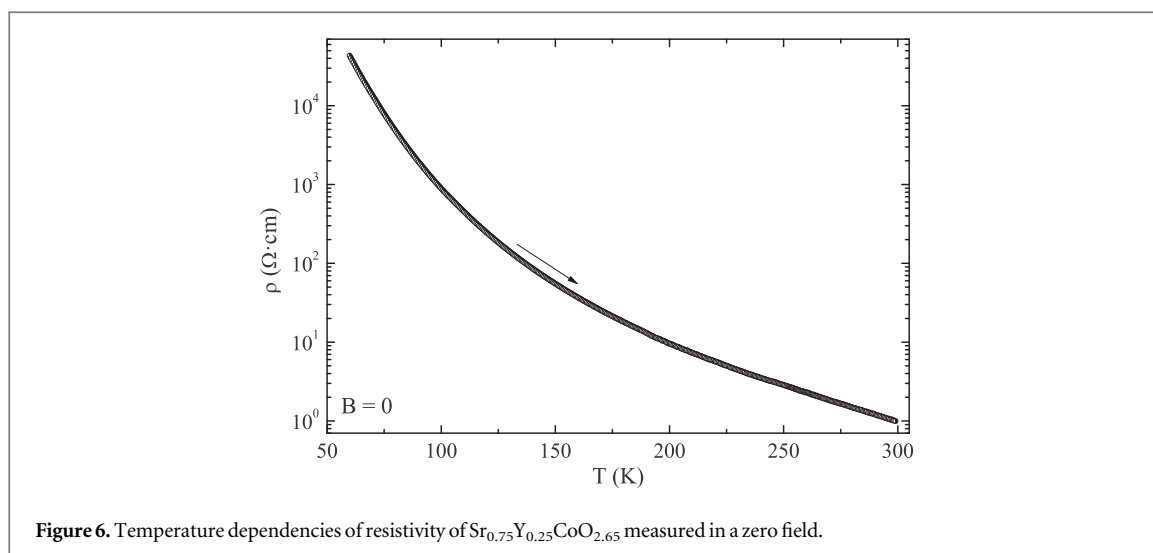


Figure 6. Temperature dependencies of resistivity of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{CoO}_{2.65}$ measured in a zero field.

between $\text{Co}^{3+}(\text{HS})\text{--O--Co}^{3+}(\text{HS})$ is in accordance with Goodenough's rules [24]. In addition only $\text{Co}^{3+}(\text{HS})$ and $\text{Co}^{3+}(\text{LS})$ ions have been revealed by NMR method in antiferromagnetic layered cobaltites [25].

The electrical resistance below 50 K is relatively large (10^4 Ohm·cm), while the magnetoresistance is almost absent, which reflects a good stability of the basic G-type antiferromagnetic state. Compounds with Co^{3+} in collective IS state are on the opposite characterized by a small electrical resistance and a ferromagnetic exchange coupling. In the octahedron CoO_6 , $\text{Co}^{3+}(\text{HS})$ is an isotropic ion, however, if the CoO_5 pyramids are articulated along the base, then ferromagnetic bonds appear due to orbital ordering in CoO_5 pyramids [26, 27]. This type of connection of the pyramids is believed to be typical for layered perovskites like $\text{YBaCo}_2^{3+}\text{O}_{5.5}$, which leads to an uncompensated canted magnetic structure due to a competition between different types of magnetic interactions and due to the presence of a strong magnetic anisotropy [26]. The ferromagnetic component coincides in magnitude ($0.25 \mu_{\text{B}}/\text{Co}$) in both classes of compounds [26–30]. Both types of compounds shows crystal structure phase transitions at the temperature of the magnetic ordering [13, 29]. Small substitution of cobalt with iron ions (2%–3%) in $\text{Sr}_{0.78}\text{Y}_{0.22}\text{CoO}_{2.65}$ completely destroys the orbital ordering and the concomitant ferromagnetic component [11]. Note that layered perovskites like $\text{YBaCo}_2^{3+}\text{O}_{5.5}$ exhibit antiferromagnet-ferromagnet transition too [26–30]. Non collinear magnetic structures have been suggested on the basis of neutron diffraction data to explain the ferromagnetic coupling between Co^{3+} in pyramids CoO_5 articulated along the base in $\text{TbBaCo}_2^{3+}\text{O}_{5.5}$ [26].

4. Conclusions

It is shown that the crystal structure of layered cobaltite $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$ can be described by the monoclinic space group $A2/m$ with a superstructure $\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ above the Neel temperature of $T_{\text{N}} = 375$ K and below 375 K with a superstructure $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$. Magnetic ordering coincides with the crystal structure phase transition. At the Neel point the unit cell is doubled along a axes apparently due to the orbital ordering in the CoO_5 pyramids, located in the anion-deficient layers. The basic magnetic structure is G-type antiferromagnetic with a small ferromagnetic component of near $0.25 \mu_{\text{B}}/\text{Co}$ due to the presence of ferromagnetic bonds and orbital ordering in the anion-deficient layers which leads to a canted magnetic structure. The stability of the canted magnetic structure is also due to the large magnetic anisotropy. Magnetic moments in the structural layers $\text{CoO}_{4+\gamma}$ are equal to $2.7 \mu_{\text{B}}/\text{Co}$ and in the CoO_6 layers equal to $1.7 \mu_{\text{B}}/\text{Co}$. The antiferromagnetic structure of G-type and the high Neel point suggest that Co^{3+} ions in both structural layers are in the HS/LS state mixture. The Neel point decreases with increasing of yttrium content. Apparently it is associated with a decrease of the unit cell volume leading to the stabilization of the LS cobalt state. The antiferromagnet-ferromagnet transition is observed in compounds with $x > 0.2$. It is associated with concurrence of different magnetic interactions and structural disorder which provoke orbital disordering. Magnetic transitions are accompanied by structural phase transitions. Spontaneous magnetization is not found for $x > 0.275$ compounds apparently due to orbital disordering and rise of crystal symmetry.

Acknowledgments

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