Magnetic and transport properties of the layered perovskite system
Sr2-yYyCoO4 (0< y < 1)

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Abstract
Layered perovskite cobalt oxides Sr2-yYyCoO4 (y=0, 0.1, 0.3, 0.5, 0.67, 0.83 and 1) were synthesized under high pressure and high temperature conditions.

Keywords
Magnetic, transport, properties, layered, perovskite, system, Sr2, yYyCoO4

Disciplines
Engineering | Physical Sciences and Mathematics

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Layered perovskite cobalt oxides Sr_{2−y}Y_{y}CoO_{4} (y=0, 0.1, 0.3, 0.5, 0.67, 0.83, and 1) were synthesized under high pressure and high temperature conditions. Structure refinement revealed that these compounds crystallize in K_{2}NiF_{4}-type structures with space group I4/mmm. The parent compound Sr_{2}CoO_{4} undergoes a ferromagnetic transition with T_{c}=255 K. The T_{c} decreases with increasing y to 150 K for y=0.5, and ferromagnetism was not observed for y≥0.67. Assessment of spin states for Co^{3+} and Co^{4+} ions suggested strongly that both are present as intermediate spin states when y≤0.67 at least for the higher temperature range above T_{c}. Fairly large negative magnetoresistance was observed for Sr_{2}CoO_{4} in the vicinity of T_{c} and in the lower temperature region.

PACS number(s): 75.30.Cr, 72.80.Ga, 75.47.–m

I. INTRODUCTION

Cobalt oxide perovskite LaCoO_{3} and its divalent substitutions have intrigued many researchers because of their complex electronic and magnetic properties (see Ref. 1). Their rich physical properties are related to the closeness of the crystal field splitting Δ_{e} and the exchange energy (Hund’s rule coupling) Δ_{ex} of Co^{3+} in the octahedral coordination, with a small energy difference between the low-spin (LS) state (t_{2g}^{3}, S=0) and the high-spin (HS) state (t_{2g}^{4}e_{g}^{2}, S=2) or the intermediate-spin (IS) state (t_{2g}^{5}e_{g}^{1}, S=1). At low temperatures, LaCoO_{3} is a nonmagnetic insulator with the LS state of Co^{3+}. Upon heating, its magnetic susceptibility increases and has a broad maximum at ~90 K, then shows a Curie-Weiss type decrease. Some theoretical and experimental studies have proposed that this behavior is caused by a spin state transformation from LS to IS, but the appearance of the IS state is still controversial and remains to be studied.

The Sr doped system of La_{1−x}Sr_{x}CoO_{3} has also been extensively studied and is well known that the hole doping affects the spin state of Co^{3+} in a similar way to temperature (see Ref. 8). Upon the Sr doping, the system changes from nonmagnetic insulator to ferromagnetic metal. For the x=0.5 phase, Goodenough proposed an intermediate-spin model with t_{2g}^{4} localized electrons and σ’ itinerant electrons at a density of 0.5 per Co atom.9 Later, his group proposed a revised model and a detailed temperature-composition (x) phase diagram of the system.8 The hole doped system may become further complicated because Co^{4+} ions can also exist in several spin-state configurations like Co^{3+}.10–12

It is well known that the dimensionality of a system is a key factor governing its electronic structure, and thus, two-dimensional (2D) layered cobalt oxides are quite interesting to compare with the three-dimensional (3D) perovskites. Thus far, various studies have been carried out on K_{2}NiF_{4}-type cobalt oxides,13–20 although the number of reports is relatively small compared with the 3D perovskite system. A K_{2}NiF_{4}-type oxide consists of CoO_{2} planes separated by rock-salt-type planes, and its 2D nature reduces the bandwidth of e_{g} electrons as compared to the 3D network. This seems a key difference between the two systems. Moritomo et al. investigated the K_{2}NiF_{4}-type system of La_{2−x}Sr_{x}CoO_{4} with a mixed valence of Co^{3+} and Co^{4+} and found steep decreases in the effective magnetic moment, Weiss temperature, and electrical resistivity with x increasing beyond ~0.7.16 In accordance with these results, they proposed a spin state transition of the Co^{3+} ion from HS to IS. However, Wang et al. have reported that the IS state never becomes the ground state of LaSrCoO_{4} according to their theoretical studies using the unrestricted Hartree-Fock approximation and the real-space recursion method.19,20

In the present study, we have developed a K_{2}NiF_{4}-type cobalt oxide with only Co^{4+} ions, Sr_{2}CoO_{4}, using a high pressure and high temperature technique. This compound exhibits a ferromagnetic transition with T_{c}=255 K. The spin state of Co^{3+} appears to be the IS state, at least in the higher temperature range above T_{c}. Negative magnetoresistance has been observed at both low temperatures and in the vicinity of T_{c}. Moreover, we carried out partial substitution of Y for Sr, i.e., electron doping, and studied the substitution effects on the structural, magnetic, and transport properties, and the spin states for the Sr_{2−y}Y_{y}CoO_{4} system.

Assessment of the spin state for the Co^{4+} (produced by introduction of Y^{3+} for Sr^{2+}) and Co^{4+} ions suggested strongly that both are present as IS states at least in the higher temperature range.

II. EXPERIMENT

Polycrystalline samples of Sr_{2−y}Y_{y}CoO_{4} (y=0, 0.1, 0.3, 0.5, 0.67, 0.83, and 1) were prepared as follows. Fine and pure powders of SrO_{2}, Co, and Y_{2}O_{3} were well mixed in the atomic ratio Sr:Y:Co=2−y:y:1. Approximately 0.2 g of each mixture was placed in a gold capsule and then compressed at 6 GPa in a high pressure apparatus which was originally developed in our institute. The samples were...
then heated at 1000 °C–1350 °C for 1–3 hours and quenched to room temperature followed by release of pressure. The high-pressure phases in the samples were identified using powder x-ray diffraction. Structure refinements were carried out by the Rietveld method using the Rietica program. Magnetic and magnetotransport properties were investigated using commercial Quantum Design MPMS and PPMS systems between 2 and 330 K in magnetic fields up to 7 T.

III. RESULTS AND DISCUSSION

Figure 1 shows the results of Rietveld refinement of the XRD pattern of Sr$_2$CoO$_4$ measured at room temperature. The pattern could be indexed when based on a tetragonal unit cell similar to that of Sr$_2$TiO$_4$. Close examination of the diffraction profile revealed the presence of a small amount of SrO$_2$ in this sample, which was included in the refinement as a second phase. The initial structural model for the refinement was taken from that of Sr$_2$TiO$_4$. The refined structure of Sr$_2$CoO$_4$ was found to be of the K$_2$NiF$_4$ type with space group I4/mmm. A schematic representation of the structure of Sr$_2$CoO$_4$ is shown in Fig. 2. The weight percentage of the impurity SrO$_2$ in the sample was refined to be 1.2%.

The structure of Sr$_2$CoO$_4$ consists of corner-sharing CoO$_6$ octahedra with 2D CoO$_2$ planes separated by insulating double layers of SrO as shown in Fig. 2. The observed Co-O(1) and Co-O(2) bond lengths of 1.898 Å and 1.994 Å indicate that the octahedron is tetragonally distorted with elongation along the c axis. The Co-O(1) bond length is slightly smaller compared to that of 3D cubic SrCoO$_3$ (a=1.912 Å) which was made under high pressure.

Next, we carried out substitution of Y for Sr under the same high pressure conditions. The Sr$_{2-y}$Y$_y$CoO$_4$ samples were found to be almost single phase but with a trace amount of Y$_2$O$_3$ in a few cases. The XRD patterns of the samples can be indexed based on the K$_2$NiF$_4$ type unit cells whose dimensions are shown in Fig. 3 as a function of y. It can be seen that both a and c decrease gradually with increasing y, except for the y=1 sample whose a-dimension is slightly larger than that of the y=0.83 sample. The decrease in the lattice parameters is in agreement with the fact that the size of the Y$^{3+}$ ion is smaller than that of Sr$^{2+}$. The XRD patterns for Sr$_{1.5}$Y$_{0.5}$CoO$_4$ and Sr$_{y}$YCoO$_4$ (y=0.5, 1) were analyzed by the Rietveld method, and the crystallographic data obtained are shown in Table I where they are compared with those for Sr$_2$CoO$_4$. Refinement results indicated that for y=0.5, the in-plane Co-O(1) bond length (1.876 Å) is slightly shorter compared to that for y=0 (1.898 Å), while the Co-O(2) bond distance along the c axis is longer (2.030 Å) compared to y=0 (1.994 Å). This indicated that the Y$^{3+}$ doping caused, at least up to y =0.5, a contraction of the Co-O bonds with the a/b plane together with elongation along the c axis, yielding more distortion of the CoO$_6$ octahedron compared with the undoped Sr$_2$CoO$_4$. However, further doping to y=1.0 makes the Co-O(2) bond length smaller so that it has nearly the same value as the Co-O(1) length as is shown in Fig. 4.

An anomalous variation is also seen in the c/a ratio in Fig. 3 where the c/a ratio decreases steeply beyond y ~0.5 consistent with the CoO$_6$ octahedron becoming less stretched along the c axis at y=1.0. We propose that these variations in the Co-O bond lengths and the lattice parameters are related to a particular spin state transition of the Co ion.

In Fig. 5, the temperature dependence of the electrical resistivity (ρ) is shown for the Sr$_{2-y}$Y$_y$CoO$_4$ system. Sr$_2$CoO$_4$ shows an almost temperature independent resistivity with a small negative coefficient. ρ at 300 K increases...
with \( y \) from \(-7 \times 10^{-2} \) cm for \( y = 0 \) to \( 2 \times 10^{3} \) cm for \( y = 1 \). Incidentally, the \( y = 0.1 \) sample in Fig. 5 breaks the trend of monotonic increase of resistivity with \( y \). The reason behind this is not clear at the moment.

Semiconducting behaviors are seen in samples with large \( y \) values. The \( \rho - T \) curves do not obey the thermal activation law, \( \rho \sim \exp(-E_a/k_BT) \) where \( E_a \) and \( k_B \) stand for the activation energy and Boltzman constant, respectively. However, high temperature resistivity data could be approximately expressed by the thermal activation law, and the activation energies calculated for the data of \( T > 250 \) K are shown in Fig. 5 as a function of \( y \). The activation energy has an almost constant value of \( 10-20 \) meV for \( y \leq 0.5 \), then steeply increases near \( x = 0.5 \) to reach \( \sim 130 \) meV for \( y = 1.0 \). As will be stated below, this \( y \) value of 0.5 corresponds to the point where ferromagnetism disappears.

The temperature dependence of the field cooled dc magnetization measured at 20 Oe is shown in Fig. 6. \( \text{Sr}_2\text{CoO}_4 \) reveals a ferromagnetic transition with \( T_c = 255 \) K, and \( T_c \) gradually decreases to 150 K for \( y = 0.5 \). Ferromagnetism disappears for \( y = 0.67 \). The field cooled magnetization was also measured at a high field of 2 kOe to obtain the inverse molar susceptibility, \( \chi^{-1} \), which is plotted against temperature in Fig. 7 for \( y = 0.67 \). The \( \chi^{-1} \) data above 250 K can be well fitted to the Curie-Weiss law; the Weiss temperature \( \Theta \) and effective number of Bohr magnetons per Co ion \( p_{\text{eff}}(\mu_B) \) are shown in Fig. 8. It can be seen that \( \Theta \) decreases from 260 K for \( y = 0 \) to \(-27.3 \) K for \( y = 0.67 \), suggesting that the interaction between the magnetic moments

### Table I. Crystal data of \( \text{Sr}_{2-w}Y_w\text{CoO}_4 \) (\( w = 0,0.5,1 \)).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wykoff site</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( B_{\text{iso}} )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>0</td>
<td>0.41</td>
</tr>
<tr>
<td>Sr/Y</td>
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<td>0</td>
<td>0.3564</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>0.30</td>
</tr>
<tr>
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<td>0.5</td>
<td>0</td>
<td>1.15</td>
</tr>
<tr>
<td>O (2)</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.1592</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1646</td>
<td>1.11</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>0.1628</td>
<td>0.83</td>
</tr>
</tbody>
</table>

\( B_{\text{iso}} \) is an isotropic thermal parameter. Data on the first, second, and last lines are for the \( w = 0,0.5,1 \) samples, respectively.

**FIG. 3.** Variations of lattice parameters of \( \text{Sr}_{2-w}Y_w\text{CoO}_4 \).

**FIG. 4.** Yttrium content \( y \) dependences of the Co—O(1) and Co—O(2) bond lengths.

**TABLE I. Crystal data of \( \text{Sr}_{2-w}Y_w\text{CoO}_4 \) (\( w = 0,0.5,1 \)).**

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<th>( B_{\text{iso}} )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>0</td>
<td>0.41</td>
</tr>
<tr>
<td>Sr/Y</td>
<td>4e</td>
<td>0</td>
<td>0</td>
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<td>0.3563</td>
<td>0.30</td>
</tr>
<tr>
<td>O (1)</td>
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<td>0</td>
<td>1.15</td>
</tr>
<tr>
<td>O (2)</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.1592</td>
<td>1.29</td>
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<td>0.83</td>
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</table>

\( B_{\text{iso}} \) is an isotropic thermal parameter. Data on the first, second, and last lines are for the \( w = 0,0.5,1 \) samples, respectively.
changes from ferromagnetic to antiferromagnetic as \( y \) increases. \( p_{\text{eff}} \) is gradually reduced from 3.72 for \( y = 0 \) to 3.01 for \( y = 0.67 \).

As stated above, we observed semiconducting resistivities for the present system in the phases with large \( y \) values. Thus, a localized electron model may be a good starting point. In Fig. 9, the LS, IS, and HS states are schematically shown for the \( d^8 \) (Co\(^{3+}\)) and \( d^9 \) (Co\(^{4+}\)) configurations in a tetrahedral crystal field. This diagram based on the ionic model suggests that the spin state of Co\(^{4+}\) in Sr\(_2\)CoO\(_4\) is the IS state because the value of \( p_{\text{eff}} \) observed (3.72) coincides with that expected for the spin only moment of the IS state Co\(^{3+}\) (3.87) whereas a very different value of 1.73 (5.92) is expected for the LS (HS) state. The \( p_{\text{eff}} \) decreases almost linearly with \( y \), or rather with the Co\(^{3+}\) substitution for Co\(^{4+}\), until \( y = 0.67 \) (Fig. 8). This linear variation suggests that no spin state transitions occur for either the Co\(^{3+}\) or the Co\(^{4+}\) ions for \( 0 \leq y \leq 0.67 \). Thus, we assumed the IS state of Co\(^{4+}\) for the entire range of \( y \) and calculated \( p_{\text{eff}} \) for combinations with the LS, IS, and HS states of Co\(^{3+}\). As shown in Fig. 9, the combination of IS-Co\(^{4+}\) and IS-Co\(^{3+}\) accounts very well for the observed values of \( p_{\text{eff}} \) up to \( y = 0.67 \). The intermediate spin states for both Co\(^{4+}\) and Co\(^{3+}\) have also been reported for the 3D perovskite of La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\).\(^{12}\)

As shown in Fig. 7, the susceptibility data for \( y = 0.83 \) or 1.0 do not obey the Curie-Weiss equation. Both sets of \( \chi^{-1} \) data describe curved lines for the entire range of temperature without any ranges of linearity. An approximate linear fitting for the data in the higher temperature region gives \( p_{\text{eff}} = 3.51 \) and 3.83, in \( y = 0.83 \) and 1.0, respectively (see right inset of Fig. 7b). On the other hand, fitting for the low-temperature data gives \( p_{\text{eff}} = 2.02 \) and 1.50 in \( y = 0.83 \) and 1.0, respectively (see a inset of Fig. 7b).

Although these \( p_{\text{eff}} \) values are the results of very rough estimation, it seems that \( p_{\text{eff}} \) increases continuously with increasing temperature from \( \sim 2.0/\sim 1.5 \) below around 30 K to \( \sim 3.5/\sim 3.8 \) at around 300 K in \( y = 0.83 \) (1.0). It has been reported that for the La\(_{3-x}\)Sr\(_x\)CoO\(_4\) system (\( 0.4 < x < 1.0 \)), the spin state transition from HS to IS occurs in Co\(^{3+}\) as \( x \) increases beyond \( x \sim 0.7 \). The high temperature \( p_{\text{eff}} \) values for \( y = 0.83 \) and 1.0 suggest that the HS state is mixed with the IS state in Co\(^{3+}\) and that the HS state becomes more dominant with increasing temperature and increasing \( y \). On the other hand, \( p_{\text{eff}} \) estimated from the low-temperature data suggests mixing of the LS state of Co\(^{3+}\) with a higher ratio for lower temperature. These results suggest complicated spin states of Co\(^{3+}\) ions for the \( y = 0.83 \) and 1.0 phases where the LS, IS, and HS states seem to be mixed depending on temperature and \( y \). Here it is worth recalling that in Figs. 3 and 4, tetrahedral distortion of the CoO\(_6\) octahedron is less pronounced for the high \( y \) range. Since IS state Co\(^{3+}\) has the largest Jahn-Teller stabilization energy, mixing of the HS and LS states of Co\(^{3+}\) would work to diminish the Jahn-Teller distortion, consistent with the tendencies in Figs. 3 and 4.

The 3D perovskite of La\(_{1-x}\)Sr\(_x\)CoO\(_3\) is a good reference system for the present one. Substitution of Sr for La in
LaCoO$_3$ brings about remarkable changes; a semiconductor-to-metal transition is induced at $x = 0.125–0.3$ and a nonmagnetic-to-ferromagnetic transition appears at $x = 0.05–0.15$ with rather wide dispersion from report to report. Thus, the $x = 0.5$ phase, La$_{0.5}$Sr$_{0.5}$CoO$_3$, is a good conductor with $\rho = 10^{-4}$ cm and a ferromagnet with a saturation moment of $1.5$ B/Co atom. Goodenough and his colleagues qualitatively explained the ferromagnetism of La$_{1-x}$Sr$_x$CoO$_3$ based on Zener’s double exchange; their model consists of localized $t_{2g}$ configurations for each Co ion and an itinerant $\sigma^*$ band which contains $1-x$ electrons per Co atom. Ferromagnetic coupling is expected between the itinerant and localized electrons, resulting in the ferromagnetic order of the localized electrons and polarization of the itinerant electrons. If we consider a pure ionic model for this situation, the system consists of the IS state of Co$^{3+}$ and the HS state of Co$^{4+}$ with a ferromagnetic coupling between them.

Compared with the 3D system, $e_g$ electrons of the present 2D system are expected to behave differently. In the 3D system, the $\sigma^*$ band is formed from hybridization of Co-3$d_{z^2}$ and O-2$p$ orbitals along the $c$ axis as well as from Co-3$d_{x^2-y^2}$ and O-2$p$ orbitals along the $ab$ plane. In the layered structure, on the other hand, the $\sigma^*$ band would be composed mainly of the $3d_{x^2-y^2}$ and O-2$p$ orbitals with a less significant contribution of the $3d_{z^2}$ orbitals due to the 2D confinement of the Co-O-Co network. Because of the tetragonal symmetry of the CoO$_6$ octahedron, both $t_2g$ and $e_g$ states are split into two levels as shown in Fig. 9. If electrons in orbitals other than $3d_{x^2-y^2}$ tend to be localized, we expect a semiconducting nature for the system with the IS or LS states of Co$^{3+}$ and Co$^{4+}$. This picture may explain the lower electrical conductivity of the present system compared with the 3D perovskite system.

Magnetization and magnetic field loops at 5 K for Sr$_{2-y}$Y$_y$CoO$_4$ are shown in Fig. 10. The magnetization increases linearly with magnetic field in the high field range for all $y$ values, i.e., the magnetization under high magnetic field can be expressed as $M = M_s + \chi_H H$ where $M_s$ and $\chi_H$ stand for the saturation magnetization and the high field susceptibility, respectively. In Sr$_2$CoO$_4$, magnetization at 50 kOe is $\sim 1.5 \mu_B$/Co atom and $M_s$ at 5 K is estimated to be $\sim 1.0 \mu_B$/Co atom, which is only 1/3 of the value of $3 \mu_B$ estimated for the saturation moment at 0 K for the IS state of Co$^{4+}$ from the ionic model or 1/2.85 of the saturation moment corresponding to the observed $p_{eff}$ of 3.72. As shown in Fig. 10, $M_s$ decreases with increasing $y$ to 0.75 $\mu_B$/Co atom for $y = 0.5$. The Rhodes-Wohlfarth relationship is well known to be valid for itinerant ferromagnets with Curie-Weiss behavior above $T_c$. This relationship...
was first given empirically, then explained theoretically based on self-consistently renormalized (SCR) spin fluctuation theory. The Rhodes-Wohlfarth ratio of \( p_c/p_s \) obeys a universal function of \( T_c \) where \( p_c \) and \( p_s \), respectively, stand for the high temperature magnetic moment corresponding to \( p_{\text{eff}} \) and the saturation magnetic moment at 0 K in units of the Bohr magneton. From a Rhodes-Wohlfarth plot using the present ferromagnetic transition temperature of \( \text{Sr}_2\text{CoO}_4 (T_c = 255 \text{ K}) \), \( p_c/p_s \) was determined to be \( \sim 2.1 \). This value is comparable with \( \sim 3 \) or \( \sim 2.85 \) of the present experimental result. This result together with the linear increase of the magnetization in the high field range might suggest itinerant electron ferromagnetism for the present system.

Inconsistent with the itinerant electron picture, the magnetic susceptibility data of the higher temperature region can be well understood assuming localized electrons with the IS states of Co\(^{4+}\) and Co\(^{3+}\) for the phases with \( y \approx 0.67 \). Moriya et al. proposed, based on the SCR theory for itinerant electron magnets, that local spin fluctuation increases with temperature until it reaches an upper limit determined by the charge neutrality condition. However, it is not clear that such a situation of temperature induced local magnetic moment is realized in the present system because its electrical resistivity is relatively high and shows semiconducting behavior even for \( y \approx 0.5 \). The ferromagnetism of the system may be explained on the basis of a localized electron picture. For instance, the saturation magnetization within the low temperature region, which is much smaller than that expected from \( p_{\text{eff}} \) in the higher temperature region may be caused by a certain temperature dependent combination of the HS and LS states. Thus, we need further studies to reach a conclusion on the origin of the ferromagnetism.

The very large coercive field of 25 kOe for \( \text{Sr}_2\text{CoO}_4 \) should be noted (Fig. 10); it implies a large anisotropy energy. The coercive field decreases with increasing \( y \) but is still large enough to be 2 kOe for \( y = 0.5 \). In initial stages of the magnetization curve just after zero-field cooling to 5 K for \( \text{Sr}_2\text{CoO}_4 \) (see Fig. 10), magnetization increases stepwise as a function of magnetic field with a first steep increase, a plateau and then a second gradual increase. This phenomenon may also reflect the large anisotropy energy.

The temperature dependences of the resistivity for \( \text{Sr}_2\text{CoO}_4 \) under 0 and 50 kOe are compared in Fig. 11. There is a kink at 255 K in the zero field \( p-T \) curve of \( \text{Sr}_2\text{CoO}_4 \) as revealed in the inset of Fig. 11. This kink corresponds to the ferromagnetic transition at \( T_c = 255 \text{ K} \) and is caused by a less pronounced increase of resistivity below \( T_c \). In the field of 50 kOe, resistance decreases, and the kink seen at 255 K disappears completely. The magnetoresistance MR is defined as \( \Delta \rho/\rho_0 = (\rho_{\text{MR}} - \rho_0)/\rho_0 \) where \( \rho_0 \) and \( \rho_{\text{MR}} \) stand for the resistivities under no magnetic field and magnetic field, respectively. The temperature variation of MR is shown in Fig. 11. It can be seen that \( \Delta \rho/\rho_0 \) is negative for the entire range of temperatures (negative magnetoresistance) and shows a sharp peak in the vicinity of the ferromagnetic transition at 255 K followed by a gradual increase with decreasing temperature. This behavior is quite similar to that observed in the 3D Co perovskite \( \text{La}_{0.3}\text{Ba}_{0.7}\text{CoO}_3 \).

The peak in \( \Delta \rho/\rho_0 \) near the ferromagnetic transition temperature is explained by the intrinsic mechanism of magnetoresistance, the ferromagnetic order is enhanced by the application of an external magnetic field, and it causes a decrease in the electrical resistivity. On the other hand, when the temperature decreases, field-hysteretic magnetoresistance corresponding to the magnetic hysteresis loop appears and becomes much more pronounced at 5 K as shown in Fig. 10. It can be seen that the maximum field-hysteretic \( \Delta \rho/\rho_0 \) occurs at a field of about 2.5 T, in coincidence with the coercive field of the magnetization process. Such a close correlation between the magnetoresistance and the magnetic domain rotation observed for our \( \text{Sr}_2\text{CoO}_4 \) sample can be well explained in terms of tunneling magnetoresistance at grain boundaries, a phenomenon that has been well established for granular manganites and other magnetoresistive oxides. Under the application of a magnetic field, the hopping of spin-polarized electrons between grains is predominantly affected by the relative angle between the magnetic moments of the grains and is controlled by the external field through the domain-rotation process. Therefore, the observed field-hysteretic magnetoresistance is ascribed to field suppression of the spin-dependent scattering at grain (or domain) boundaries.

**IV. CONCLUSION**

Layered perovskite cobalt oxides \( \text{Sr}_{2-x}\text{Y}_x\text{CoO}_4 \) \((y = 0, 0.1, 0.3, 0.5, 0.67, 0.83, \text{ and } 1) \) were synthesized under high pressure and high temperature conditions. Structure refinement revealed that these compounds crystallize in \( \text{K}_2\text{NiF}_4 \)-type structures with space group \( \text{I}4/\text{mmm} \). The parent compound \( \text{Sr}_2\text{CoO}_4 \) undergoes a ferromagnetic transition with \( T_c = 255 \text{ K} \). The \( T_c \) decreases with increasing \( y \) to 150 K for \( y = 0.5 \), and ferromagnetism was not observed for \( y > 0.67 \). Magnetic susceptibilities above \( T_c \) of the samples with \( y = 0.67 \) can be well fitted by the Curie-Weiss law and the effective number of Bohr magnetons, \( p_{\text{eff}} \), determined from the Curie-Weiss constants, suggesting intermediate spin states for both the Co\(^{3+}\) and Co\(^{4+}\) ions. On the other hand, low
temperature magnetization data suggest itinerant electron ferromagnetism. Fairly large negative magnetoresistance was observed for Sr$_2$CoO$_4$ near the ferromagnetic transition temperature of 255 K and in the lower temperature region. The magnetoresistance near $T_c$ is explained by the intrinsic mechanism while that at lower temperatures is ascribed to the field suppression of the spin-dependent scattering at grain (or domain) boundaries.

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