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

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The $\text{Sr}_{1-x}\text{Y}_x\text{CoO}_{2.65}$ ($x=0.2$) 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 $\text{A}_2/m$ with the superstructure $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ ($a_p$ is a primitive cell) however basic diffraction peaks well indexed in $\text{I}_4/\text{mmm}$ ($2a_p \times 2a_p \times 4a_p$) space group. Around the Neel point $T_N = 375$ K there is a doubling of the unit cell parameter along $a$ axis in the framework of the space group $\text{A}_2/m$. A basic magnetic structure is $\text{G}$ type antiferromagnetic with average magnetic moments of $2.7\mu_\text{B}/\text{Co}$ and $1.7\mu_\text{B}/\text{Co}$ in anion-deficient $\text{CoO}_4 + \gamma$ and stoichiometric $\text{CoO}_6$ layers, respectively. The ferromagnetic component determined from the magnetization measurements is about $0.27\mu_\text{B}/\text{Co}$ at 8 K. $\text{Sr}_{0.8}\text{Y}_{0.2}\text{CoO}_{2.65}$ shows almost standard magnetization vs. temperature dependence whereas $\text{Sr}_{0.75}\text{Y}_{0.25}\text{CoO}_{2.65}$ exhibits antiferromagnet-ferromagnet transition accompanied by structural transformation. There is practically no spontaneous magnetization in $x=0.3$. The basic magnetic structure and high $T_N$ suggest that $\text{Co}^{3+}$ ions in both structural layers are predominantly in the low-spin/high-spin states mixture. It is assumed that the ferromagnetic component is due to the orbital ordering occurring at $T_N$ in the $\text{CoO}_5$ pyramids and concomitant appearance of ferromagnetic exchange coupling between the $\text{Co}^{3+}(\text{HS})$ ions located in $\text{CoO}_5$ pyramids in anion-deficient $\text{CoO}_4 + \gamma$ layer.

Introduction

Cobaltites of rare-earth elements with a perovskite-like structure are of considerable interest, both from the point of view of technological applications and a research in the area of physics of magnetic phenomena [1-2]. The basic compound $\text{LaCoO}_3$ up to 30 K is very close to a diamagnetic insulator with paramagnetic defects, above 30 K a partial spin crossover of $\text{Co}^{3+}$ ions occurs from the low-spin (LS) state to the high spin/low spin (HS/LS) states mixture which is paramagnetic [3-4]. However LS state is still dominant at least to 400 K. Both magnetic and orbital ordering has not been reliably observed at any temperature. The substitution of $\text{La}^{3+}$ with $\text{Sr}^{2+}$ ions leads to the drop of resistivity and appearance of a long-range ferromagnetic order above 18% replacement of $\text{La}^{3+}$ ions [5]. Subsequently, $T_C$ and magnetization increase almost linearly from 170 K and $M_s = 1.2\mu_\text{B}/\text{Co}$ ($x=0.18$) up to $T_C \sim 305$ K.
and $M_s = 2.5\mu_B /\text{Co}$ in practically stoichiometric metallic SrCo$^{4+}$O$_3$, which can be obtained only under high oxygen pressure [6]. Taking into account the magnitude magnetic moment $M_s$ it was suggested that Co$^{3+}$ and Co$^{4+}$ ions are in intermediate spin state [6]. Deviation in stoichiometry of oxygen in cobaltites leads to antiferromagnetic ordering with $T_N$, which can be much higher than room temperature [7]. For example SrCoO$_{2.5}$ containing only Co$^{3+}$ in HS state both in tetrahedral and octahedral surrounding is G-type antiferromagnet with $T_N=537$ K [7]. The observed magnetic moments are about $3\mu_B /\text{Co}$ for both tetrahedral and octahedral oxygen surrounding [7]. It is incompatible with IS spin state of Co$^{3+}$ ions. So the magnetic interactions between Co$^{3+}$ ions in HS state regardless from oxygen surrounding are strongly antiferromagnetic. It was shown in [8-10] that relatively small substitution of Sr$^{2+}$ by Y$^{3+}$ leads to the stabilization of Sr$_{1-x}$Y$_x$CoO$_{3.6}$ ($0.05 < x < 0.35$) 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 CoO$_{4+y}$ [9-10]. A basic antiferromagnetic ordering of the G type arises substantially above room temperature and accompanied by the appearance of a small ferromagnetic component [9-10]. Composition $x=0.25$ exhibits anomalous decrease of magnetization with temperature decreasing [9,10]. Small substitution of Co with Fe almost completely destroys the ferromagnetic component in spite of growth of $T_N$ and magnetic moment per unit cell thus underlining structural factor [9].

A number of scenarios for the appearance of the ferromagnetic component have been described: for example, orbital ordering in Co$^{3+}$ (IS) ions located in oxygen-stoichiometric CoO$_6$ layers is proposed as the reason for ferrimagnetic component [11,12]. Ferrimagnetic structure in anion deficient layers due to oxygen vacancies ordering [13]. Ferromagnetic Co$^{3+}$ chains in oxygen-stoichiometric CoO$_6$ layers [14], spin "bags" in CoO$_6$ layers [15] and a uncompensated canted magnetic structure [16]. The questions are still actually: whether or not the magnetic ordering is accompanied by a structural transition [11-12] and crystal structure impact on stability of ferromagnetic component. Note, that majority theoretical studies of magnetic properties have been performed in frame of space group I4/mmm. However, correct symmetry seems to be much lower [12]. Oxygen vacancies ordering observed in anion deficient layers correspondsto general chemical formula Sr$_3$YCo$_4$O$_{10.5}$ with very large superstructure [12]. So the origin of ferromagnetic component is not clear. Therefore, we have conducted a comprehensive study of the crystal structure, magnetic and elastic properties of the composition Sr$_{0.8}$Y$_{0.2}$CoO$_{2.65}$. Compounds with larger yttrium content have been studied also in order to establish effect of Sr$^{2+}$ with Y$^{3+}$ substitution on magnetic properties.

**Experimental part**

Polycrystalline samples of compositions Sr$_{1-x}$Y$_x$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$_2$O$_3$, Co$_3$O$_4$ 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 minutes at a speed of 250 rpm. Before weighing, the Y$_2$O$_3$ 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 hours. The samples were then cooled for 7 hours down to a temperature of 300 °C. X-ray diffraction studies (95 K ≤ $T$ ≤ 420 K) were performed at a 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
Results and discussion

The crystal structure of Sr$_{0.8}$Y$_{0.2}$CoO$_{2.65}$ was studied using the diffraction of synchrotron X-ray radiation in temperature range 90-400 K. Space groups I4 / mmm, Cmna and A2 / m were used for refinement of crystal structure. X-ray diffraction peaks were much better indexed in the monoclinic space group A2 / m with the superstructure 2V2a$_p$ × 2V2a$_p$ × 4a$_p$ at 400 K and with 4V2a$_p$ × 2V2a$_p$ × 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 rising indicating stability of ground spin state of cobalt ions. Figure 1 shows the parts of x-ray diffraction patterns at small angles at 400 and 350 K. 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 was proposed [12]. Figure 2 shows parts of neutron diffraction patterns at small angles recorded at 10 and 400 K. At 400 K, the magnetic contribution to neutron scattering was not 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$_p$ × 2a$_p$ × 4a$_p$. These peaks are marked by arrows with the designation AF. Very weak diffraction peaks that can be indexed within the space group Cmna or A2 / m are marked with asterisks. The crystal and magnetic structures were calculated within the more simple tetragonal space group I4 / mmm (2a$_p$ × 2a$_p$ × 4a$_p$), since the peaks which cannot be indexed in I4 / mmm group are very small. According to the refinement by Rietveld method, the magnetic structure is of the G type antiferromagnetic with magnetic moments of 1.7μ$_B$ / Co in the stoichiometric layers of CoO$_6$ and in the anion-deficient layers 2.7μ$_B$ / Co (Table). The inset to Fig. 2 shows the temperature dependence of the magnetic contribution in the diffraction peak 112 (I4/mmm). One can see that the Neel point is about 375 K. Judging by the fact that the intensity of the reflexes marked with an asterisk depends strongly on temperature, the magnetic cell is much larger than that considered in Table. However, the intensity of the three reflexes marked with an asterisk is very small. Therefore, the presented approximation describes a fairly well of basic magnetic structure. According to the refined oxygen content, cobalt ions are dominantly in the trivalent state because the chemical formula is Sr$_{0.8}$Y$_{0.2}$CoO$_{2.65}$. Figure 3 shows temperature dependences of Young's modulus. One can see that the well pronounced minimum of Young's modulus of Sr$_{0.8}$Y$_{0.2}$CoO$_{2.65}$ coincides with the Neel point T$_N$. This indicates that the crystal structure phase transformation take places at the temperature of magnetic ordering. The compound Sr$_{0.75}$Y$_{0.25}$CoO$_{2.65}$ exhibits two minima of Young's modulus: below and above room temperature. The minimum observed at 350 K corresponds to temperature of magnetic ordering. Fields and temperatures dependencies of magnetization for Sr$_{1-x}$Y$_x$CoO$_{2.65}$ are shown in figures 4 and 5. From the field dependence of the magnetization x=0.2 composition, it is difficult to precisely estimate the spontaneous magnetization, since saturation of the magnetization in fields up to 14 T is not observed below magnetic ordering temperature (Fig.4). However, one can conclude that the spontaneous magnetization for Sr$_{0.8}$Y$_{0.2}$CoO$_{2.65}$ is near 8 emu / g or 0.27 μ$_B$ / Co. Magnetization vs. 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 (Fig5). One can seethat the composition of x=0.25 shows well pronounced antiferromagnet-ferromagnet transition slightly below room temperature(Fig.5). This transition is a first order because there is a large temperature magnetization hysteresis and a metamagnetic behavior (Figs.4 and 5). Magnetic fields transform compensated antiferromagnetic phase into new antiferromagnetic with ferromagnetic component. The antiferromagnet-ferromagnet phase transition is accompanied by well pronounced minimum of Young's modulus thus indicating a concomitant structural transition (Fig.3). Maximum of magnetization for x=0.275 shifts to room temperature (Fig.5). Temperature hysteresis was observed too. There is no noticeable spontaneous magnetization in Sr$_{0.7}$Y$_{0.3}$CoO$_{2.65}$ below room temperature. Apparently a very small spontaneous magnetization is resulted from a tiny structural (chemical) inhomogeneity.

Recently, we investigated the effect of cation and anion ordering on the crystal structure and magnetic properties of substituted rare-earth cobalt oxides Gd$_{0.1}$Sr$_{0.9}$CoO$_{3-\delta}$ [1]. The solid solutions considered can be in an ordered and disordered state. The disordered sample Gd$_{0.1}$Sr$_{0.9}$CoO$_{3-\delta}$ is a cubic perovskite phase with a uniform random distribution of Sr$^{2+}$/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 Sr$^{2+}$/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 [Sr$_{0.5}$O$_{0.5}$]-[CoO$_{2.5}$]-[Gd$_{0.1}$Sr$_{0.4}$O$_{5.5}$]-[CoO$_{2.6}$]. An important circumstance is that the anion-deficient layered cobaltites of the type Sr$_{3}$YCo$_{4}$O$_{10.5}$ and ordered Gd$_{0.1}$Sr$_{0.9}$CoO$_{3-\delta}$ excluding the paramagnetic contribution from gadolinium ions Gd$^{3+}$ have similar magnetic properties [1-3]. In addition, the magnetic and thermodynamic values of the ordered samples Gd$_{0.1}$Sr$_{0.9}$CoO$_{3-\delta}$ have pronounced anomalies [1, 2], therefore we consider that analogous to layered cobaltites of the Sr$_{3}$YCo$_{4}$O$_{10.5}$ type with different oxygen content [3] in the ordered compounds Gd$_{0.1}$Sr$_{0.9}$CoO$_{3-\delta}$ there is a first-order phase transition from the high-temperature "ferromagnetic" state to the low-temperature antiferromagnetic state.

The electrical resistivity in the temperature range 5-315 K shows a semiconductor-like behavior. Resistivity at 5 K is relatively large $\rho = 10^4$ Ohm cm. The magnetoresistance is small and amounts to $\sim 2\%$ at temperature range 5-300 K in a field of 14 T.

To explain the magnetic properties, it is necessary to know the spin state of cobalt ions in both structural layers. We assume that all Co$^{3+}$ ions are in the LS/HS states mixture. This assertion is supported by the following facts. The basic antiferromagnetic structure is of the G-type. It means that magnetic moments of the all nearest neighbors are directed oppositely to each other in both layers. Observed the 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 small the Curie point. For example, in ferromagnetic epitaxial thin films of LaCoO$_3$ shows maximal $T_C$ around 90 K regardless of sign of volume unit cell change due to strains arising from mismatch between lattices of film and substrate[18]. So ferromagnetism is associated with strains. It is known that Co$^{3+}$ (IS) ions can be Jahn-Teller active in contrast to isotropic Co$^{3+}$ (HS) ones. So strains should stabilize Co$^{3+}$ (IS) state. Note that SrCoO$_{2.5}$ with Co$^{3+}$ ions in the HS state shows G-type antiferromagnetic ordering at temperature around of 540 K [7]. Strong antiferromagnetic interaction between Co$^{3+}$(HS)-O-Co$^{3+}$(HS) is in accordance with Goodenough's rules [19]. In addition only Co$^{3+}$(HS) and Co$^{3+}$(LS) ions have been revealed by NMR method in antiferromagnetic layered cobaltites [20]. The electrical resistance at 5 K is relatively large (10$^4$ Ohm cm), while the magnetoresistance is almost absent, which correspond a good stability of the basic G-type antiferromagnetic state. The compounds with Co$^{3+}$ in collective IS state are characterized by a small electrical resistance and a ferromagnetic exchange coupling.
In octahedron CoO₆, Co³⁺ (HS) is an isotropic ion, however, if the CoO₆ pyramids are articulated along the base, then ferromagnetic bonds appear due to orbital ordering in CoO₅ pyramids [21,22]. This type of connection of the pyramids is believed to be typical for layered perovskites like YBaCo₂³⁺O₅.5, which leads to uncompensated canted magnetic structure due to different types of magnetic interactions competition and large magnetic anisotropy [21]. Ferromagnetic component coincides in magnitude (0.25 μₐ / Co) in both classes of compounds [21-25]. Both types of compounds shows crystal structure phase transition at temperature of magnetic ordering [12,24]. Small substitution of cobalt with iron ions (2-3%) in Sr₀.78Y₀.22CoO₂.65 completely destroys the orbital ordering and concomitant ferromagnetic component [9]. Note that layered perovskites like YBaCo₂³⁺O₅.5 exhibit aniferromagnet-ferromagnet transition too [21-25]. Non collinear magnetic structure have been suggested on the base of neutron diffraction data to explain ferromagnetic coupling between Co³⁺ in pyramids CoO₅ articulated along the base in TbBaCo₂³⁺O₅.5. The ferromagnetic coupling has been deduced from magnetic 4aₚ structure along c crystal axes. Apparently orbital ordering is very sensitive to concurrence of the different types of magnetic interactions and structural order/disorder and chemical composition.

Conclusions
It is shown that the crystal structure of layered cobaltite Sr₀.8Y₀.2CoO₂.65 can be described by the monoclinic space group A2 /m with a superstructure v2aₚ x 2v2aₚ x 4aₚ above the Neel temperature of Tₐ = 375 K and below with a superstructure 4v2aₚ x 2v2aₚ x 4aₚ. Magnetic ordering coincides with a crystal structure phase transition. At Neel point the unit cell is doubled along a axes apparently due to the orbital ordering in the CoO₅ pyramids, located in the anion-deficient layers. The basicmagnetic structure is G type antiferromagnetic with a small ferromagnetic component of near 0.25 μₐ /Co due to the presence of ferromagnetic bonds and orbital ordering in the anion-deficient layers which lead to canted magnetic structure. The stability of the canted magnetic structure is also due to the large magnetic anisotropy. Magnetic moments in the structural layers CoO₄⁺ γ are equal to 2.7μₐ/Co and in the CoO₆ layers are 1.7μₐ/Co. Antiferromagnetic structure of G-type and high Neel point suggest that Co³⁺ ions in both structural layers are in HS/LS states mixture. The antiferromagnet-ferromagnet transition is observed in compounds with x>0.2. It is associated with concurrence of 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.

References


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Figure caption

Fig. 1 Small angle parts of X-ray patterns of Sr$_{0.8}$Y$_{0.2}$CoO$_2$ at 350 and 400 K. Diffraction peaks are indexed in A2/m space group with superstructure $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ (400 K) and with $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ (350 K).

Fig. 2 NPD patterns of Sr$_{0.8}$Y$_{0.2}$CoO$_2$ at 10 and 400 K. Diffraction peaks indexed in A2/m space group are marked with asterisks. The inset shows temperature dependencies of intensity of (112) diffraction peak (I4/mmm).

Fig. 3 Temperature dependencies of Yang’s modulus of Sr$_{1-x}$Y$_x$CoO$_2$ ($x=0.2$ and $0.25$).

Fig. 4 Field dependencies of magnetization of Sr$_{1-x}$Y$_x$CoO$_2$ ($x=0.2$; $0.25$; $0.275$ and $0.35$). For $x=0.25$ compound magnetization vs. field dependencies presented at different temperatures.

Fig. 5 Temperature dependencies of magnetization of Sr$_{1-x}$Y$_x$CoO$_2$ ($x=0.2$; $0.25$; $0.275$ and $0.3$).

Field field dependencies

Table. Crystal and magnetic structure parameters of Sr$_{0.8}$Y$_{0.2}$CoO$_2$ at 10 and 400 K refined in I4/mmm space group.