Magnetotransport properties of $SrRuO_3$ epitaxial thin films on (100) $LaAlO_3$: Presence of localized magnetic moments

J. H. Cho,* Q. X. Jia, X. D. Wu, S. R. Foltyn, and M. P. Maley
Superconductivity Technology Center, MS K763, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
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We report temperature and magnetic field dependences of the longitudinal and transverse magnetoresistances of high-quality epitaxial $SrRuO_3$ thin films. We also report Hall effect measurements in the paramagnetic and ferromagnetic states. The magnetic field dependence of the longitudinal magnetoresistivity shows a simple scaling $\sim H^2/(T-T_c)^2$ far above the ferromagnetic transition temperature T_c. This observation supports a presence of localized magnetic moments above T_c. [S0163-1829(96)07825-3]

Compared with $3d$ transition-metal oxide compounds, only a few studies of $4d$ transition-metal oxide compounds have been made. In a crystal environment, it is generally believed that $4d$ and $5d$ transition-metal compounds follow a low-spin state instead of the high-spin state of $3d$ transition-metal compounds. According to a band calculation,[1] $4d$ transition-metal compounds have been regarded to follow a spin-independent band calculation, indicating a nonmagnetic ground state. However, $SrRuO_3$ shows metallic conductivity and ferromagnetism below 160 K. In addition, $Ca_{1-x}Sr_xRuO_3$ systems show physical properties ranging from a metallic ferromagnetism in $SrRuO_3$ to short-range metallic antiferromagnetism in $CaRuO_3$ with the same cation valence. This suggests that there exists a subtle interplay of crystal symmetry.[2] Magnetically, both compounds show Curie-Weiss paramagnetism at high temperatures with a Curie constant equivalent to $S \approx 1$ $(2.87\mu_B)$. In the ferromagnetic state of $SrRuO_3$, the saturation moment is $\sim 1.1\mu_B$,[3] which is significantly lower than the obtained Curie constant from the paramagnetic state.

In addition, giant magnetoresistances have been observed recently on doped $LaMnO_3$ oxide compounds,[4] and have generated renewed interest in the electrical transport properties of ferromagnetic compounds. Similar magnetoresistances were also observed in metallic $La_{1-x}Sr_xCoO_3$ compounds, where a close relationship between magnetotransport and spontaneous magnetization was inferred.[5] Therefore, it is our purpose to study the nature of magnetotransport of the $4d$ transition-metal oxide compound $SrRuO_3$ with respect to an itinerant or a localized magnetic moment.

In this paper, we will report temperature and magnetic field dependences of longitudinal and transverse magnetotransport properties of high-quality epitaxial $SrRuO_3$ thin films, where the temperature dependence and magnitude of resistivity are comparable to single crystals.[6] We will also report Hall effects on paramagnetic and ferromagnetic states. The magnetic field dependence of the longitudinal magnetotransport shows a simple scaling $\sim H^2/(T-T_c)^2$ far above the ferromagnetic transition temperature T_c. This observation supports a presence of localized magnetic moments above T_c.

$SrRuO_3$ thin films are deposited on (100) single-crystal $LaAlO_3$ substrates using an excimer laser (XeCl, 308 nm) with a pulse rate 10 Hz. Based on structural and electrical properties of our $SrRuO_3$ films, the optimal deposition temperature was 775 °C at 200 mTorr oxygen atmosphere. Immediately after the deposition, the oxygen pressure of the chamber was increased to $\sim$300 Torr, and the films were cooled to room temperature. The epitaxial growth of the film was verified by x-ray diffraction with a ϕ scan and by scanning tunneling microscopy.[7] The ϕ scan indicates that the orthorhombic (110) direction equivalent to the pseudocubic a or b axis is aligned with the (100) direction of $LaAlO_3$. We used two films with 90 Å (F1) and 750 Å (F2) thickness. The deposition rate of the films was calibrated by Rutherford backscattering spectroscopy. Using temperature dependences of remanent magnetizations (not shown), we obtained ferromagnetic transition temperatures (T_c) $\sim$140 K and 160 K for F1 and F2, respectively. The temperature dependences of the magnetizations show different behaviors for the two films. The magnetization of F1 shows a rather fast decrease with increasing temperature, indicative of superparamagnetism. The magnetization of F2 shows a typical ferromagnetic transition. At 5 K, the remanent magnetizations for the field perpendicular and parallel to the film are almost identical for F2.

From now on, we will focus on the magnetotransport properties of these films, especially F2. Here, $\mathbf{H}\|c$, $\mathbf{H}\|b$, and $\mathbf{H}\|a$ represent the magnetic field direction perpendicular to the film (transverse), the magnetic field parallel to the film but perpendicular to the applied current (transverse), and the magnetic field parallel to the film and parallel to the applied current (longitudinal), respectively.

Figure 1 shows temperature and magnetic field dependences of resistivities of F1 and F2. The overall resistivity of F1 is larger than that of F2. F1 also shows an upturn at low temperatures indicating a localization effect. On the other hand, the magnitude of resistivity of F2 is almost identical to the value of a single crystal,[6] and the temperature dependence is also similar except at very low temperatures. There are changes of slopes at the T_c's of both films. The magnetic field dependences of both films at $H = 7$ T with $\mathbf{H}\|c$ show maximum changes at the T_c's ($\sim$140 K for F1 and $\sim$160 K for F2). Such negative magnetoresistances are characteristics

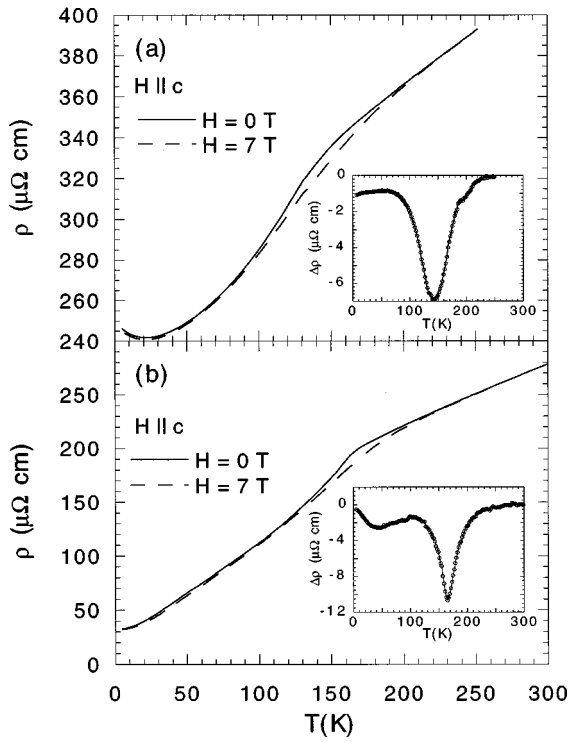

FIG. 1. (a) Temperature dependence of resistivity of the 90 Å thick film at $H = 0$, 7 T with $\mathbf{H}\|c$. At low temperatures, it shows a localization effect. (b) Temperature dependence of resisitivity of the 750 Å thick film at $H = 0$, 7 T with $\mathbf{H}\|c$. The temperature dependence and the magnitude are similar to those of single crystals. The inset shows the temperature dependence of difference resistivities.

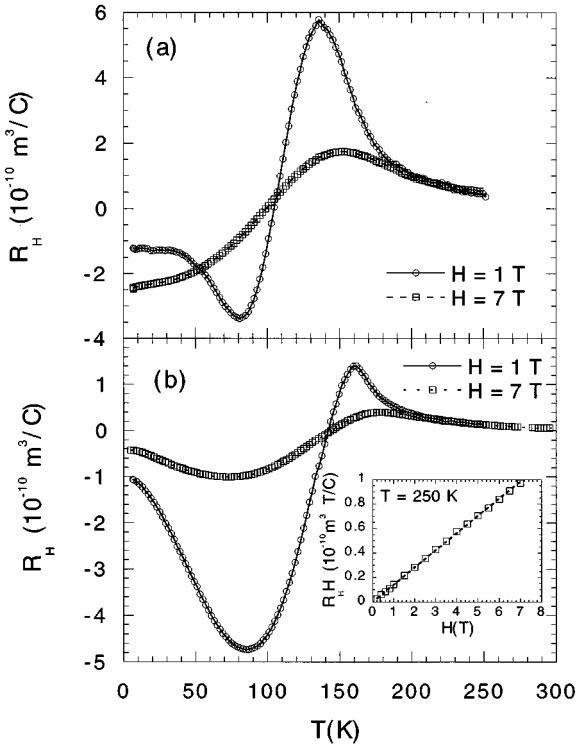

FIG. 2. (a) Temperature dependence of the Hall coefficient of the 90 Å thick film at $H = 1$, 7 T with $\mathbf{H}\|c$. (b) Temperature dependence of the Hall coefficient of the 750 Å thick film at $H = 1$, 7 T with $\mathbf{H}\|c$. The inset shows a linear magnetic field dependence of the Hall resistivity at 250 K. This indicates that there is no contribution from the spontaneous magnetization.

of ferromagnetic compounds. The insets show difference resistivities $[\Delta\rho = \rho(H) - \rho(0)]$ between $H = 7$ and 0 T. The narrower full width at half maximum (FWHM) of F2 than of F1 indicates a different nature of ferromagnetic fluctuations, as seen in the remanent magnetizations.

Figure 2 shows the temperature and magnetic field dependences of the Hall coefficients for F1 and F2. The magnetic field was along the c axis and the current along the a axis. Above $\sim$200 K, no magnetic field dependence is observed between $H = 1$ T and $H = 7$ T. Below $\sim$200 K, the Hall coefficients between 1 T and 7 T start to deviate. Compared with the behavior of 7 T, there is a large enhancement of the Hall coefficient of 1 T around T_c on both films. As the temperatures decrease further, we observe a change of sign of the Hall coefficient. Below T_c, the temperature dependence of the Hall coefficient of F1 is different from that of F2. Above T_c, the Hall coefficient is positive (hole type), and shows a strong temperature dependence following a Curie-Weiss-like behavior. The inset of Fig. 2(b) shows a linear magnetic field dependence of the Hall resistivity of F2 at 250 K.

Figure 3 shows the temperature dependences of the $\Delta\rho$'s of F2 for three different field orientations at $H = 7$ T. For the magnetic field $\mathbf{H}\|a$, i.e., the longitudinal magnetoresistivity ($\Delta\rho_\|$), the magnitude of the negative magnetoresistivity is larger than those of the transverse ones ($\Delta\rho_\perp$). The behaviors of the two field orientations for $\mathbf{H}\|c$ (perpendicular to the film) and $\mathbf{H}\|b$ (parallel to the film) are similar. This coincides with the observed isotropic orientation dependence of the remanent magnetization if this effect results from the spontaneous magnetization. The two curves on the positive side of Fig. 3 represent the difference $\Delta\rho_\perp(\mathbf{H}\|c,b) - \Delta\rho_\|(\mathbf{H}\|a)$. The difference results from the fact that a Lorentz force also contributes to the transport property in the transverse directions, where the Lorentz force bends the trajectory of the carriers. As seen in Fig. 3, there is a large contribution from the scattering by the Lorentz force,

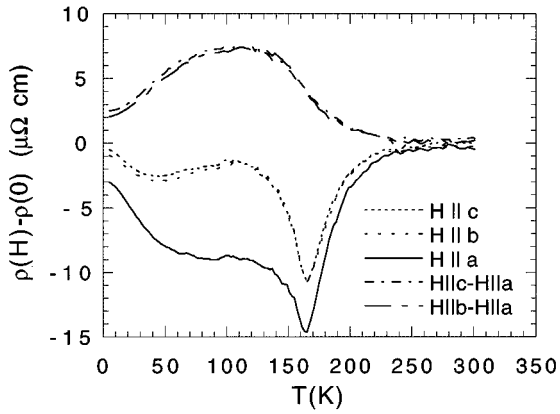

FIG. 3. Temperature dependence of the transverse and longitudinal magnetoresistivities at $H = 7$ T for the 750 Å film. The two curves on the positive side of the figure indicate the contribution from the Lorentz force acting on the carriers.

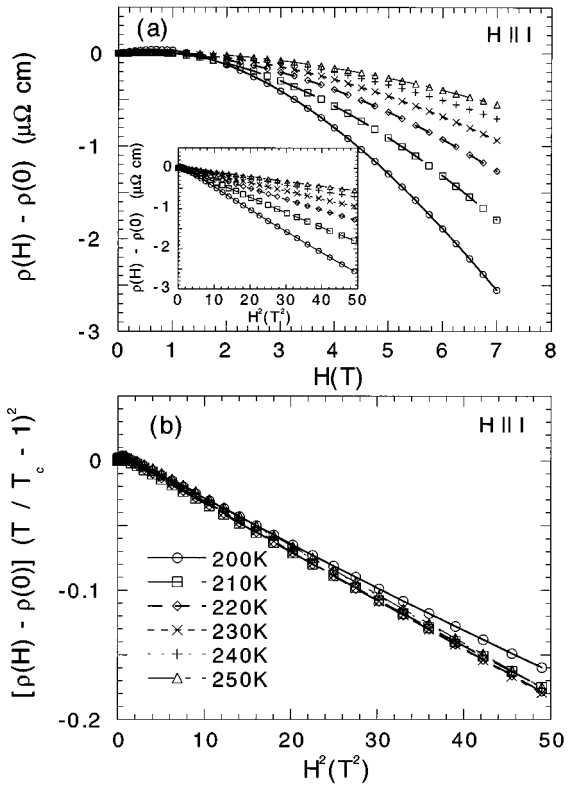

FIG. 4. (a) Magnetic field dependence of the longitudinal magnetoresistivity for the 750 Å film at 200, 210, 220, 230, 240, and 250 K. The magnetic field dependence is quadratic. The inset shows a difference resistivity vs quadratic magnetic field. (b) Scaling of the difference resistivity vs H^2.

i.e., an orbital contribution. This indicates that the magnetotransport in this system consists of spin-dependent and orbital-dependent terms.

Figure 4(a) shows magnetic field dependences of longitudinal magnetoresistivities of F2 above T_c. The magnetoresistivity shows a negative magnetic field dependence. At a temperature closer to the T_c, the negative magnetoresistance is enhanced. The magnetic field dependence is proportional to H^2 as seen in the inset of the Fig. 4(a). Figure 4(b) shows a scaling of $\Delta\rho_{\parallel}$. The meaning of the scaling function $[\rho(H)-\rho(0)](T/T_c-1)^2$ will be discussed later. The magnetic field dependences of the transverse magnetotransports show a similar behavior with a smaller change than that of the longitudinal case (not shown).

As seen in Fig. 1, F1 has a lower ferromagnetic transition temperature (140 K) than that of F2. The apparent decreases of T_c's are also observed in $Ca_{1-x}Sr_xRuO_3$ compounds with increasing Ca (Refs. 2, 8) and in the pressure dependence of T_c of $SrRuO_3$.[9,10] The decrease of T_c in our thinner film also coincides with the fact that the lattice mismatch between the pseudocubic lattice constant 3.93 Å of $SrRuO_3$ and 3.793 Å of $LaAlO_3$ induces a compression in the film. As the film gets thicker, the compression will decrease, and T_c recovers to the bulk and single-crystal value. The transition widths shown in the insets of Fig. 1 also demonstrate that F1 has a broader transition at T_c than does F2. This might be related to the nature of the magnetic transition, where F1 shows the remanent magnetization similar to a behavior of a superparamagnetism, while F2 shows a spin-wave-excited magnetization.[11]

The Hall effect shows strong temperature and magnetic field dependences in both films. Above T_c, the Hall coefficient is positive, and increases with decreasing temperature. Below T_c, the Hall coefficient starts to decrease, and changes sign. Comparing F1 with F2, the behavior of the Hall coefficient below T_c seems to depend on details of the ferromagnetic state, i.e., the spontaneous magnetization. Above $\sim$200 K, the Hall coefficients with $H=1$ and 7 T coincide with each other as shown in the inset of Fig. 2(b) by the linear magnetic field dependence of the Hall resistivity at 250 K. Below $\sim$200 K, the Hall coefficients of the two magnetic fields deviate from each other. This kind of behavior is typically seen in ferromagnetic compounds. In ferromagnetic UGe_2, Yun *et al.*[12] also observed a large enhancement of the Hall coefficient at a low magnetic field without any change of sign. It is believed that the Hall coefficient of a ferromagnetic system consists of two terms, where one originates from the Lorentz force and the other from the anomalous Hall effect due to spontaneous magnetization.[13,14]

On the other hand, the change of the sign in the Hall coefficient is not directly related to the spontaneous magnetization. Around $\sim$250 K, where no magnetic field dependence of the Hall coefficient is observed, the Hall coefficient of F1 and F2 is $\sim 5.3\times10^{-11}$ and $\sim 1.3\times10^{-11}$ m^3/C, respectively. The deduced number of carrier concentrations is $\sim 1.2\times10^{23}/cm^3$ and $\sim 5\times10^{23}/cm^3$, respectively. We can expect smaller carrier concentrations in F1 due to localization and to its larger value of resistivity. However, compared with photoemission data[15] and the crystallographic density with one carrier per formula unit ($\sim 1.7\times10^{22}/cm^3$), the deduced carrier concentration obtained from the Hall coefficient is far too large. At $\sim$300 K, the deduced number of carrier concentration is $\sim 1.3\times10^{24}/cm^3$ for F2. Considering the above facts and the change of sign of the Hall coefficient, it is reasonable to consider $SrRuO_3$ as a two-band system with holes and electrons. Therefore, the anomalously small value of the Hall coefficient results from the compensation effect of holes and electrons by the Lorentz force. A preliminary result indicates that there is another change of the sign around $\sim$380 K. This supports the two-band model.

The octahedral cubic crystal field of Ru($4d$) in $SrRuO_3$ splits the Ru $4d$ states into a lower threefold degenerate t_{2g} level and a higher twofold degenerate e_g one. Ru^{+4} has four electrons in the $4d$ shell. The high-spin state is $t_{2g}^3 e_g^1$ with $S=2$, where as the low-spin state is t_{2g}^4 with $S=1$. In $4d$ transition-metal compounds, there exists a stronger spin-orbit interaction, since the effect of the crystal field is not as strong as in $3d$ transition-metal compounds. As seen in Fig. 3, the difference between $\Delta\rho_{\parallel,\perp}$ results from spin-orbit scattering, where the orbital quenching is not suppressed. Below $\sim$200 K, there exists a strong contribution from the spin-orbit scattering acting opposite to the spin-only contribution. This coincides with Hund's rule, where there exists an opposite effect between the spin and the orbital contribution below half-filled d states, though we should notice the large enhancement of the spin-orbit contribution below the ferromagnetic state. This indicates that this effect is directly related to the ferromagnetic state.

Negative magnetoresistances are predicted for both itinerant weakly ferromagnetic states[16] and localized ferromagnetic states,[17] and have been observed experimentally. In a Kondo system, a negative magnetoresistance is also observed.[18] In fact, the negative magnetoresistance is realized if a magnetic field suppresses spin-dependent scattering. The scaling observed in Fig. 4(b) is predicted in a system with spin fluctuations through a localized d and itinerant s interaction,[17] and we demonstrate such a scaling quantitatively. It was predicted that the negative magnetoresistance should vary as $H^2/(T-T_c)^2$ far above the ferromagnetic transition temperature. This coincides with our observation. Since the temperature range of the scaling is far above the ferromagnetic transition temperature, we can safely use a mean-field approximation. The susceptibility $\chi(T)$ of this system above T_c follows a Curie-Weiss paramagnetism and can be described as $(T-T_c)^{-1}$.[3] In another words, the scaling is proportional to $H^2\chi(T)^2$. As seen in Fig. 2, the Hall coefficient has no magnetic field dependence from 210 K to 250 K. This indicates that this scaling does not result from field-induced spontaneous magnetic moments, where the ensemble average $\langle S\rangle$ is finite (S denotes a spin.). This differs from the observed relation in $La_{1-x}Sr_xCoO_3$ Ref. (5) that the magnetotransport is proportional to $\langle S\rangle^2$. Rather, the negative magnetoresistance results from the suppression of fluctuations of the Edwards-Anderson order parameter by the magnetic field, where the mean value $\langle S\rangle = 0$ but $\langle S^2\rangle$ is finite. This shows that the magnetotransport is directly coupled to the local spin fluctuations, and shows that, above T_c, the magnetic moments are localized, as the Curie-Weiss law indicates.

To summarize, we here measured the magnetotransport properties of high-quality epitaxial $SrRuO_3$ thin films. The magnetoresistance data scale and the scaling is well described by suppression of s-d spin fluctuations by the magnetic field. In this case, the spin of the d state is well localized. The scaling indicates that the negative magnetoresistance is governed by the suppression of fluctuations of the Edwards-Anderson order parameter in $SrRuO_3$, and shows the existence of localized magnetic moments above T_c.

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*Present address: Research Center for Dielectric and Advanced Matter Physics (RCDAMP), Pusan National University, 30 Jangjun-Dong, Kumjeong-Ku, Pusan 609-735, Rep. of Korea.

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