Metallic Ferromagnet with Square-Lattice CoO_2 Sheets

J. Matsuno,[1,*] Y. Okimoto,[1] Z. Fang,[2,3] X. Z. Yu,[2] Y. Matsui,[4] N. Nagaosa,[1,5] M. Kawasaki,[1,6] and Y. Tokura[1,2,5]

[1]*Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8562, Japan*
[2]*Spin SuperStructure Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Corporation, c/o AIST, Tsukuba Central 4, Tsukuba 305-8562, Japan*
[3]*Institute of Physics, Chinese Academy of Science, Beijing 100080, China*
[4]*Advanced Materials Laboratory, National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan*
[5]*Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*
[6]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

(Received 28 February 2004; published 13 October 2004)

A single-crystalline film of Sr_2CoO_4 with square-lattice CoO_2 sheets (K_2NiF_4-type structure) was synthesized, and its electronic properties were characterized. The compound exhibited both ferromagnetic and metallic behaviors, with a fairly high Curie temperature T_C of $\sim$250 K, in contrast to the superconductivity recently found in a triangular-lattice CoO_2-sheet compound. The film's large magnetoresistance with current perpendicular to the CoO_2 plane showed field-hysteretic behavior analogous to tunneling magnetoresistance. The electronic structure of Sr_2CoO_4 was also investigated to characterize the quasi-two-dimensional ferromagnetic metal state in terms of optical spectroscopy and first-principles calculation.

DOI: 10.1103/PhysRevLett.93.167202 PACS numbers: 75.70.–i, 71.20.–b, 75.47.–m, 78.20.–e

Since the discovery of high-temperature superconductors, most of the extensive studies of strongly correlated electronic systems have been devoted to superconductivity and magnetism. For example, the role of frustration and the spin-singlet formation, i.e., the resonating valence bond state [1,2], have been discussed for many years. In this context, the recent discovery of superconductivity in Co oxides with two-dimensional triangular-lattice CoO_2 sheets [3] has aroused much interest, since this superconductivity appears in a magnetically frustrated system with low dimensionality, similar to high-temperature cuprate superconductors. Therefore, it is essential to study Co oxides with different two-dimensional structures. In this Letter, we report a novel compound, Sr_2CoO_4 (SCO), which has an identical crystal structure (a K_2NiF_4-type structure) to superconducting Cu oxides of the form $La_{2-x}Sr_xCuO_4$. Compounds with the K_2NiF_4-type structure are well known to exhibit various intriguing physical phenomena, such as high-temperature superconductivity in cuprates, spin-triplet superconductivity in ruthenates [4], and spin/charge stripes in nickelates and manganites [5]. We have succeeded in fabricating a single-crystalline thin film of Sr_2CoO_4, which has never before been synthesized even in a form of bulk polycrystal, by employing the pulsed-laser deposition (PLD) method. We have found both ferromagnetic and metallic behaviors, with a fairly high Curie temperature T_C of $\sim$250 K, rather than superconductivity. Hence, Sr_2CoO_4 may be regarded as a quasi-two-dimensional metallic ferromagnet, which has never been observed in the K_2NiF_4-type family. A previous study of single crystals of $La_{2-x}Sr_xCoO_4$ ($0.0 \le x \le 1.0$) found neither metallic nor ferromagnetic behavior [6], while three-dimensional $La_{1-x}Sr_xCoO_3$ ($0.18 \le x \le 0.5$) is a well-known ferromagnetic metal [7,8].

By applying PLD with a KrF excimer laser ($\lambda = 248$ nm), a-axis-oriented epitaxial thin films of Sr_2CoO_4 with a thickness of 40 nm were grown. Targets with a nominal composition of Sr_2CoO_4 were prepared by a conventional solid-state reaction from stoichiometric mixtures of $SrCO_3$ and Co_3O_4. The films were epitaxially grown on $LaSrAlO_4(100)$ [(LSAO), $a = b = 0.3755$ nm and $c = 1.263$ nm] substrates with a K_2NiF_4 structure. For these LSAO (100) substrates, there are two film-plane lattice constants, namely, a and c. We denote the film-plane a axis as the b axis in order to distinguish it from the a-axis normal to the film plane [see Fig. 1(d)]. The typical growth temperature was around 700–750 °C, and the oxygen pressure was $\sim$3 Pa. The resistivity was measured by a standard four-probe method. For measurements of anisotropy, we cut the films into thin pieces and evaporated silver electrodes so as to limit the current direction to the respective film-plane axes, namely, the b axis and the c axis. Optical measurements were performed at 7 K with a Fourier transform interferometer and a grating monochromator equipped with a microscope to cover the photon energy region of 0.2–4.1 eV, in which the LSAO substrate is transparent. Optical conductivity spectra $\sigma(\omega)$ were obtained from the reflectance $R(\omega)$ and transmittance spectra $T(\omega)$.

Figure 1(a) shows a transmission electron microscope (TEM) image of a $Sr_2CoO_4(100)$ thin film grown on a $LaSrAlO_4(100)$ substrate. The CoO_2 layers in the grown

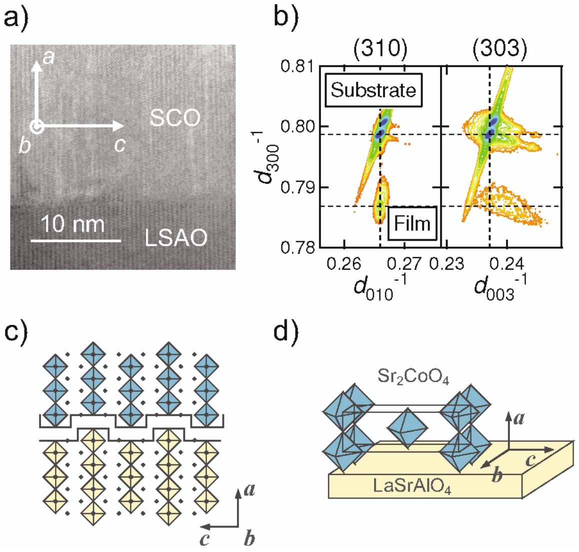

FIG. 1 (color). (a) Cross-sectional transmission electron micrograph of the interface between $Sr_2CoO_4(100)$ and $LaSrAlO_4(100)$, observed along the (010) direction. (b) Reciprocal-space mapping of the (310) (left panel) and (303) (right panel) x-ray diffraction (XRD) peaks for an SCO film grown on an LSAO (100) substrate. (c) Schematic of atomic-scale graphoepitaxy. (d) Definitions of each axis.

film are aligned perpendicular to the substrate surface, without any trace of c-axis-oriented growth. This can be also confirmed by the reciprocal-space mapping of the XRD for an SCO film, as shown in Fig. 1(b). The mapping data indicate that the film grew epitaxially with a film-plane orientation such as $\mathbf{b}_{\mathrm{SCO}} \parallel \mathbf{b}_{\mathrm{LSAO}}$ and $\mathbf{c}_{\mathrm{SCO}} \parallel \mathbf{c}_{\mathrm{LSAO}}$. The data also indicate that the c-axis lattice constant almost matched that of the substrate ($c_{\mathrm{SCO}} = c_{\mathrm{LSAO}}$). These results support the idea that the film growth was enabled by "atomic-scale graphoepitaxy" [9], as shown schematically in Fig. 1(c). We expect that, as indicated by the thick lines, atomic-scale trenches constructed by AlO_6 octahedra run in plane along the b-axis direction. Then, the interface would have a tendency to be commensurate with such atomic grooves, promoting epitaxy with respect to the c-axis direction. On the other hand, the b-axis lattice constant was identical to that of the substrate. This lattice clamping along the b axis may have also contributed to the epitaxial growth. Thus, the PLD method employing atomic graphoepitaxy enables us to synthesize single-crystalline Sr_2CoO_4 films, even though the compound itself has never been synthesized.

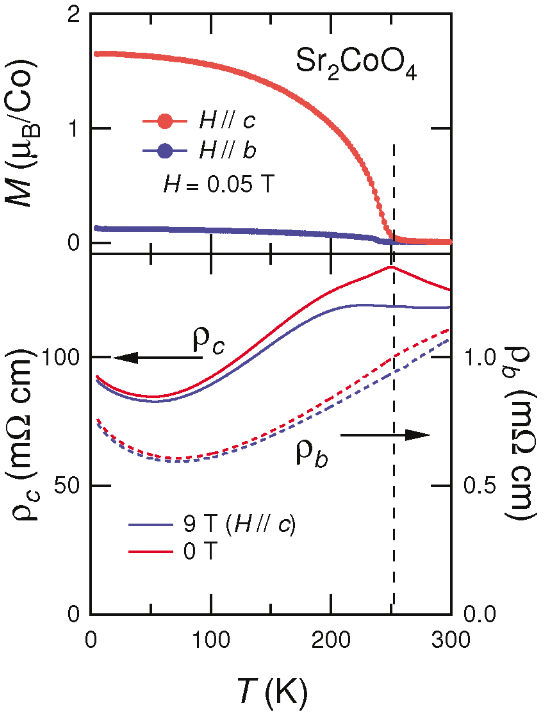

FIG. 2 (color). Temperature dependence of the magnetization M (upper panel) and in-plane resistivity ρ_b and interplane resistivity ρ_c (lower panel) for Sr_2CoO_4 thin films. The magnetization was measured with the magnetic field directions $H \parallel b$ and $H \parallel c$, where both the b and c axes are within the film plane. Thus, the observed magnetic anisotropy was not affected by geometrical factors.

Magnetization measurements revealed a ferromagnetic transition around $T_C \simeq 250$ K, as shown in Fig. 2. In addition, we found large magnetic anisotropy where the magnetic easy axis was the c axis. The temperature dependence of the inter-CoO_2-plane resistivity ρ_c shows a sharp maximum at $T_C = 250$ K, with a semiconducting T dependence above T_C and metallic behavior below T_C. In contrast, the resistivity ρ_b within the CoO_2 plane shows metallic characteristics even above T_C [10]. The metallic behavior below T_C for both ρ_c and ρ_b is thus dominated by ferromagnetic spin ordering. The anisotropy, defined as ρ_c/ρ_b, ranges from 120–150 over the whole temperature region that was investigated, revealing the quasi-two-dimensional electronic nature of Sr_2CoO_4. Among the quasi-two-dimensional oxides, very few have been known to show both ferromagnetic and metallic behaviors. The highest Curie temperature reported so far is ~130 K for a bilayered manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.4$) [11], while no ferromagnetism has been observed in single-layered (K_2NiF_4-type structure) manganite $La_{1-x}Sr_{1+x}MnO_4$ [12]. Our results indicate that this newly synthesized Sr_2CoO_4 may be regarded as a quasi-two-dimensional ferromagnetic metal, which has never been found among the K_2NiF_4-type (single-layered) compounds.

Large magnetic anisotropy is also clearly seen in the magnetization curves shown in Fig. 3. For $H \parallel c$, we can observe magnetic hysteresis with a rather large coercive force $\mu_0 H_C$ of ~2.2 T, whereas no hysteresis is observed for $H \parallel b$. For the Co-oxide perovskites, the possibility of various spin configurations has long been discussed [5]: $LaCoO_3$(Co^{3+}, d^6) is known to show a gradual crossover from a high-temperature intermediate-spin state to a low-

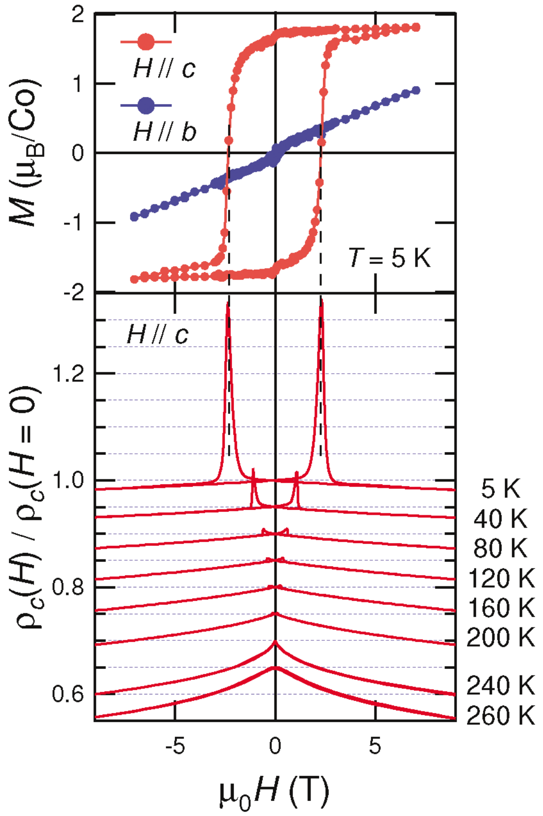

FIG. 3 (color). Field dependence of the magnetization M (upper panel) and the interplane resistivity ρ_c (lower panel) for Sr_2CoO_4 thin films. The resistivity is normalized by the value without the magnetic field.

temperature low-spin state [13]. In the present case of $Sr_2CoO_4(Co^{4+}, d^5)$, there are three possible spin states, namely, low spin (t_{2g}^5), intermediate spin ($t_{2g}^4 e_g^1$), and high spin ($t_{2g}^3 e_g^2$). The observed saturated moment of the $1.8\mu_B$/Co site is close to what would be expected for the intermediate-spin configuration in accordance with the case of $SrCoO_3(Co^{4+})$ [14]. In the lower panel of Fig. 3, we show the isothermal magnetoresistance (MR) along the c axis at various temperatures. Basically, negative MR is observed, as shown in the lower panel of Fig. 2; the magnitude of the MR reaches its maximum around T_C. At lower temperatures, however, it shows an anomalous increase up to 30% at H_C. Across H_C, the magnetic domain flips over, and hence, there should be a maximum number of magnetic domain boundaries at H_C. The observed anomaly in $\rho_c(H = H_C)$ can be regarded as the interdomain tunneling resistance, suggesting that some of the magnetic domain boundaries intervene between the ferromagnetic CoO_2 layers as being perpendicular to the c axis. This situation contrasts with the *negative* interplane magnetoresistance observed in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.30$) [15], where the anomaly is derived from interlayer tunneling between the weakly antiferromagnetically coupled MnO_2 bilayers.

To gain insight into the electronic structure of ferromagnetic Sr_2CoO_4, we performed a first-principles band-structure calculation. The plane-wave pseudopotential calculations were done based on the density functional theory with local spin density approximation (LSDA) for the exchange-correlation potential [16]. The ferromagnetic solution is much lower in energy than the nonmagnetic solution, by about 296 meV/cell. The calculated density of states (DOS), shown in Fig. 4(a), clearly indicate that both the majority spin e_g states and the minority spin t_{2g} states are partially occupied around the Fermi level, suggesting nonfull spin polarization of the conduction electrons. This stands in contrast to the full spin polarization, i.e., half metallicity, postulated for $La_{1-x}Sr_xMnO_3$ [17] and Sr_2FeMoO_6 [18]. The partial filling in the t_{2g} manifold (in particular, in the d_{yz} and d_{zx} states) can render the compound active in spin-orbit interaction, which is consistent with the fairly strong

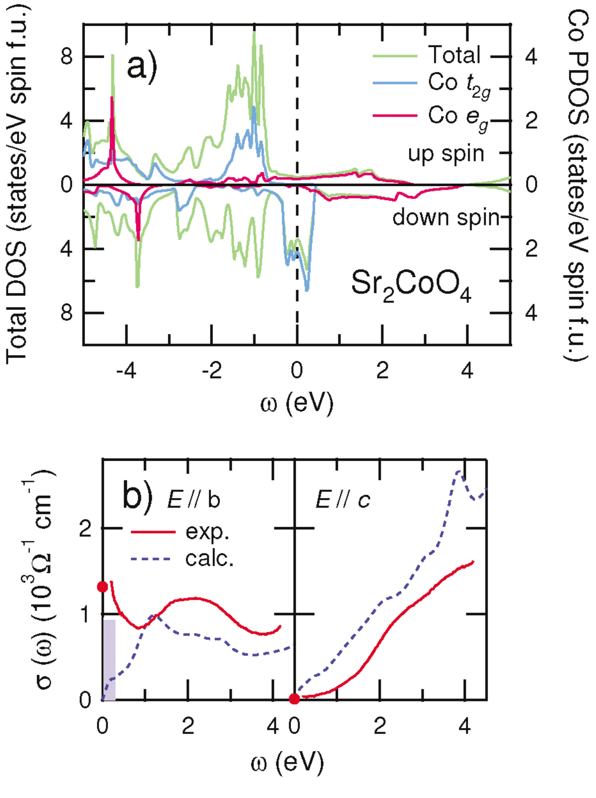

FIG. 4 (color). (a) Calculated density of states for ferromagnetic Sr_2CoO_4. The projected densities of states (PDOS) for Co t_{2g} and e_g are also shown. (b) Optical conductivity spectra $\sigma(\omega)$ for a Sr_2CoO_4 thin film with light polarizations $E \parallel b$ (left panel) and $E \parallel c$ (right panel). Values of dc conductivity calculated from Fig. 2 (lower panel) are also shown by red circles at 0 eV for both polarizations. The spectra calculated by the Kubo formula are denoted by dotted lines for both polarizations. For the case of $E \parallel b$, the shaded rectangle at 0 eV schematically indicates the intraband contribution (the Drude component), which was not included in the calculated spectra.

magnetic anisotropy that we observed. The calculated total spin moment is $1.97\mu_B$/cell, with $0.20\mu_B$/oxygen coming from in-plane oxygen and $0.11\mu_B$/oxygen from apical oxygen. This value is close to the experimentally obtained value of $1.8\mu_B$, which is consistent again with the picture of the intermediate spin state. The electronic structure was also clarified by obtaining optical conductivity spectra, as shown in Fig. 4(b). The highly anisotropic nature of the electronic state in this compound was confirmed: we observed a metallic response for the polarization $E \parallel b$, while a nominally insulating (gapped) feature appeared for $E \parallel c$. We also note that dc conductivity obtained from the resistivity in Fig. 4(b) is consistent rather well with the optical conductivity for both polarizations. The anisotropy is well reproduced by the LSDA calculation, as denoted by the dotted lines in Fig. 4(b). (Although the discrepancy between the experimental and theoretical results in the low-energy region of $\sigma(\omega)$ for $E \parallel b$ appears large, it is due to the Drude components, which is not shown in the theoretical curve.) The broad structure around 2 eV observed for $E \parallel b$ was attributed to the charge-transfer transition from the O $2p$ to the Co t_{2g} states among the down-spin electron bands. The agreement between the experimental and calculated spectra verifies that the electronic structure can be essentially described within the framework of the present LSDA calculation.

In conclusion, we have succeeded in synthesizing Sr_2CoO_4 in the form of a single-crystalline thin film with square-lattice CoO_2 sheets (K_2NiF_4-type structure). The new compound was found to be a metallic ferromagnet, with appreciable magnetic anisotropy and quasi-two-dimensional transport properties. We have thus demonstrated that the CoO_2 layers can act as a stage for two-dimensional ferromagnetism as well as superconductivity. The fairly high T_C (250 K) of Sr_2CoO_4 may provide intriguing opportunities to explore the spintronic functionality of CoO_2 layers.

---

*Electronic address: j-matsuno@aist.go.jp

[1] L. Pauling, Proc. R. Soc. London A **196**, 343 (1949).

[2] P.W. Anderson, Science **235**, 1196 (1987).

[3] K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature (London) **422**, 53 (2003).

[4] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994).

[5] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).

[6] T. Matsuura, J. Tabuchi, J. Mizusaki, S. Yamauchi, and K. Fueki, J. Phys. Chem. Solids **49**, 1403 (1988).

[7] P. M. Raccah and J. B. Goodenough, J. Appl. Phys. **39**, 1209 (1968).

[8] G. H. Jonker and J. H. Van Santen, Physica (Amsterdam) **19C**, 120 (1953).

[9] S. Miyazawa and M. Mukaida, Appl. Phys. Lett. **64**, 2160 (1994).

[10] We note that the ρ_b shows a slight upturn below 50 K. The conductivity σ_b ($\equiv 1/\rho_b$) below 20 K obeys $T^{1/2}$ dependence, indicating the weak localization effect. The $\sigma_b(T \rightarrow 0)$ is, however, well above $1 \times 10^3\ \Omega^{-1}\,\mathrm{cm}^{-1}$, suggesting the metallic ground state.

[11] Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, Nature (London) **380**, 141 (1996).

[12] Y. Moritomo, Y. Tomioka, A. Asamitsu, Y. Tokura, and Y. Matsui, Phys. Rev. B **51**, 3297 (1995).

[13] S. Yamaguchi, Y. Okimoto, and Y. Tokura, Phys. Rev. B **55**, R8666 (1997).

[14] R. H. Potze, G. A. Sawatzky, and M. Abbate, Phys. Rev. B **51**, 11 501 (1995).

[15] T. Kimura, Y. Tomioka, H. Kuwahara, A. Asamitsu, M. Tamura, and Y. Tokura, Science **274**, 1698 (1996).

[16] The crystal structure of thin film is slightly orthorhombically distorted (i.e., a is different from b); however, as the first approximation, we assume that the crystal has the tetragonal symmetry of the K_2NiF_4 structure and fix the lattice parameters to be $a = b = 0.3755$ nm and $c = 1.26$ nm. Then the internal coordinates of apical oxygen and Sr atoms are optimized self-consistently, which gives 0.157 78 and 0.145 62 for the relative c-axis positions of O and Sr in the ferromagnetic solutions.

[17] J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Nature (London) **392**, 794 (1998).

[18] K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, Nature (London) **395**, 677 (1998).