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# Magnetoresistance effect in layered cobaltite $Sr_{0.9}Y_{0.1}CoO_{2.63}$

## 1.    Introduction

Complex oxides of cobalt with a perovskite structure have attracted great interest due to different spin states of the $Co^{3+}$ ion, the existence of interplay between the magnetic and transport properties [1] and the effect of colossal magnetoresistance [2]. The character of the magnetic interactions in cobaltites depends on the spin state of $Co^{3+}$ ions, which can be found in the low spin ( $t_{2g}^6$ , S = 0), intermediate spin ($t_{2g}^5 e_g$ , S = 1), and high spin ($t_{2g}^4 e_g^2$ , S = 2) states. In the parent compound $LaCoO_3$, a gradual semiconductor-metal transition is associated with a change in the spin state of $Co^{3+}$ ions. On the surface of crystallites in powders and inside epitaxial $LaCoO_3$ films, ferromagnetism with $T_C \sim 85$ K was observed [3]. The replacement of La ions by Sr ions in the $La_{1-x}Sr_xCoO_3$ system leads to ferromagnetism with the Curie temperature gradually increasing up to 305 K ($SrCoO_3$) [4,5]. The end compound $SrCoO_{3-\gamma}$ can have various structural distortions depending on the conditions of synthesis and oxygen content [4]. The decrease of the oxygen content leads to a transition from the ferromagnetic state with $T_C \approx 305$ K ($\gamma \approx 0$) to the antiferromagnetic state with $T_N \approx 537$ K ($\gamma \approx 0.5$) [5]. It was shown in [6] that a small substitution of Sr ions by rare-earth ions (near 5%) can stabilize the cubic phase $Sr_{0.95}Y_{0.05}CoO_{3-\gamma}$ under air synthesis conditions, whereas the

cubic phase $SrCoO_{3-\gamma}$ is obtained only under high oxygen pressure [4]. Depending on the oxygen content, the sample $Sr_{0.95}Y_{0.05}CoO_{3-\gamma}$ can also be tetragonal ($a_p \times a_p \times 2a_p$, $a_p$ - primitive unit cell parameter, space group *P4/mmm*).

Relatively recently anion-deficient layered cobaltites $Sr_3YCo_4O_{10.5+\delta}$ (the reduced chemical formula is $Sr_{0.75}Y_{0.25}CoO_{3-\gamma}$) were obtained in which rare-earth ions can be ordered [6, 7]. These compounds are predominantly antiferromagnetic with a Neel temperature well above room temperature [7, 8]. A relatively small ferromagnetic component occurs simultaneously with the antiferromagnetic ordering [7, 8]. The basic crystal structure of layered cobaltites $Sr_3LnCo_4O_{10.5+\delta}$ (Ln - lanthanide) consists of alternating anion-deficient layers $CoO_{4+\delta}$ and layers formed by $CoO_6$ octahedra touching the apexes [6-9]. The oxygen vacancies are ordered in the $CoO_{4+\delta}$ layers [6].

A study of layered cobaltite $Sr_3YCo_4O_{10.5}$ by X-ray spectroscopy was carried out in [15], which indicated the presence of ordering of the some 3d orbitals of cobalt ions below the Neel point. So it was suggested that the ferrimagnetic component of this compound was explained by the ordering of the 3d orbitals of $Co^{3+}$ ions in the intermediate spin state in the layers having a stoichiometric content of oxygen ions. However, the ordering of the 3d orbitals of cobalt ions may be associated with anion-deficient layers. Since there are different points of view on the nature of the ferromagnetic component in the layered cobaltites $Sr_{3-x}Ln_xCo_4O_{10.5+\delta}$, we have carefully studied the structure, magnetic and magnetotransport properties of cobaltite $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$, in which the yttrium and oxygen content is intermediate between oxygen vacancies ordered $SrCoO_{2.5}$ and $Sr_3YCo_4O_{10.5+\delta}$.

## 2.     Experimental procedures

Polycrystalline samples of the sample $Sr_{1-x}Y_xCoO_{2.65}$ ($0.05 \leq x \leq 0.3$) were obtained by conventional ceramic technology in air. The stoichiometric amounts of $Y_2O_3$ and $Co_3O_4$ oxides and $SrCO_3$ carbonate of high purity were thoroughly ground in a planetary ball mill from RETSCH PM-100 for 30 min at a rate of 250 rpm. The $Y_2O_3$ oxide was heated to 1000°C to remove moisture prior to weighing. The synthesis of the samples was carried out in two stages. Preliminary synthesis was performed at a temperature of 1000 °C. The final synthesis was performed at 1150 – 1200 °C for 7 – 8 h. Then the sample was cooled for 12 h to 300°C. Scanning electron microscope (SEM) LEO 1455 VP was used to study the microstructure. To determine the elemental composition of the samples X-ray microanalysis was conducted using energy dispersive X-ray spectroscopy microanalyzer Aztec Energy Advanced X-Max 80 (EDX). Synchrotron X-ray diffraction studies (95 K $\leq$ T $\leq$ 420 K) were carried out using the powder diffraction station of the Materials Sciences beamline on Swiss Light Source at the Paul Scherrer Institut (Willigen, Switzerland). Neutron diffraction studies in the temperature range from

10 to 420 K were performed on the D2B high-resolution diffractometer at the Laue-Langevin Institute (Grenoble, France). The FullProf software package was used for the refinement of the crystal and magnetic structure by the Rietveld method [18]. Magnetic and magnetotransport measurements were performed using physical property measurement system (Cryogenic Ltd.) in magnetic fields up to 14 T in the temperature range 5 – 315 K. Conductivity measurements were performed using a four-contact method with indium contacts deposited by ultrasound.

## 3.     Results and discussion

The shape and size of the particles of ceramic samples Sr$_{1-x}$Y$_x$CoO$_{2.65}$ ($0.05 \leq x \leq 0.3$) were examined using scanning electron microscope. The investigation of the composition of synthesized samples by registration of element distribution along any given line on the surface has shown a good accordance with prescribed parameters (Fig.1). There is an insignificant variation of the observed of Y, Sr, Co content in different crystallites so it can regard the sample as practically homogeneous on the composition.
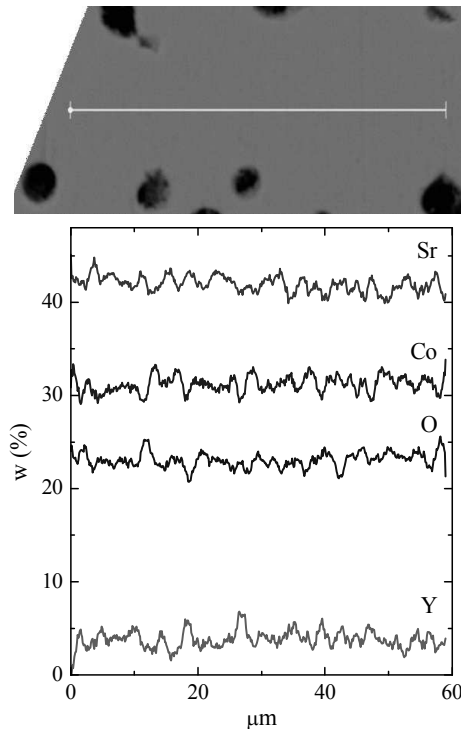


**Fig. 1.**    SEM image and EDX line scan of the surface area of the sample Sr$_{0.9}$Y$_{0.1}$CoO$_{2.63}$

Synchrotron X-ray diffraction studies of $Sr_{0.9}Y_{0.1}CoO_{2.63}$ composition were carried out in the temperature range 95-420 K. The crystal unit cell parameters of the main structural phase of $Sr_{0.9}Y_{0.1}CoO_{2.63}$ were calculated in the tetragonal space group *I4/mmm* with a superstructure of the type $2a_p \times 2a_p \times 4a_p$ ($a_p$ is the parameter of the primitive cubic cell). It can be seen from figure 2 that the parameters and volume of the unit cell increase monotonically with increasing temperature. The gradual increase of the unit cell volume indicates the absence of any crystal structure or spin transition.

With the increase of the yttrium ion content to 20%, additional diffraction peaks with *hkl* indices 111 and $\bar{1}11$ appear on the X-ray patterns, which disappear at temperatures above 350 K. These peaks can be described within the framework of the monoclinic space group *A2/m* (superstructure $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$) (Fig. 3). The appearance of these peaks has been associated with the spin transition of Co ions or 3d orbital ordering in $CoO_6$ layers [8-9]. With an increase in temperature above 350 K, a first-order phase transition is observed, accompanied by a crystal structure transition to a cell of the type $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ (space group *A2/m*).
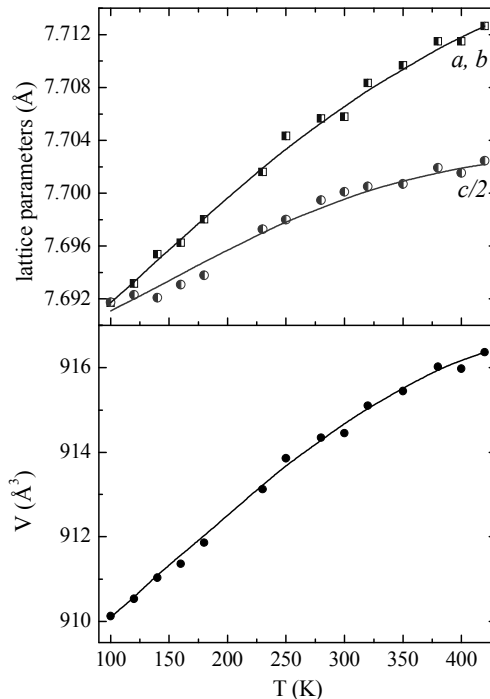


**Fig. 2.**   Temperature dependences of lattice parameters and unit cell volume V for the sample $Sr_{0.9}Y_{0.1}CoO_{2.63}$ (space group *I4/mmm*)
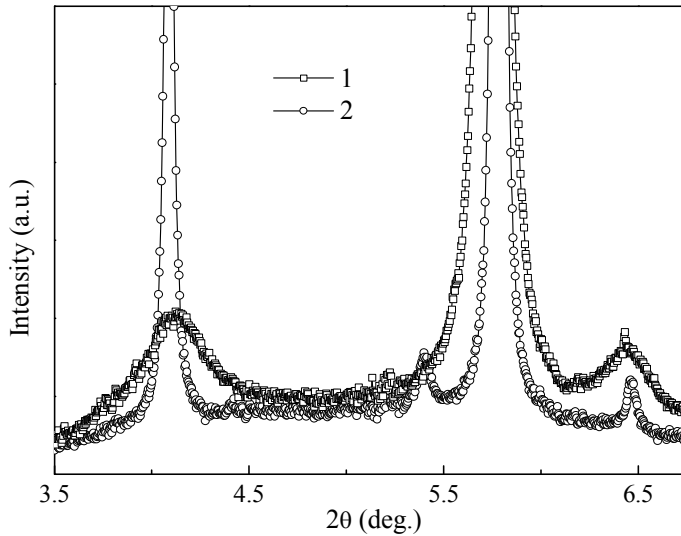
**Fig. 3.** X-ray powder diffraction patterns for the samples $Sr_{0.9}Y_{0.1}CoO_{2.63}$ (space group *I4/mmm+ A2/m*) (1) and $Sr_{0.8}Y_{0.2}CoO_{2.65}$ *(A2/m)* (2) at 100 K over the range of angles 3.5-6.5

Neutron diffraction studies of $Sr_{0.9}Y_{0.1}CoO_{3-\gamma}$ were carried out at 10 K, 260 K, and 400 K. The calculations of the crystal and magnetic structure of the major phase of the sample $Sr_{0.9}Y_{0.1}CoO_{2.63}$ at 10 K and 400 K were carried out within the framework of the space group *I4/mmm* and unit cells of the type $2a_p \times 2a_p \times 4a_p$. According to the obtained data, the crystal structure consists of layers alternating along the *c* axis of $CoO_6$ octahedra and anion-deficient $CoO_{4+\gamma}$ layers, like what has been previously shown for other layered cobaltites $Sr_{0.75}Y_{0.25}CoO_{3-\gamma}$ [7]. At 400 K the monoclinically distorted phase is absent. Refined from the neutron diffraction data, the oxygen content in the sample is close to 2.63, which means that the cobalt ions are in the trivalent state. Analysis of the neutron diffraction data obtained at 10 K showed that the basic magnetic structure can be described by an antiferromagnetic ordering of the G type with a magnetic cell of the type $2a_p \times 2a_p \times 4a_p$ with two different magnetic positions in the layers of $CoO_6$ octahedra and anion-deficient layers. The magnetic moments in anion-deficient layers and in layers of $CoO_6$ octahedra at 10 K are equal to $\sim 2\ \mu_B$ and $\sim 1.5\ \mu_B$, respectively. The magnetic contribution to the diffraction pattern is no longer present at 400 K.
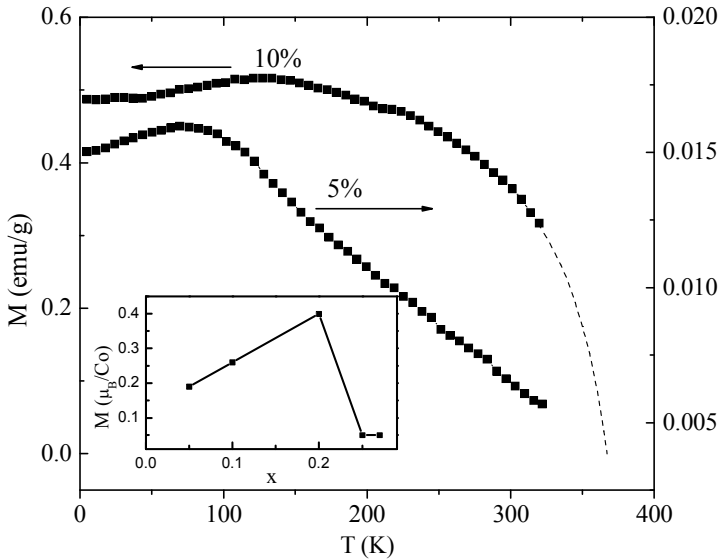
**Fig. 4.**   Temperature dependences of the magnetization for the samples $Sr_{0.95}Y_{0.05}CoO_{2.63}$ and $Sr_{0.9}Y_{0.1}CoO_{2.63}$. The Inset shows the concentration dependence of the magnetization for $B = 14$ T at 5 K for $Sr_{1-x}Y_xCoO_{3-\gamma}$

From the magnetic measurements, the Néel temperature was roughly estimated to about $T_N \approx 380$ K using M(T) approximation by dashed curve in figure 4. As the temperature decreases from 320 K to 5 K, first the magnetization increases, reaching a maximum value of 0.5 emu/g at $T \approx 130$ K, and then decreases slightly. The residual magnetization is $\sim 0.022$ $\mu_B$ per cobalt ion at 5 K and slightly decreases to 0.017 $\mu_B$ per cobalt ion at 220 K. The magnetization is not saturated in magnetic fields up to 14 T. The sample $Sr_{0.95}Y_{0.05}CoO_{2.63}$ exhibits much smaller magnetization. The magnetization as function of the Y content for $B = 14$ T at 5 K is plotted in the Inset of the figure 4 and shows a growth up to x=0.2 and then drops (x=0.25) apparently due to the crystal structure transition.
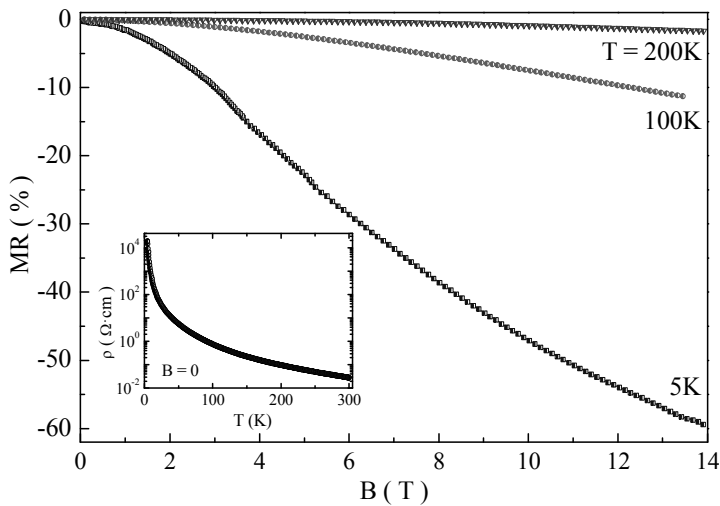
**Fig. 5.** Dependence of the magnetoresistance for the sample Sr$_{0.9}$Y$_{0.1}$CoO$_{2.63}$ at 5K, 100K and 200K (the Inset shows temperature dependence of electrical resistivity B = 0)

The measurement of the electric transport properties of the sample Sr$_{0.9}$Y$_{0.1}$CoO$_{2.63}$ shows that the temperature dependence of the electrical conductivity in this temperature range has a semiconductor character (see the inset of Fig. 5). The magnitude of the resistivity increases from ~ 0.02 Ω·cm at 300 K to ~ 20 kΩ·cm at helium temperature. Anomalies of the temperature dependence of the electrical resistivity were not found. The negative magnetoresistance (MR = (ρ(0) - ρ(H))/ρ(0) • 100%) reaches 58% at 5 K in a magnetic field B=14 T (Fig.5). With increasing temperature, the magnetoresistance strongly decreases to 1.6% in a field of 14 T at 200 K.

## 4.     Conclusions

The obtained data indicate that the crystal structure changes from tetragonal *P4/mmm* ($a_p \times a_p \times 2a_p$) to monoclinic *A2/m* through the intermediate tetragonal phase *I4/mmm* ($2a_p \times 2a_p \times 4a_p$) in the system Sr$_{1-x}$Y$_x$CoO$_{3+\gamma}$ (the γ value corresponds to finding the majority of cobalt ions in the oxidation state 3+) with increasing yttrium content. The simultaneous disappearance of the monoclinic phase and of the spontaneous magnetization evidence that the type of crystal structure determines the occurrence of the ferromagnetic component.

## Acknowledgments

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## Abstract

The structure and the magnetic and magnetotransport properties of the perovskite sample Sr$_{0.9}$Y$_{0.1}$CoO$_{2.63}$ have been studied using different diffraction methods and magnetization and conductivity measurements. Synchrotron X-ray diffraction shows that the sample is structurally two-phase. The majority phase has a tetragonally distorted unit cell and is described by the space group *I4/mmm*. A very strongly broadened superstructure peak observed at small angles in X-ray diffraction patterns at temperatures below 400 K are explained by the existence of a monoclinic phase with large unit cell whose phase fraction is much smaller than that of the tetragonal phase, but which is dominant in the sample Sr$_{0.8}$Y$_{0.2}$CoO$_{2.65}$. The spontaneous magnetization strongly increases with increasing the Y content up to 20% due to formation of the monoclinic phase. The magnetic structure is predominantly antiferromagnetic G-type with magnetic moments 1.5 $\mu_B$ in the layers of CoO$_6$ octahedra and 2 $\mu_B$ in the anion-deficient CoO$_{4+\gamma}$ layers. The electrical conductivity of the sample Sr$_{0.9}$Y$_{0.1}$CoO$_{2.63}$ has semiconducting character. The magnetoresistance reaches 58% for the field B = 14 T at 5 K and decreases strongly with the increasing temperature and Y content.

## Streszczenie

Struktura i właściwości magnetyczne i magnetotransportowe perowskitu Sr$_{0.9}$Y$_{0.1}$CoO$_{2.63}$ zostały zbadane przy użyciu różnych metod dyfrakcyjnych oraz pomiarów namagnesowania i przewodnictwa. Dyfrakcja rentgenowska mierzona na synchrotronie pokazuje, że próbka ma strukturę dwufazową. Główna faza ma tetragonalnie zniekształconą komórkę elementarną i jest opisana przez grupę przestrzenną I4 /mmm.

Pik o bardzo mocno poszerzonej superstrukturze obserwowano pod niewielkimi kątami w dyfraktogramach rentgenowskich w temperaturach poniżej 400 K i jest związany z istnieniem fazy monoklinowej o dużej komórce elementarnej, której frakcja fazowa jest znacznie mniejsza niż faza tetragonalna, ale która jest dominujący w próbce Sr$_{0.8}$Y$_{0.2}$CoO$_{2.65}$. Spontaniczne namagnesowanie silnie wzrasta wraz ze wzrostem zawartości Y do 20% z powodu tworzenia się fazy monoklinowej.

Struktura magnetyczna jest w przeważającej mierze antyferromagnetyczną typu G z momentami magnetycznymi 1,5 $\mu_B$ w warstwach oktaedrycznych $CoO_{4+\gamma}$ i 2 $\mu_B$ w warstwach $CoO_{4+\gamma}$ z niedoborem anionów. Przewodność elektryczna próbki $Sr_{0.9}Y_{0.1}CoO_{2.63}$ ma charakter półprzewodnikowy. Magnetooporność osiąga 58% dla pola B = 14 T przy 5 K i silnie się zmniejsza wraz ze wzrostem temperatury i zawartością Y.

**Słowa kluczowe:** struktura krystaliczna; struktura magnetyczna; magnetyzacja; magnetooporność