Scaling of the anomalous Hall effect in Sr$_{1-x}$Ca$_x$RuO$_3$

R. Mathieu$^{1,3,4}$, A. Asamitsu$^{1,2}$, H. Yamada,$^3$ K. S. Takahashi,$^2$
M. Kawasaki,$^{3,4}$ Z. Fang,$^{1,5}$ N. Nagaosa,$^{2,3,6}$ and Y. Tokura$^{1,2,3}$

$^1$Spin Superstructure Project (ERATO-SSS), JST, AIST Central 4, Tsukuba 305-8562, Japan
$^2$Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan
$^3$Correlated Electron Research Center (CERC), AIST Central 4, Tsukuba 305-8562, Japan
$^4$Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
$^5$Institute of Physics, Chinese Academy of Science, Beijing 100080, China
$^6$CREST, Japan Science and Technology Agency (JST)

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The anomalous Hall effect (AHE) of ferromagnetic thin films of Sr$_{1-x}$Ca$_x$RuO$_3$ ($0 \leq x \leq 0.4$) is studied as a function of $x$ and temperature $T$. As $x$ increases, both the transition temperature $T_c$ and the magnetization $M$ are reduced and vanish near $x \sim 0.7$. For all compositions, the transverse resistivity $\rho_H$ varies non-monotonously with $T$, and even changes sign, thus violating the conventional expression $\rho_H = R_0 B + 4\pi R_s M(T)$ ($B$ is the magnetic induction, while $R_0$ and $R_s$ are the ordinary and anomalous Hall coefficients). From the rather complicated data of $\rho_H$, we find a scaling behavior of the transverse conductivity $\sigma_{xy}$ with $M(T)$, which is well reproduced by the first-principles band calculation assuming the intrinsic origin of the AHE.

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It has been known that the Hall resistivity $\rho_H$ in a ferromagnet has some extra contribution originated from the spontaneous magnetization, which is assumed and often observed experimentally to be fitted by $\rho_H = R_0 B + 4\pi R_s M$, where $B$ is the magnetic induction and $M$ is the magnetization of the material. $R_0 B$ represents the ordinary Hall contribution, which is related to the nature and amount of charge carriers. It is a linear function of the applied magnetic field $H$ as in the Hall measurement geometry, $B = H$. $R_s M$ is referred to as the anomalous Hall term, and is usually associated with the spin polarization of the conduction carriers and the relativistic spin-orbit interaction. According to the above definition of $\rho_H$, the anomalous Hall term is proportional to the magnetization of the material. However the quantitative analysis of the AHE has seldom been completed since its mechanism has not yet been established, and theories give much smaller values compared with the experiments. Furthermore, most of the theories regard the AHE as from extrinsic origins, involving processes such as skew scatterings and side-jump mechanisms. Therefore the magnitude of the AHE depends on the concentration and scattering strength of impurities, thermal spin-agitation, etc. In contrast to these extrinsic mechanisms, several works regard AHE of the intrinsic origin. Namely the phase of the Bloch wave-function in the momentum space determines the Hall conductivity $\sigma_{xy}$, which is largely determined by the band crossing points acting as “magnetic monopoles". As an explicit example, the AHE and magneto-optical effect of SrRuO$_3$ have been studied, and a good agreement was obtained between theory and experiments. In the present paper, we report the extensive study of the AHE in Sr$_{1-x}$Ca$_x$RuO$_3$ ($0 \leq x \leq 0.4$) as a function of $T$ and $x$ to reveal its systematics. We have found the scaling behavior of the transverse conductivity $\sigma_{xy}$ in terms of the $T$- and $x$-dependence of the magnetization $M(x, T)$, which is in fairly good agreement with the first-principles band calculation. This gives a firm evidence for the intrinsic origin of the AHE.

Several members of the Ruddelson-Popper-type Sr$_{n+1}$Ru$_n$O$_{3n+1}$ series show metallic properties, as well as superconductivity and magnetic order. SrRuO$_3$ ($n = \infty$, perovskite) is ferromagnetic with a Curie temperature ($T_c$) around 160 K, and a fairly large spin orbit coupling. The 4d orbitals of Ru$^{4+}$ are rather extended, and the Coulomb repulsion is small compared to the band width. The ferromagnetic properties of SRO are usually associated with a narrow itinerant band resulting from the hybridization between the Ru($t_{2g}$) and O(2p) orbitals.

While similar structurally, and as well metallic, CaRuO$_3$ (CRO) does not exhibit ferromagnetism and its magnetic state is still under discussion. In Sr$_{1-x}$Ca$_x$RuO$_3$, the ferromagnetic interaction becomes weaker with increasing $x$. For the compounds with larger Ca-doping ($x \geq 0.7$), no clear phase transition is discerned, and only some irreversibility is observed in the magnetization curves of these materials. The disappearance of the long range magnetic order is commonly related to the distortion of the RuO$_6$ octahedra associated with the partial or total replacement of Sr by Ca, and the corresponding narrowing of the 4d bandwidth.

It is difficult to grow clean single crystals of Ca-doped SRO, although it is possible to prepare high quality single crystals of the end compounds, SRO and CRO. On the other hand, it is nowadays possible to grow high quality epitaxial films of SrRuO$_3$ and Sr$_{1-x}$Ca$_x$RuO$_3$. In the
present article, we study the anomalous Hall resistivity of epitaxial films of Sr$_{1-x}$Ca$_x$RuO$_3$ ($0 \leq x \leq 0.4$), and its evolution as the ferromagnetic interaction decreases with $x$. The Hall resistivity contains an anomalous component, associated with the ferromagnetic ordering of the samples at low temperatures. This component is not simply proportional to the $M$, as usually assumed. The results reveal a close relation between $\sigma_{xy}$ and the spin polarization of the system. Such a correlation was predicted by first-principles calculations taking account of the spin-orbit interaction in terms of the Berry phase connection. The calculations successfully reproduce the non-monotonous variation of $\sigma_{xy}$ with temperature (via its magnetization), as well as its sign change. The effects of disorder and structural changes on the anomalous conductivity are discussed.

FIG. 1: (color online) Temperature dependence of the resistivity of the Sr$_{1-x}$Ca$_x$RuO$_3$ films (main frame) and single crystals of SrRuO$_3$ and CaRuO$_3$ (lower inset). The upper inset shows the variation of the out-of-plane lattice parameter of the films (squares). The lattice parameter of the SrTiO$_3$ substrate $a_{STO}$ is indicated, as well as the average lattice parameter obtained for Sr$_{1-x}$Ca$_x$RuO$_3$ polycrystalline samples, for $a=b=c$ ($V^{1/3}$, $V$ is the unit cell volume), and for a perfect elastic strain (Poisson ratio of 0.5; $V/a_{STO}^2$). The parameters of $x=0, 0.1,$ and 0.2 ideally lie between the $V^{1/3}$ and $V/a_{STO}^2$ values; the small deviation observed from $x=0.3$ and 0.4 may be related to a minor Ru deficiency; ruthenium oxides are very robust against oxygen deficiencies, so that the oxygen content should be stoichiometric.

Thin ($\sim$ 500 Å) films of Sr$_{1-x}$Ca$_x$RuO$_3$ ($x=0, 0.1, 0.2, 0.3,$ and 0.4) were epitaxially grown on the (001) surfaces of high quality SrTiO$_3$ single-crystal substrates by pulsed laser deposition (PLD). Bulk single crystal SrRuO$_3$ and CaRuO$_3$ were prepared using a flux method for comparison. The quality of the films and phase-purity of the single crystals were confirmed by x-ray diffraction. Both single crystals have orthorhombic structure; SrRuO$_3$ has a relatively small orthorhombicity ($c/a=1.003, c/b=0.996$), while it is larger for CaRuO$_3$ ($c/a=1.01, c/b=0.980$). The epitaxial thin films are coherently strained by the SrTiO$_3$ substrate, yielding a tetragonal distortion in the [001] direction ($c/a=c/b=1.01$ for $x=0$). As a result, the out-of-plane lattice constants of the films are elongated (c.f. inset of Fig. 1), and due to the spin-orbit interaction, the easy axis of magnetization is perpendicular to the film plane. Magnetic and transport measurements were performed on the Sr$_{1-x}$Ca$_x$RuO$_3$ thin films and the single crystals of SRO and CRO. The magnetization data was recorded on a MPPMS5S SQUID magnetometer using a magnetic field applied normal to the plane of the films. The films were then patterned in a six-lead Hall bar geometry using conventional photo-lithography and Ar ion etching for transport measurements. The Hall resistivity $\rho_H$ was measured with a PPMS6000 system together with the longitudinal resistivity $\rho_{xx} = \rho$ as a function of $H$ and $T$. The anomalous resistivity $\rho_{xy}$ was extrapolated to $H = 0$ from $\rho_H$ vs $H$ measurements up to $H = \pm 9$ T at constant temperatures (from 2 K to 200 K) after subtraction of the ordinary Hall contribution, and the transverse conductivity $\sigma_{xy}$ was estimated as $-\rho_{xy}/\rho_{xx}^2$. A small (as the patterned leads are nearly symmetric) magnetoresistance was removed by subtracting $\rho_H(0) - \rho_H(H)$. First-principles calculations of $\sigma_{xy}$ were performed assuming orthorhombic and cubic crystal structures. The plane-wave pseudo-potential calculations were performed based on the local spin density approximation (LSDA), and the spin-orbit coupling was treated self-consistently by using the relativistic fully separable pseudo-potentials in the framework of non-collinear magnetism formalism. The finite life-time broadening was estimated from the experimental residual resistivity and the extended Drude analysis of the longitudinal conductivity.

All the investigated samples are metallic as seen in Fig. 1 and inset. The residual resistivity at low temperatures is very low ($\sim$ 2.5 $\mu\Omega$cm) for the single crystals, and increases for the films from 26 ($x = 0$) to 232 $\mu\Omega$cm ($x = 0.4$). A kink is observed in the resistivity curves, around the paramagnetic-to-ferromagnetic transition temperatures ($T_c$) of the films. No long range magnetic order is observed in CRO, and as seen in inset, the resistivity curve has no anomaly in the measured range of temperature. Due to the above mentioned strain effects, the epitaxial film of SRO has a slightly lower $T_c$ than the single crystal, near 150 K. The substitution of Sr by Ca in Sr$_{1-x}$Ca$_x$RuO$_3$ weakens the ferromagnetic interaction, and $T_c$ is greatly reduced. It is reduced to $\sim$ 110 K for $x = 0.2$, and $\sim$ 70 K for $x = 0.4$. 
of the anomalous Hall resistivity $\rho_{xy}$ for all the films and the SRO single crystal. At a constant temperature, $\rho_H$ is a linear function of $H$ at high fields, with a negative proportionality constant ($R_0 < 0$), indicating charge carriers of electron-like nature. As seen in the figure, $\rho_{xy}$ of the films varies non-monotonically with $T$. No AHE is observed at high temperatures. The AHE appears just above $T_c$: $\rho_{xy}$ is negative, and show a maximum near $T_c$. At lower temperatures, $\rho_{xy}$ changes sign (near 120 K for $x = 0$, and 60 K for $x = 0.2$), and remain positive down to the lowest temperature. For $x = 0.4$ with a lower $T_c$, however, the sign change is not observed. Similar features are observed for the single crystal of SRO; the resistivity of the single crystals was too low below 40 K to estimate $\rho_{xy}$ (and thus $\sigma_{xy}$). As seen in the bottom panel of Fig. 2, the anomalous conductivity remains fairly large at low temperatures, amounting to $\sim -100$ Scm$^{-1}$ at 2 K for the undoped and $x = 0.1$ films. $\sigma_{xy}(T)$ shows a similar high-temperature peak, which, as $T_c$, is

The top panel of Fig. 2 shows the temperature dependence of the magnetization (top panel), transverse resistivity (middle panel), and transverse conductivity (bottom panel) of the Sr$_{1-x}$Ca$_x$RuO$_3$ films. In the SQUID experiments, the samples are cooled in $H = 7$ T, and the magnetization is recorded on re-heating in $H = 0.05$ T applied normal to the film planes. The results for the single crystal (SC) are included for comparison in dashed lines. The top inset shows the monotonous increase of the coercivity $H_c$ with increasing Ca doping; $H_c$ was determined from $M - H$ measurements at $T = 5$ K.

![FIG. 2: (color online) Temperature dependence of the magnetization (top panel), transverse resistivity (middle panel), and transverse conductivity (bottom panel) of the Sr$_{1-x}$Ca$_x$RuO$_3$ films. In the SQUID experiments, the samples are cooled in $H = 7$ T, and the magnetization is recorded on re-heating in $H = 0.05$ T applied normal to the film planes. The results for the single crystal (SC) are included for comparison in dashed lines. The top inset shows the monotonous increase of the coercivity $H_c$ with increasing Ca doping; $H_c$ was determined from $M - H$ measurements at $T = 5$ K.](image)

![FIG. 3: (color online) Top panel: The transverse conductivity $\sigma_{xy}$ data obtained for the films is plotted against the magnetization $M$, using the data from Fig. 2. Typical errors bars are indicated. As the areas of the films are well defined by patterning, the uncertainty on the magnitude of $\rho$ is mainly determined by the error in thickness determination, which amounts to $\sim 5$ % of the actual thickness. Including measurement and determination errors, there is an uncertainty of $\sim 15$ % on $\sigma_{xy}$. The uncertainty on the magnitude of $M$ is, as $\rho$, of $\sim 5$ %. Bottom panel: First-principles calculations for cubic and orthorhombic structures. Results obtained using different broadening parameters are shown in the orthorhombic case.](image)
shifted to lower temperatures as the Ca doping increases. If the anomalous conductivity data in Fig. 2 is plotted against the magnetization instead of the temperature, as in the top of Fig. 3, one observes, within the measurement uncertainties, a similar or universal behavior of the Hall conductivity for all the samples.

Now we discuss the physical origin of these behaviors. The scaling \( \rho_{xy} \propto \rho_{xx}^2 \) itself is often observed experimentally and is even derived considering extrinsic mechanisms. In these conventional theories, a simple proportionality relation \( \rho_{xy} \propto M \) is derived in terms of the perturbative expansion in the spin-orbit coupling \( \lambda \) and \( M \). However, this simple relation is violated because the band crossing occurs in the band structure, and \( \lambda M \) lifts this degeneracy. This degeneracy point is known to act as a monopole for the gauge field representing the Berry phase curvature, producing its singular distribution. This non-perturbative feature causes the rapid change of \( \sigma_{xy} \) including sign reversal as a function of \( M \) because the Fermi energy crosses this monopole energy as \( M \) changes. First-principles calculations confirm this scenario as shown in the inset of Fig. 3 for SRO (undoped case), using the orthorhombic structure obtained for the bulk SRO crystal. As seen in this inset, the calculations reproduce closely the non-monotonous variations, as well as the sign change of \( \sigma_{xy} \) with \( M \) (or \( T \)). The first-principles calculations (bottom panel of Fig. 3) show how the anomalous Hall conductivity depends on the crystal structure and lifetime of the electrons. Results obtained by considering a cubic structure are indeed quite different from those obtained in the orthorhombic case, even though they qualitatively show a similar non-monotonous behavior. It is also shown in the figure how \( \sigma_{xy} \) is reduced upon increasing the scattering rate in the calculations; the broadening parameters were chosen so as to reflect the increase of longitudinal resistivity shown in Fig. 1.

The Ca doping of the \( \text{Sr}_1-x \text{Ca}_x \text{RuO}_3 \) films also induces slight structural changes, such as a smaller orthorhombicity or more correctly tetragonality, c.f. inset of Fig. 1. It is thus expected that the temperature dependence of \( \sigma_{xy} \) of the doped films should differ, more or less, from that of the undoped SRO film, reflecting the changes in the local lattice-structure of the system and their effect on the band structure. Nevertheless, if the additional electron scattering effects arising from the Ca doping are taken into account as the broadening-induced reduction of the magnitude of \( \sigma_{xy} \), the anomalous Hall conductivity of the \( \text{Sr}_1-x \text{Ca}_x \text{RuO}_3 \) films shows a good scaling to \( M \), while changing \( T \) and \( x \). This indicates that the AHE is mainly of intrinsic origin, as described in terms of the Berry phase connection.

In summary, the anomalous Hall effect was investigated for thin films of \( \text{Sr}_1-x \text{Ca}_x \text{RuO}_3 \), in which the ferromagnetic interaction is weakened with increasing Ca content \( x \). The Hall resistivity of the films vary in a similar fashion with the temperature \( T \). The obtained anomalous Hall conductivity varies non-monotonously and non-trivially with \( T \), and even changes sign. The results however, show a good scaling solely to the \( T \) and \( x \)-dependent magnetization \( M \), which can be reproduced by first-principles calculations. The anomalous Hall effect appears, as asserted by Fang et al., as a hallmark of the presence of magnetic monopoles in the momentum space of the crystal.

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