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Uniaxial colossal magnetoresistance in the Ising magnet $SrCo_{12}O_{19}$

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A new type of colossal magnetoresistance, which is extremely sensitive to the magnetic-field direction, was discovered in a magnetoplumbite-type hexagonal cobalt oxide $SrCo_{12}O_{19}$ synthesized under a high pressure of 3 GPa. $SrCo_{12}O_{19}$ has a unique combination of physical properties (i.e., uniaxial magnetic anisotropy originating from Ising spins on $Co^{3+}O_5$ bipyramids and a metal-insulator transition taking place on a three-dimensional network of $Co^{3+/4+}O_6$ octahedra). The resistivity decreases by a factor of 1000 when a magnetic field of 10 T is applied along the hexagonal axis (magnetic easy axis) in the insulating phase, whereas it is rather robust against the field perpendicular to this axis. These results demonstrate a metal-insulator crossover dominated by the orientation order of built-in Co^{3+} Ising spins embedded in the conductive $Co^{3+/4+}$-O matrix lattice.

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Magnetoresistance, a change in resistance in response to external magnetic field H, has been of prime importance in the field of solid state science as well as electrical engineering. In the late 1980s a giant magnetoresistance in Fe/Cr multilayer films was discovered, which has been developed to be utilized in the form of magnetic head of hard disk drives.[1,2] Some bulk materials, such as perovskite manganites,[3–6] EuO (Ref. 7), and λ-$(BETS)_2FeCl_4$ (Refs. 8,9), are known to show a much larger change near their metal-insulator transition temperatures, hence they are termed colossal magnetoresistance (CMR) effects. While this effect has been studied in several systems, all of them are phenomenologically similar (i.e., resistivity decreases drastically by the application of H in any direction).

On the other hand, materials, in which spins are either up or down, can be regarded as Ising magnets. They are important from practical viewpoints as exemplified by Co-based alloys and FePt suitable for ultrahigh-density perpendicular magnetic recording because of the strong uniaxial magnetic anisotropy, which allows high thermal stability of small magnetic domains.[10] One of the most commonly used magnets, a magnetoplumbite-type ferrite $(Sr,Ba)Fe_{12}O_{19}$ is also an Ising magnet and a candidate for high-density perpendicular magnetic recording.[11,12] A new cobalt oxide $SrCo_{12}O_{19}$ crystallizing in the same structure to be reported here is a special Ising system featured by quite a unique type of coupling to electrical conductivity. $SrCo_{12}O_{19}$ consists of the alternate stacking of the $SrCo_6O_{11}$-type (R) block and the spinel-type (S) block (see the inset of Fig. 1) which have the Co(1)-O Kagomé lattice in common.[13] The R block bears the Ising-type magnetism, while the electrical conductivity has its paths involving both the R and S blocks. The performance of the three-dimensional (3D) conductive lattice being controllable by the application of H directed along the c axis only, we named this effect "uniaxial colossal magnetoresistance."

Single crystals of $SrCo_{12}O_{19}$ with hexagonal morphology (0.4 × 0.4 × 0.2 mm in dimension, typically) were grown under high pressure (HP) using a conventional cubic anvil-type high-pressure apparatus as described elsewhere.[13] The synchrotron x-ray diffraction data at low temperatures were collected at BL-4 C in the Photon Factory. The wavelength of the incident beam was 0.6888 Å. Electrical resistivity was measured between 2 and 300 K at a rate of 2 K/min by a four-probe method using a physical property measurement system (PPMS, Quantum Design). Heat capacity was measured by the thermal-relaxation method using the PPMS. Thermopower was measured by a steady-state technique with a typical temperature gradient of 1 K/mm, and the contribution of the voltage leads was carefully subtracted.

With H parallel to the c axis, the in-plane magnetoresistance defined as $\rho_a(0)/\rho_a(H)$ reaches approximately five thousands at 1.6 K and 18 T as shown in Fig. 1. This is, as far as we know, the largest value ever observed in cobalt oxides [cf., $\rho(0)/\rho(H) \sim 7$ in a Bi-Ca-Co-O system at 2.5 K and at 7 T (Ref. 14)], and is comparable to those of the other CMR materials.[3–9] Figures 2(a) and 2(b) show that the magnetoresistance (MR) strongly depends on the direction of H. Both the in-plane and the out-of-plane resistivities, ρ_a and

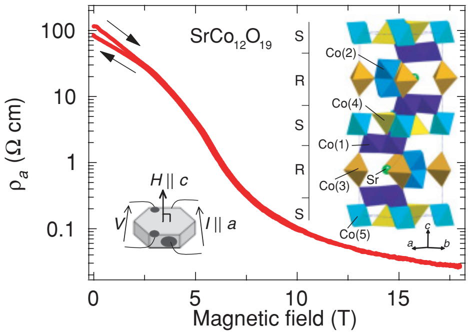

FIG. 1. (Color online) In-plane resistivity of $SrCo_{12}O_{19}$ as a function of external magnetic field applied along the c axis at 1.6 K. The sample was cooled down to 1.6 K under zero field and then measured on sweeping the magnetic field in the order 0 T → 18 T → 0 T. Crystal structure of $SrCo_{12}O_{19}$ consisting of Co-O polyhedra is shown as the inset. S and R denote a spinel-type block and a $SrCo_6O_{11}$-type block, respectively.

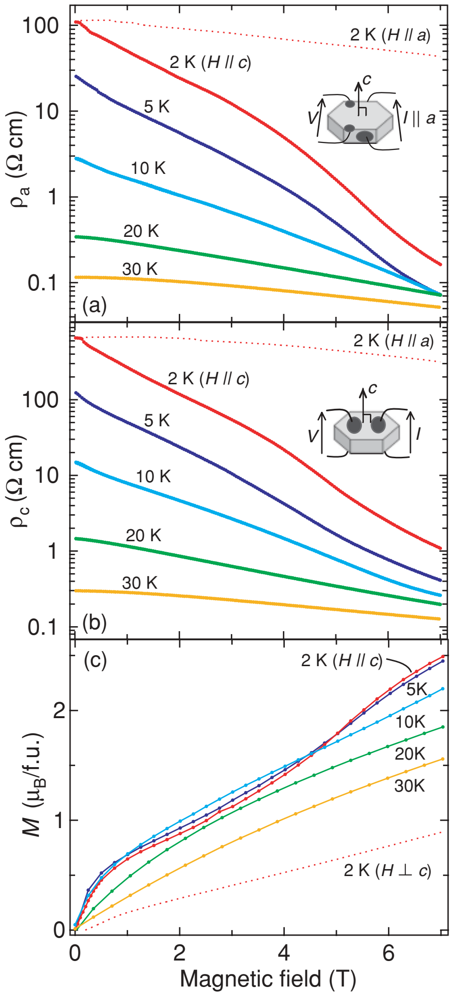

FIG. 2. (Color online) (a) In-plane resistivity ρ_a and (b) out-of-plane resistivity ρ_c of $SrCo_{12}O_{19}$ under magnetic field along the *c* axis at 2, 5, 10, 20, and 30 K and that under the magnetic field along the *a* axis at 2 K. (c) Out-of-plane magnetization curves ($H \parallel c$) at 2, 5, 10, 20, 30, and 50 K and in-plane magnetization curve ($H \perp c$) at 2 K. All data were measured on increasing magnetic fields after zero-field cooling. The magnetization data at 2 K were taken from Ref. 13.

ρ_c, drastically decrease with increasing H parallel to the c axis, whereas they are rather robust against H parallel to the a axis (perpendicular to the c axis). The MR anisotropy measured in terms of $\rho_a(H||a)/r_a(H||c)$ and $\rho_c(H||a)/r_c(H||c)$ is about 400 and 600, respectively, at $H = 7$ T and 2 K. The MR anisotropy is much larger than that of $GdBaCo_2O_{5.5}$ with Ising-like spins.[15]

The uniaxial and colossal MR is closely related to the field dependence of magnetization as shown in Fig. 2(c). The out-of-plane magnetization increases nonlinearly at low H below 30 K, suggesting the development of correlations between the localized spins. Below 5 K a metamagnetic-like anomaly is observed at around 5 T, which corresponds to the also mild kinks in the $\rho-H$ curves. On the other hand, the in-plane magnetization is much smaller and almost linear to H. These results indicate that the magnetic anisotropy with the easy axis along the c axis becomes significant below about 30 K. The uniaxial magnetic anisotropy can be attributed to the trigonal bipyramidal site Co(3) with Ising-like spins stabilized by the spin-orbit coupling under the uniaxial crystal field (see the inset of Fig. 1).

Despite the anisotropic crystal structure, the resistivity is rather isotropic and shows interesting temperature-dependent and field-dependent behavior. As can be seen in Figs. 3(a) and 3(b) a metal-insulator (MI) transition takes place at 80 K ($=T_{MI}$), and it is not accompanied either by thermal hysteresis nor by discontinuity, as is characteristic of the first-order transition. The negative MR is small near T_{MI} but becomes gigantic as temperature decreases below about 30 K [see the inset of Figs. 3(a) and 3(b)]. Notably, the insulating behavior is interrupted between 6 and 12 K under the external magnetic field as most clearly observed for ρ_a at H ($\parallel$ c) = 7 T, which may be regarded as a "magnetic-field-induced insulator to metal transition." However, such a field effect is weakened near the lowest measured temperature.

Another transport property, thermopower, and also magnetic properties show corresponding anomalies. The in-plane

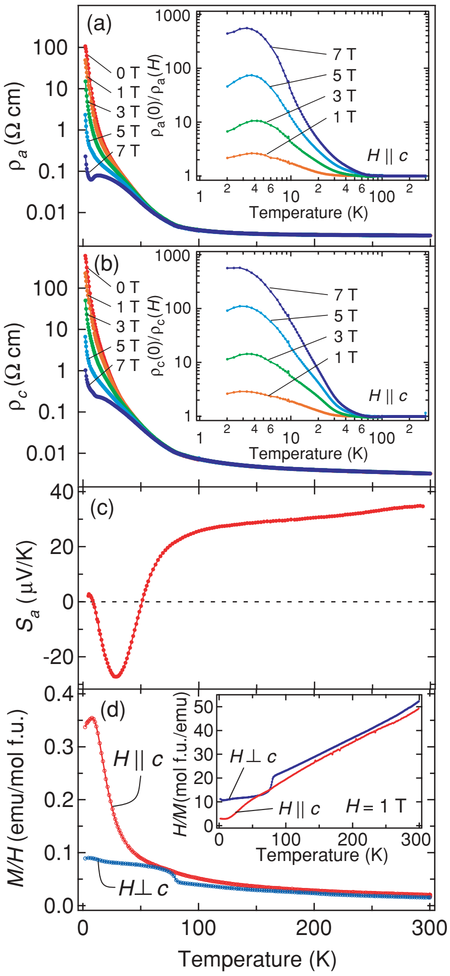

FIG. 3. (Color online) Temperature dependence of (a) in-plane resistivities, (b) out-of-plane resistivities under selected magnetic fields applied along the *c* axis (insets show temperature dependence of magnetoresistances), (c) in-plane Seebeck coefficient, and (d) in-plane ($H \perp c$) and out-of-plane ($H||c$) magnetization divided by an external magnetic field of 1 T for $SrCo_{12}O_{19}$ (inset shows temperature dependence of the inverse of M/H). The magnetization data were taken from Ref. 13. All the data were measured on heating.

thermopower shown in Fig. 3(c) decreases significantly below around T_{MI}, even changing its sign at 50 K, which implies that the density of states near the Fermi level is reconstructed. Upon the MI transition at 80 K, an antiferromagnetic order takes place and the magnetic anisotropy is enhanced as lowering the temperature. At high temperatures both the in-plane and the out-of-plane magnetization obey the Curie-Weiss law [see Fig. 3(d)]. The simultaneous occurrence of the MI and the magnetic transitions indicates a strong spin-charge coupling. It is notable that the anomaly at T_{MI} can be found only for the in-plane magnetization, whereas another anomaly at 8 K, where the MR effect and the magnetic anisotropy are nearly maximized, is clearly seen for the out-of-plane magnetization.

The T_{MI} is specific with respect to the structural features also. As shown in Fig. 4(a) the in-plane lattice parameter a quite unusually increases below about 70 K, while the out-of-plane lattice parameter c decreases more rapidly below 80 K. Correspondingly, the heat capacity exhibits a small lambda-like peak just below T_{MI} [see Fig. 4(b)], which is the evidence for the second-order nature of the phase transition. At around 8 K a broad peak in the heat capacity, or more clearly in the heat capacity divided by temperature [see the inset of Fig. 4(b)], was observed. This broad peak can be associated with the enhancement of the uniaxial MR and thus the ordering of the Ising spins being muddled by the phase competition as will be explained later.

We note here some important features of $SrCo_{12}O_{19}$ that differentiate it from other CMR materials. First, as shown in Fig. 1, the H-dependent hysteresis of MR is absent in the high-H region, suggesting that the CMR effect can be characterized as a second-order transition or a crossover. Second, the CMR effect is observed far below T_{MI}, at around 5 K. Third, the presence of Ising-like spins plays an important role on the highly anisotropic character of the MR effect.

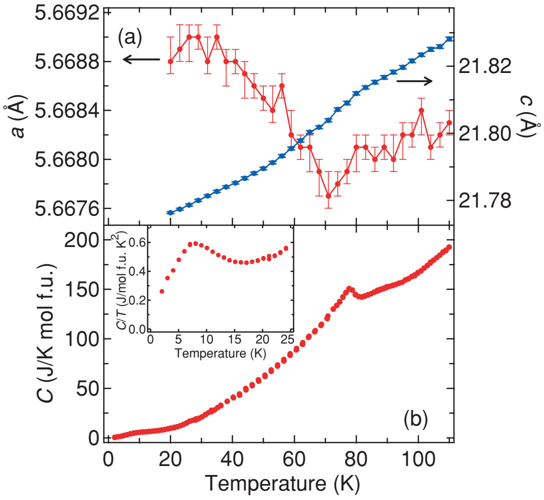

FIG. 4. (Color online) (a) Lattice parameters and (b) total specific heat of $SrCo_{12}O_{19}$ as a function of temperature on heating run are shown. The lattice parameters at 300 K were estimated to be $a = 5.66$ Å and $c = 21.897$ Å on the basis of hexagonal symmetry ($P6_3/mmc$) (Ref. 13). The total specific heat divided by temperature below 25 K is shown as the inset.

Considering the complicated crystal structure of $SrCo_{12}O_{19}$, a simplified qualitative picture deduced from the experimental facts would be a better starting point rather than a quantitative picture based on first-principle calculations. According to the bond-valence calculations, the valences of the cobalt ions are $Co(1)^{3.5+}$, $Co(2)^{3.4+}$, $Co(3)^{2.8+}$, $Co(4)^{2.2+}$, and $Co(5)^{3.5+}$ (Ref. 13). First, we assume that the electronic state of Co(4) with the tetrahedral coordination in the spinel block is Co^{2+} with nearly isotropic spins of $S = 3/2$, as in the case of the spinel Co_3O_4 having essentially the same site.[16] The slight nonlinearity of the in-plane magnetization at low H can be ascribed to the canted spin components of this site. Second, the Co(3) site with the trigonal bipyramidal coordination is in a trivalent state with a high-spin configuration and carries Ising-like spins of $S = 2$, on the analogy of the related hexagonal compound $SrCo_6O_{11}$ having essentially the same trigonal bipyramidal site.[17–19] As a result, because the valences of strontium and oxygen ions are expected to be $+2$ and -2, respectively, the rest of cobalt ions with the octahedral coordination, Co(1), Co(2), and Co(5), should adopt a valence of $+3.22$ in average, which is close to $+3.25$. On the other hand, based on the bond-valence calculations, the valences of these Co ions were estimated to be about $+3.5$.

Keeping the above picture in mind, we will address the origin of the phase transition at 80 K. As is similar to the other conducting Co oxides, the Co^{4+} ions should be responsible for the electrical conduction. If this is the case, the conduction paths are formed by the 3D network of $Co^{3+/4+}O_6$ octahedra containing Co(1), Co(2), and Co(5), which is consistent with the nearly isotropic resistivity shown in Figs. 3(a) and 3(b). Because the formal Co valence of the $Co^{3+/4+}$-O sublattice is estimated to be in the range $+3.22$– $+3.5$, we expect that the conduction carriers are unstable against a charge ordering of Co^{3+} and Co^{4+} in the ratio of $3:1$ ($Co^{3.25+}$), $2:1$ ($Co^{3.33+}$), or $1:1$ ($Co^{3.5+}$). Actually, there exist many similarities between $SrCo_{12}O_{19}$ and a charge-ordering system $Na_{0.5}CoO_2$ with regard to the anomalies observed at or below T_{MI}, that is, the insulating ground state confirmed by the resistivity, the simultaneous onset of the antiferromagnetic and the MI transitions, the negative hump in the thermopower,[20] and the anomalous thermal changes in the lattice parameters.[21] However, as yet we have found neither the lowering of symmetry nor the appearance of superlattice peaks indicating a charge order by x-ray diffraction measurements. In fact, as for $Na_{0.5}CoO_2$, in which the ordering tendency of Co^{3+} and Co^{4+} is enhanced by the orthogonally ordered Na ions,[22] it was barely detected by diffraction techniques.[23–25] Thus, it is no wonder that the detection of a charge order driven by a purely electronic mechanism in $SrCo_{12}O_{19}$ ends in failure.

Finally, we will address a possible origin for the uniaxial CMR effect. Previously we found a ferromagnetic (or ferrimagnetic) metallic state with spin-polarized conduction electrons in the related compound $SrCo_6O_{11}$ with hexagonal R-type structure, in which the large negative MR appears below about 20 K as the ferromagnetic correlation between Ising-like spins develops.[26] Because the formal Co valence averaged over the octahedral sites in $SrCo_6O_{11}$ is about $+3.5$ (Ref. 17), the $Co^{3+/4+}$-O network consisting of the octahedral sites in $SrCo_{12}O_{19}$ is expected to have a similar ferromagnetic metallic state. As seen in Fig. 3(d), the out-of-plane magnetization rapidly increases below about 30 K, where the enhancement of the negative MR sets in, suggesting the development of ferromagnetic (or ferrimagnetic) state with the easy axis along the *c* axis. Given that such a ferromagnetic metallic state competes with the charge-ordered state, the application of external magnetic fields, which enhances internal magnetic fields by the Ising spin sublattice, should destabilize the antiferromagnetic state and the concomitant charge order, and stabilize the nearly degenerate ferromagnetic metallic phase through changes in the Zeeman energies. Accordingly, the CMR effect in this material can be ascribed to the magnetic-field-induced crossover between two competing states, which is dominated by the Ising-like spin sublattice. $SrCo_{12}O_{19}$ allows us to explore a new class of gigantic response with directional sensitivity to external magnetic fields by making use of Ising-like spins in electronic systems with competing phases.

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