Low-Temperature Hall Effect in Substituted Sr$_2$RuO$_4$

Naoki Kikugawa, Andrew Peter Mackenzie  
School of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife KY16 9SS, United Kingdom

Christoph Bergemann  
Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom

Yoshiteru Maeno  
International Innovation Center, Kyoto University, Kyoto 606-8501, Japan  
Department of Physics, Kyoto University, Kyoto 606-8502, Japan  
(Dated: March 22, 2022)

We report the results of a study of the Hall effect and magnetoresistance in single crystals of Sr$_2$RuO$_4$ in which Sr$^{2+}$ has been substituted by La$^{3+}$ (Sr$_{2-n}$La$_n$RuO$_4$) or Ru$^{4+}$ by Ti$^{4+}$ (Sr$_2$Ru$_{1-x}$Ti$_x$O$_4$). For undoped Sr$_2$RuO$_4$, the purity is so high that the strong-field Hall coefficient can be measured for fields above 4 T. The conventional weak-field Hall coefficient as a function of doping shows a sharp jump and sign change at $y \sim 0.01$ that is unrelated to either a sharp change in Fermi-surface topography or a magnetic instability. The implications of these results are discussed.

PACS numbers: 74.70.Pq, 74.62.Dh, 74.25.Fy

I. INTRODUCTION

Transport properties under magnetic field such as Shubnikov-de Haas oscillations, magnetoresistance, and Hall resistivity reflect the Fermi-surface topology in metals [1]. In principle, the Hall effect provides information regarding both the orbital contribution from quasiparticles tracing the Fermi surface and the magnetic contribution (the "anomalous" Hall effect). It is therefore a widely-used probe in the investigation of highly correlated electron systems, where the ground states are dominated by interactions among d- and f-electrons [2]. Recently, there has been specific interest in using it as a probe for the Fermi-volume changes that have been predicted to occur near some magnetic quantum critical points [4, 5, 6].

Although it is commonly studied, the Hall effect is a difficult experiment to interpret. Separating the anomalous and orbital parts is not always easy, and even when this can be done, extracting information from the orbital part has a number of important complications. In the commonly-used weak field limit ($\omega_c \tau \ll 1$, $\omega_c$: band-averaged cyclotron frequency, $\tau$: band-averaged relaxation time), the Hall conductivity is a weighted Fermi-surface integral involving the square of the mean free path $\ell$, biased towards regions of high curvature. At high temperatures, where $\ell$ is expected to be $k$-dependent, it is hard to use the weak field Hall effect to obtain quantitative volume information on even simple Fermi surfaces. For multi-band materials, extracting quantitative information is next to impossible in this regime.

There is, however, a limit in which more quantitative analysis should in principle be possible. At very low temperatures, where elastic scattering dominates, $\ell$ is assumed to be $k$-independent, in the so-called "isotropic-$\ell$" limit [7]. In this limit, the Hall conductivity is dominated by curved parts of the Fermi surface. In two dimensions, an analysis introduced by Ong [7] yields a simple expression for Hall coefficient $R_H$ for a multi-band material [8]:

$$R_H = \frac{2\pi d \sum_i (-1)^n \ell_i^2}{e(\sum_i k_i^f \ell_i)^2}. \quad (1)$$

Here, $k_i^f$ is the average Fermi wave-vector of the $i$-th Fermi-surface sheet, $\ell_i$ the mean free path of the quasiparticle on that sheet, $d$ the distance between adjacent RuO$_2$ layers, $n_i = 0$ if $i$ is a hole pocket and 1 if it is an electron one. If $\ell$ is isotropic, it is independent of the sheet and disappears from Eq. (1), allowing an analysis of the Hall coefficient purely in terms of the Fermi-surface topography.

Inspection of Eq. (1) shows that although it is possible to calculate $R_H$ on the basis of known Fermi-surface topography for a material with more than one Fermi-surface sheet, the inverse is not in general true. However, that is not a very important constraint on the use of the Hall effect in studies of quantum criticality, because the key prediction is that of a sudden change in $R_H$ at the critical points as a tuning parameter is varied [4, 6]. One of the questions that we address with the experiments reported here is whether a sudden change in Fermi-surface topography is the only physics that can give a sudden change in $R_H$ in a multi-band material as a function of doping in the low temperature limit. In the course of our work, we have also studied the Hall effect and magnetoresistance in the regime $\omega_c \tau > 1$, thus making one of the first observations, to our knowledge, of the strong-field Hall coefficient of a correlated electron material.

For our study, we concentrate on the two-dimensional metal and unconventional superconductor [3, 10], Sr$_2$RuO$_4$, because the evolution of its Fermi surface has been traced by direct experimental measurement of the de Haas-van Alphen effect [11, 12], even in the presence...
of chemical doping [13]. Using the known Fermi-surface parameters, it was possible for "pure" Sr$_2$RuO$_4$ to obtain accurate agreement between the value of $\rho_H$ calculated using Eq. (1) with the isotropic-$\ell$ approximation and direct measurement [8]. A later Hall effect study of Ca-substituted Sr$_2$RuO$_4$ showed a strong dependence on the Ca concentration which was assumed to reflect a changing Fermi-surface topography coupled with the known changes in the crystal structure [14]. It was not, however, possible to prove that the Hall coefficient changes with doping were the result purely of a change in the Fermi-surface topography, because the high levels of disorder in the samples precluded independent measurement by quantum oscillations.

Recently, the opportunity has arisen to check the behavior of the low temperature Hall effect in doped samples of Sr$_2$RuO$_4$ in a highly controlled situation. If La$^{3+}$ is substituted for Sr$^{2+}$ in Sr$_{2-x}$La$_x$RuO$_4$, the electrons that are doped onto the conduction band give a change in the Fermi-surface topography. It was possible to observe quantum oscillations over the range $0 \leq y \leq 0.06$, confirming that the doping resulted in a simple rigid-band shift of the Fermi level even in a strongly correlated, multi-band metal [13]. Further analysis showed that the same rigid-band model gave a successful description of the measured specific heat to even higher values of $y$, motivating us to calculate the behavior of the Hall effect in the simplest model (rigid-band shift and isotropic-$\ell$) and then perform experiments to see the extent to which the measured Hall coefficient agreed with the prediction. Here we report the results of these measurements and a further data set acquired on single crystals of the Ti$^{4+}$ substituted system (Sr$_2$Ru$_{1-x}$Ti$_x$O$_4$). A further motivation for the work was studying the Hall effect in the presence of magnetic instabilities which previous work has shown to exist at $y \sim 0.20$ [13] and $x \sim 0.025$ [14].

II. EXPERIMENTAL

A series of single crystals of Sr$_{2-y}$La$_y$RuO$_4$ with $y$ up to 0.27 and Sr$_{2-x}$Ru$_{1-x}$Ti$_x$O$_4$ with $x$ up to 0.09 were grown by a floating-zone method in an infrared image furnace (NEC Machinery, model SC-E15HD) in Kyoto, using procedures described in detail elsewhere [13, 17]. The La and Ti concentrations in the crystals were determined by electron-probe microanalysis (EPMA). For the measurements described here, the crystals were cut into rectangles with a typical size of $2 \times 0.3 \times 0.03$ mm$^3$, with the shortest dimension along the $c$ axis. Silver paste (Dupont, 6838) cured at 450°C for 5 minutes was used for attaching 8 electrodes onto each crystal in the Hall geometry; contact resistances were confirmed as below 0.3 Ω at room temperature. Before measuring the Hall effect, we carefully checked the crystal homogeneity by multi-configuration resistivity measurements down to 4.2 K in zero magnetic field. The temperature dependences of resistivity and residual resistivities $\rho_{ab0}$ reproduce well the results of previous studies [13, 15, 16, 18]. Here, the $\rho_{ab0}$ was defined as the low-temperature resistivity extrapolated to $T = 0$. The Hall and magnetoresistance measurements were performed in a dilution refrigerator at stabilized temperature between 40 mK and 1.6 K, sweeping the magnetic field (applied $\parallel c$ axis) between $-12$ T and 12 T, and deducing $\rho_H$ from the gradient of the Hall resistivity $\rho_H$ at low fields. $\rho_H$ in all samples is almost temperature-independent below 1.6 K.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the Hall resistivity $\rho_H$ for all the La-doped crystals that we have studied, along with an example from the Ti-doped system ($x = 0.01$). In the Ti-doped sample, whose residual resistivity is $5 \mu \Omega$cm, $\omega_c \tau \ll 1$ over the whole field range, and the Hall resistivity remains field linear. This field linearity is shared by the La-doped crystals with high $y$ ($y > 0.10$), for which $\rho_{ab0} > 3 \mu \Omega$cm. As $y$ and $\rho_{ab0}$ decrease, more and more curvature is seen in the Hall resistivity, due to increasing influence of the next order cubic term in the Zener-Jones expansion. All data for $y > 0.02$ can be fitted very well by an expression of the form:

$$\rho_H = R_H B + R_3 B^3. \tag{2}$$

Here, $R_3 \propto \tau^2 \propto 1/\rho_{ab0} \propto 1/(n_{imp} \sin^2 \delta_0)^2$ as discussed in Eq. (3) of ref. 8 ($\delta_0$: phase shift, $n_{imp}$: impurity concentration). For $x = y = 0$, however, no fit based on a Zener-Jones expansion matches the data well over the entire field range. The reason for this is simple: in contrast to those used in the original Hall effect work with $\rho_{ab0} = 0.9 \mu \Omega$cm [8], the best modern crystals with $\rho_{ab0} = 90 \mu \Omega$cm are so pure ($\ell = 1.1 \mu$m) that the strong-field regime ($\omega_c \tau > 1$) can be reached at fields as low as 4 T. This high value of $\omega_c \tau$ completely invalidates the use of any fitting based on the Zener-Jones expansion. Instead, we observe almost perfect linearity of $\rho_H$ at high fields (shown as dashed line), with a value of $R_H$ of $-2.1 \times 10^{-10}$ m$^3$/C. In line with the results of classic measurements on pure elemental metals [11, 19], this is in much better agreement with a calculation based on the full Fermi volume (i.e. the volume of the hole Fermi-Surface sheet minus that of the two electron sheets) than the weak-field value of $-0.71 \times 10^{-10}$ m$^3$/C.

The fact that the Hall resistivity can be accounted for so well in terms of an analysis based on orbital effects already gives good evidence that such effects dominate the transport properties of doped Sr$_2$RuO$_4$. This assertion is further confirmed by analysis of the transverse magnetoresistance $\Delta \rho_{ab}/\rho_{ab}$, which we show in Fig. 2. Just as in the case of the Hall effect, the next term in the Zener-Jones expansion (a negative term in $(\omega_c \tau)^2$) is seen to play an increasing role as $y$ is decreased. For $y = 0$, saturation is seen in the magnetoresistance, and the data can be fitted very well with the simplest form of an expression for magnetoresistance going beyond the
FIG. 1: The magnetic field dependence of the Hall resistivity $\rho_H$ in Sr$_{2-y}$La$_y$RuO$_4$. The dashed line emphasizes the linear field dependence of $\rho_H$ at high fields in pure Sr$_2$RuO$_4$ with $\rho_{ab0}=90$ n$\Omega$cm. For comparison, the Hall resistivity in Sr$_2$Ru$_{1-x}$Ti$_x$O$_4$ with $x=0.01$ is also shown. It is linear over the whole field range, because $\rho_{ab0}=5$ $\mu$$\Omega$cm and so only the weak-field regime can be accessed in fields up to 12 T.

Zener-Jones expansion, namely that based on two fluids (one of electrons and one of holes) [20]:

$$\frac{\Delta \rho_{ab}}{\rho_{ab}} = \frac{p(\omega_c\tau)^2}{1 + q(\omega_c\tau)^2}. \quad (3)$$

The overall conclusion drawn from the analysis of the data shown in Figs. 1 and 2 is that orbital effects mainly dominate the magnetotransport of Sr$_2$RuO$_4$.

In order to set the scene for the discussion of the weak-field Hall coefficient, we show in Fig. 3 the rigid-band shift prediction for the evolution of $k_F$ as a function of $y$ in Sr$_{2-y}$La$_y$RuO$_4$. Although these are predicted values, they are based on an empirically constrained band structure [12] and have been verified by direct measurement of quantum oscillations for $y \leq 0.06$ [13]. The main feature is the change in $k_F$ for the $\gamma$ band at $y=0.23$, which

FIG. 2: Magnetoresistance of Sr$_{2-y}$La$_y$RuO$_4$ with $y$ up to 0.27 as a function of $(\omega_c\tau)^2$. The inset shows the magnetoresistance in pure Sr$_2$RuO$_4$ as a function of $\omega_c\tau$. The curve running through the data is a fit using Eq. 3.

FIG. 3: Theoretical prediction of the dependence of the Fermi wave-vectors of the $\alpha$, $\beta$ and $\gamma$ bands on additional electron doping in Sr$_2$RuO$_4$, obtained using a tight-binding calculation. Note that the $\gamma$ Fermi surface changes from electron-like (solid lines in the inset) to hole-like (dotted lines in the inset) when the Fermi energy moves beyond the van Hove singularity for $y > 0.23$. In that case, the sign of the Hall coefficient $R_H$ is predicted to change from negative to positive.
corresponds to crossing of the van Hove singularity that lies approximately 49 meV above the Fermi level in the undoped material \[21\].

As shown in the inset to Fig. 3, the sharp change in the \(k_F\) of the \(\gamma\) sheet coincides with its change from an electron pocket centered on \(\Gamma\) to a hole pocket centered on \(X\). Within the isotropic-\(\ell\) approximation discussed in the introduction, this would lead to a sign reversal not just of the contribution of \(\gamma\) band to \(\sigma_{xy}\) but also of the overall Hall coefficient. The predictions for \(R_H\) deduced from Eq. (1) with "isotropic-\(\ell\)" model (denoted \(R_H^{\text{iso}}\)) are shown as a thin line in Fig. 4. It is expected to be only very weakly \(y\)-dependent everywhere except the point at which \(\gamma\) changes in character from electron-like to hole-like. The disagreement between the prediction of this simple model and the experimental data is clear. A sign reversal is seen in the data, but rather than being at the predicted value of \(y = 0.23\), it occurs centered on \(y ∼ 0.01\).

This observation serves as a topical warning against reading too much into simplified interpretations of the Hall effect in correlated electron metals. Not only does the sign change but the relative change in \(\text{mod}(R_H)\) is as large as a factor of three. All this occurs at a value of \(y\) for which we have already obtained direct experimental proof that there is neither a large change in Fermi-surface topography nor a large change in the magnetic behavior of the system. There is no evidence at all for a quantum critical point at \(y ∼ 0.01\).

In constructing simplified models for the analysis of the Hall effect, two approximations are most commonly used. We have adopted the "isotropic-\(\ell\)" approach in which the assumption is that \(\ell = v_F\tau\) (\(v_F\): Fermi velocity) is the essential quantity in determining transport properties if impurity scattering dominates the relaxation processes, i.e. that \(v_F\) and \(\tau\) are no longer independent in this regime. An alternative that is also sometimes used is to factorize into \(v_F\) and \(\tau\) and then to assume that \(\tau\) is independent of \(k\) in performing the transport integrals \[17\]. In our opinion this latter approach is harder to justify when analyzing low temperature data, but it is also important to point out that its adoption would not account for our observation, because the \(y\) dependence of the Fermi velocities is known to be very weak in this range of doping \[13\].

The results for La doping came as a considerable surprise, because the simple analysis had worked well for both undoped crystals and crystals containing Al impurities \[14\]. In order to obtain a better overall experimental picture of the effect of doping, we have also studied a series of crystals in which non-magnetic Ti\(^{4+}\) has been substituted for the in-plane Ru\(^{4+}\). The results are also shown in Fig. 4. Although there is variation in \(\text{mod}(R_H)\), there is neither a sharp step nor a sign change \[22\].

The interpretation that can be drawn within an orbital analysis of the Hall effect is that each substitution has some band- or even \(k\)-specific effect on the mean free path, invalidating the use of the isotropic-\(\ell\) approxima-

![FIG. 4: The Hall coefficient \(R_H\) (closed circles) plotted against La and Ti concentration. The higher-order contribution \(R_3\) (open circles) obtained by fitting using Eq. (2) is also plotted. The calculated \(R_3\) (denoted \(R_3^{\text{cal}}\)) is based on Eq. (3) of ref. \[3\] (see text for details).](image)
dependent scattering in Sr$_2$RuO$_4$, it would probably end up with so many free parameters that it would be difficult to make a firm judgement on its validity. That is probably the main message from the work reported here. Although the weak-field Hall effect is often referred to as a simple probe of Fermi-surface topography, its simplicity relates more to the ease with which it can be measured than with which it can be interpreted. Even in the low-temperature limit in which its relationship to Fermi-surface topography should be at its clearest, its results can be seriously misleading. Here, we have given a concrete example of a sudden jump in the value of $R_H$ as a function of doping which definitely does not signal a correspondingly large change in Fermi-surface topography.

IV. SUMMARY

We have presented detailed measurements of the Hall effect in La- and Ti-doped single-crystals of Sr$_2$RuO$_4$. Analysis of data taken to high fields argues strongly in favor of an interpretation based dominantly on the orbital Hall effect. In spite of this, we report a pronounced anomaly as a function of La doping that is not simply related to a change in the Fermi surface.

Acknowledgments

The authors thank A.J. Schofield, M. Sing and S.R. Julian for useful discussions. They also thank R.A. Borzi and S.A. Grigera for technical supports and useful comments, Y. Shibata, J. Hori, Takashi Suzuki, and Toshizo Fujita for electron-probe micro-analysis (EPMA) measurements at Hiroshima University. This work was supported by the Grant-in-Aid for Scientific Research (S) from the Japan Society for Promotion of Science (JSPS), by the Grant-in-Aid for Scientific Research on Priority Area ‘Novel Quantum Phenomena in Transition Metal Oxides’ from the Ministry of Education, Culture, Sports, Science and Technology. One of the authors (N.K.) is supported by JSPS Postdoctoral Fellowships for Research Abroad.

[1] C.M. Hurd, The Hall Effect in Metals and Alloys (Plenum Press, 1972).
[2] W. Lee, S. Watauchi, V.L. Miller, R.J. Cava, and N.P. Ong, Science 303, 1647 (2004).
[3] Y. Nakajima, K. Izawa, Y. Matsuda, S. Uji, T. Terashima, H. Shishido, R. Settai, Y. Onuki, and H. Kontani, J. Phys. Soc. Jpn. 73, 5 (2004).
[4] P. Coleman, C. Pépin, Q. Si, and R. Ramazashvili, J. Phys. Condens. Matter 13, R723 (2001).
[5] A. Yeh, Y. Soh, J. Brooke, G. Aeppli, T.F. Rosenbaum, and S.M. Hayden, Nature 419, 459 (2002).
[6] M.R. Norman, Q. Si, Y.B. Bazailly, and R. Ramazashvili, Phys. Rev. Lett. 90, 116601 (2003).
[7] N.P. Ong, Phys. Rev. B 43, 193 (1991).
[8] A.P. Mackenzie, N.E. Hussey, A.J. Diver, S.R. Julian, Y. Maeno, S. Nishizaki, and T. Fujita, Phys. Rev. B 54, 7425 (1996).
[9] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz, and F. Lichtenberg, Nature 372, 532 (1994).
[10] A.P. Mackenzie and Y. Maeno, Rev. Mod. Phys. 75, 657 (2003).
[11] A.P. Mackenzie, S.R. Julian, A.J. Diver, G.J. McMullan, M.P. Ray, G.G. Lonzarich, Y. Maeno, S. Nishizaki, and T. Fujita, Phys. Rev. Lett. 76, 3786 (1996).
[12] C. Bergemann, A.P. Mackenzie, S.R. Julian, D. Forsythe, and E. Ohmichi, Adv. Phys. 52, 639 (2003).
[13] N. Kikugawa, A.P. Mackenzie, C. Bergemann, R.A. Borzi, S.A. Grigera, and Y. Maeno, unpublished. (cond-mat/0403337)
[14] L.M. Galvin, R.S. Perry, A.W. Tyler, A.P. Mackenzie, S. Nakatsuji, and Y. Maeno, Phys. Rev. B 63, 161102(R) (2001).
[15] N. Kikugawa, C. Bergemann, A.P. Mackenzie, and Y. Maeno, unpublished. (cond-mat/0211248 v2)
[16] N. Kikugawa and Y. Maeno, Phys. Rev. Lett. 89, 117001 (2002).
[17] M. Minakata and Y. Maeno, Phys. Rev. B 63, 180504(R) (2001).
[18] N. Kikugawa, A.P. Mackenzie, and Y. Maeno, J. Phys. Soc. Jpn. 72, 237 (2003).
[19] N.W. Ashcroft and N.D. Mermin, Solid State Physics (Thomson Learning, 1976).
[20] A.W. Tyler, Y. Ando, F.F. Balakirev, A. Passner, G.S. Boebinger, A.J. Schofield, A.P. Mackenzie, and O. Laborde, Phys. Rev. B 57, 728(R) (1998), and references therein.
[21] According to ref. 18, the instability point occurs for $y \approx 0.20$. The difference from $y = 0.23$ is probably because the decrease of the $c$-axis lattice parameter with La doping, which lowers the $\gamma$ band relative to the others, might not be negligible for higher concentration.
[22] For simplicity, $R_H^{\text{cal}}$ in Sr$_x$Ru$_{1-x}$Ti$_2$O$_4$ assumes that the Fermi wave-vector is unchanged with $x$ for all bands, although a (tiny) SDW gap should be opened for $x \geq 0.025$.
[23] We note that the $R_H$ as a function of both La and Ti concentrations shows cusps corresponding to each magnetic instability point at $y \approx 0.20$ and $x \approx 0.025$.
[24] Y. Sidis, M. Braden, P. Bourges, B. Hennion, S. NishiZaki, Y. Maeno, and Y. Mori, Phys. Rev. Lett. 83, 2520 (1999).
[25] M. Braden O. Friedt, Y. Sidis, P. Bourges, M. Minakata, and Y. Maeno, Phys. Rev. Lett. 88, 197002 (2002).
[26] I.I. Mazin and D.J. Singh, Phys. Rev. Lett. 82, 4324 (1999).
[27] M. Sing, private communication.