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<td>Citation</td>
<td>Physical Review Letters (2013), 110(7)</td>
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<tr>
<td>Issue Date</td>
<td>2013-02</td>
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<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/170062">http://hdl.handle.net/2433/170062</a></td>
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<td>Rights</td>
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<td>Type</td>
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First-Order Superconducting Transition of Sr$_2$RuO$_4$

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(Received 5 June 2012; revised manuscript received 31 October 2012; published 14 February 2013)

By means of the magnetocaloric effect, we examine the nature of the superconducting-normal (S-N) transition of Sr$_2$RuO$_4$, a most promising candidate for a spin-triplet superconductor. We provide thermodynamic evidence that the S-N transition of this oxide is of first order below approximately 0.8 K and only for magnetic field directions very close to the conducting plane, in clear contrast to the ordinary type-II superconductors exhibiting second-order S-N transitions. The entropy release across the transition at 0.2 K is 10% of the normal-state entropy. Our result urges an introduction of a new mechanism to break superconductivity by magnetic field.

DOI: 10.1103/PhysRevLett.110.077003

PACS numbers: 74.70.Pq, 74.25.Bt, 74.25.Dw, 75.30.Sg

The order of a phase transition provides one of the most fundamental pieces of information of the long-range ordered state accompanied by the phase transition. In the case of superconductivity, the order of the superconducting-normal (S-N) transition in magnetic fields reflects how the superconductivity interacts with the magnetic field and how it is destabilized. For example, for a type I superconductor, the in-field S-N transition is a first-order transition (FOT) [1], because of an abrupt disappearance of the superconducting (SC) order parameter caused by the excess energy for magnetic-flux exclusion. For a type II superconductor, in contrast, the in-field S-N transition is ordinarily a second-order transition (SOT) [1]. In this case, penetration of quantized vortices with accompanying kinetic energy due to orbital currents leads to a continuous suppression of the SC order parameter up to the upper critical field $H_{c2}$. This type of pair breaking is called the orbital effect.

A well-known exception for type II superconductivity is the case where the superconductivity is destroyed by the Zeeman spin splitting [2]. When the spin susceptibility in the SC state, $\chi_{sc}$, is lower than that in the normal state, $\chi_n$, the SC state acquires higher energy $\Delta E_Z = (1/2)(\chi_n - \chi_{sc})\mu_0H^2$ with respect to the normal state, due to the difference of polarizability of the electron spin. This destroys superconductivity at the Pauli limiting field $\mu_0H_p \sim [2\mu_0E_{cond}/(\chi_n - \chi_{sc})]^{1/2}$, where $\Delta E_Z$ reaches the SC condensation energy $E_{cond}$. Such a pair-breaking effect is called the Pauli effect. It is theoretically predicted that a strong Pauli effect leads to a first-order S-N transition at temperatures sufficiently lower than the critical temperature $T_c$ [3]. This prediction has been confirmed in a few spin-singlet superconductors [4-6].

The type II superconductor Sr$_2$RuO$_4$ ($T_c = 1.5$ K) is one of the most promising candidates for spin-triplet superconductors [7-9]. Due to its unconventional superconducting phenomena originating from the orbital and spin degrees of freedom as well as from the nontrivial topological aspect of the SC wave function, this oxide continues to attract substantial attention [10-14]. The spin-triplet state has been directly confirmed by extensive spin susceptibility measurements by means of the nuclear magnetic resonance (NMR) using several atomic sites [15-17] and the polarized neutron scattering [18]: Both experiments have revealed $\chi_{sc} = \chi_n$ in the entire temperature-field region investigated. This means that $H_p \propto (\chi_n - \chi_{sc})^{-1/2}$ is infinite and the Pauli effect is irrelevant in this material.

Interestingly, several properties of the S-N transition of Sr$_2$RuO$_4$ have not been understood for more than 10 years within the existing scenarios for the spin-triplet pairing. For example, $H_{c2}(T)$ is more suppressed than the expected behavior for the orbital effect, when the field is parallel to the conducting $ab$ plane [19-21]. In addition, several quantities such as the specific heat $C$ [20], thermal conductivity $\kappa$ [20], magnetization $M$ [22], exhibit sudden recovery to the normal-state values near $H_{c2}$ for $H \parallel ab$ and at low temperatures.

To resolve the origin of such unusual behavior, we performed measurements of the magnetocaloric effect (MCE) of Sr$_2$RuO$_4$. The MCE is a change of the sample temperature $\tilde{T}$ in response to a variation of the external magnetic field $H$; we measure $\tilde{T}$ while sweeping $H$ at a constant rate. The thermal equation of the MCE is written as [23]

$$\left(\frac{\partial S}{\partial H}\right)_T = -\frac{C}{\tilde{T}}\frac{d\tilde{T}}{dH} - k\frac{T - T_{bath}}{\tilde{T}} - \frac{1}{\tilde{T}}\frac{dQ_{loss}}{dH},$$

where $S$ is the entropy, $C$ is the heat capacity of the sample, $k$ is the thermal conductance between the sample and thermal bath, $\tilde{H}$ is the sweep rate of the magnetic field, $T_{bath}$ is the temperature of the thermal bath, and $dQ_{loss}$ is the dissipative loss of the sample. When $k$ is small so that the second term is negligible, the equation reduces to the relation for the conventional adiabatic MCE. In the other limit where the thermal coupling between the sample and bath is strong, the first term in turn becomes negligible, leading to the “strong-coupling limit” relation [23] $\partial S/\partial H \approx -(k\Delta t/H) - T^{-1}(dQ_{loss}/dT)$ with $\Delta t = (T - T_{bath})/T$ [24]. In this
limit, the measured $\Delta t$ is linearly dependent on $(\partial S/\partial H)_T$. Thus, it is expected that $T$ and $\Delta t$ exhibit peak-like anomalies at a FOT and step-like anomalies at a SOT. Because of this qualitative difference, the strong-coupling MCE is suitable to distinguish a FOT and a SOT. We found that our calorimeter indeed works almost in this strong-coupling limit, with the first term in Eq. (1) amounting to at most 10% of the second term. We however didn’t neglect the first term in the evaluation of the entropy discussed below.

For the present study, we used single crystals of Sr$_2$RuO$_4$ grown by the floating-zone method [25]: Sample 1 weighing 0.684 mg with $T_c = 1.45$ K and sample 2 weighing 0.184 mg with $T_c = 1.50$ K. The value of $T_c$ of sample #2 is equal to the ideal Sr$_2$RuO$_4$ in the clean limit [26], indicating its extreme cleanness. The MCE was measured using a hand-made sensitive calorimeter. Magnetic field was applied using a vector magnet system [27]. Details of the experimental method is described in the Supplemental Material [24].

We first present the MCE for $H \parallel ab$ ($H \sim |100|$) and $T \sim 0.2$ K measured at $\mu_0 H = \pm 1.02$ mT/sec in Figs. 1(a) and 1(b). Obviously, $T(H)$ exhibits peak-like behavior near $H_{c2}$, rather than a single step-like behavior. This feature becomes clearer in the background-subtracted $\Delta t(H)$ (up-sweep) and $\Delta t(H)$ (down-sweep) curves shown in Figs. 1(c) and 1(d) [24]. The observed peak provides indication of a FOT in Sr$_2$RuO$_4$. Note that a slight asymmetry in the MCE signal (i.e., $|\Delta t_1(H)| < |\Delta t_1(H)|$) is attributed to the energy dissipation mainly due to vortex motion causing a heating in both the field up-sweep and down-sweep measurements [28]. More importantly, $H_{c2}$ is clearly different between the up-sweep and down-sweep curves. The difference between the up-sweep onset $H_{c2}$ and the down-sweep onset $H_{c2}$ is approximately $\mu_0 \Delta H_{c2} = \mu_0 (H_{c2} - H_{c2}) = 20$ mT for sample #1 and 15 mT for sample #2. This difference corresponds to 15–20 sec for $\mu_0 H = 1.02$ mT/sec. The difference cannot be attributed to an extrinsic delay of the temperature measurement, since the delay time of our apparatus is much shorter than 15–20 sec [29]. We have also confirmed that a finite $\Delta H_{c2}$ is observed for lower sweep rates such as $\mu_0 H = \pm 0.2$ mT/sec. Therefore, this difference of $H_{c2}$ is indeed intrinsic, and provides definitive evidence that the S-N transition is a FOT accompanied by supercooling (or possibly superheating). Note that the very sharp peak in $\Delta t(H)$ at $H_{c2}$ for sample #2 demonstrates the cleanness and homogeneity of this sample.

Next, we focus on the variation of the MCE with temperature and field angle. As represented in Figs. 1(c) and 1(d), both the peak in $\Delta t(H)$ and the supercooling becomes less pronounced as temperature increases. Around 0.8 K, these features totally disappear and the S-N transition becomes a SOT as expected for ordinary type II superconductors. In Fig. 2, we present several MCE curves for fields tilted away from the $ab$ plane toward the $c$ axis by the amount which we define as $\theta$. When the field is tilted only by $\sim 2$ degrees, the FOT features disappear.

From the MCE data for $H \parallel ab$, we deduce the entropy using Eq. (1) [24]. Figure 3(a) again characterizes the FOT with a huge peak in $(\partial S/\partial H)_T$ and supercooling or

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**FIG. 1** (color online). (a), (b) Representative raw data of the MCE of Sr$_2$RuO$_4$ for $T \sim 0.2$ K at $H \parallel ab$ ($H \sim |100|$). The dotted curves indicate $T_{bg} - T_0$ for the up sweep (pink or darker gray) and the down sweep (cyan or lighter gray), which corresponds to the background contribution [24]. (c), (d) Relative temperature change $-\Delta t_1$ (red or lighter gray) and $\Delta t_1$ (blue or darker gray) due to the MCE for the same field condition at different temperatures. For clarity, each pair of curves is shifted vertically by 0.25% and 0.4% for panels (c) and (d), respectively. The high-temperature ($T > 0.6$ K) data in (d) are multiplied by 5.

**FIG. 2** (color online). Field angle $\theta$ variation of the MCE of sample #2 at $T \sim 0.2$ K. The red (lighter gray) and blue (darker gray) curves indicate $-\Delta t_1(H)$ and $\Delta t_1(H)$, respectively. Each curve is shifted vertically by 0.5% and the data for $\theta \geq 2.0^\circ$ are multiplied by 3 for clarity.
tency of this value using the Clausius-Clapeyron equation

diagrams presented in Figs. 4 and 5. The region for
explained in the Supplemental Material [24].
(b) illustrates the jump
we obtain
R
S=T
axis of (b) indicates
curves present up- and down-sweep data, respectively. The right
S=T
[30]. The jump in
FIG. 3 (color online). (a) Field dependence of
ðµ0T Þ−1 × (δS/δH)T ’ of Sr2RuO4 deduced from the MCE. (b) Field dependence of ΔS/T. In both (a) and (b), the main panels present data for sample 2 and the insets for sample 1; the solid and broken curves present up- and down-sweep data, respectively. The right axis of (b) indicates S/T obtained by assuming Sn/T = 37.5 mJ/K²mol [30]. The double-headed arrow in (b) illustrates the jump ΔS/T = −3.5 ± 1 mJ/K²mol at the transition.

superheating. In Fig. 3(b), we present ΔS = S − Sn = ∫Hc2(δS/δH)γdH divided by temperature. Here, Sn is the entropy in the normal state. The total entropy S can be calculated with the assumption Sn/T = γe, where γe = 37.5 mJ/K²mol is the electronic specific heat coefficient [30]. The jump in S/T across the FOT is approximately δS/T = −3.5 ± 1 mJ/K²mol at the lowest measured temperatures. This value of δS/T amounts to approximately 10% of Sn/T, and the latent heat L = TδS at 0.2 K is 0.14 ± 0.04 mJ/mol. We can check the consistency of this value using the Clausius-Clapeyron equation

μ0dHc2/dT = −δS/δM, where δM is the jump in M across the FOT. Using the values μ0dHc2/dT ~ −0.20 ± 0.05 T/K estimated from our Hc2 data for sample #2 and δM ~ −0.014 emu/g from the magnetization study [31], we obtain δS/T = −4.7 ± 1.2 mJ/K²mol for 0.2 K. This value reasonably agrees with the value from our MCE experiment. In addition, S at lower fields also exhibits agreement with other thermodynamic studies [20,22], as explained in the Supplemental Material [24].

We summarize the present observations in the phase diagrams presented in Figs. 4 and 5. The region for which the FOT emerges is limited to temperatures below T_FOT ~ 0.8 K for θ = 0° and field angles within |θ| < 2° for T ~ 0.2 K. Interestingly, the FOT region is included in a wider region in which the behavior of Hc2 cannot be described solely by the conventional orbital effect [21]: Hc2(T) substantially deviates from the linear behavior and Hc2(θ) cannot be fitted with the effective mass model (Fig. 5). These facts indicate that the ordinary orbital effect cannot be an origin of the FOT.

Let us compare the present results with previous observations. The rapid recoveries of κ/τ [20] and M [22] near Hc2 for H ∥ ab have been observed in the region where the S-N transition is revealed to be of first order. Thus, it now turns out that these recoveries are actually consequences of the FOT. However, supercooling (or superheating) at the S-N transition in Sr2RuO4 has never been reported in previous studies. This is probably because the supercooled metastable normal state easily nucleates into the SC state. Thus, a fast and continuous sweep is helpful to observe the supercooling, rather than point-by-point measurements.

FIG. 4 (color online). Superconducting phase diagram of Sr2RuO4 for H ∥ ab (H ~ [100]) deduced from the MCE for sample 2. The red squares and the blue crosses indicate the onset Hc2 for the up- and down-sweeps, respectively. The inset presents Hc2 and ΔHc2 (triangles) in the low-temperature region.

FIG. 5 (color online). Field-angle dependence of Hc2 (squares) and ΔHc2 (circles) at T ~ 0.2 K. The green curve indicates the fitting to the data of sample #1 in the range |θ| > 2.0° [21] with the effective mass model Hc2(θ) = Hc2(90°)/(sin²θ + cos²θ/Γ²)½, where Γ is the anisotropy parameter and is obtained to be 25 from the fitting.
The smallness and cleanness of the present samples have also assisted the observation, because the number of nucleation centers (e.g., surface defects, lattice imperfections) is reduced for small and clean samples. In contrast to the previous studies on the bulk SC phase, a hysteresis in the in-field S-N transition was observed for the interfacial 3 K phase superconductivity in the Sr$_2$RuO$_4$-Ru eutectic [32,33]. Possible relation between this hysteresis and the spectroscopy [41]. Such a pinning of the spin direction may be directly applied as long as the orbital motion is assumed to be purely two dimensional. As another macro- or mesoscopic mechanism, the kinematic polarization discussed in the context of the stability of the half-quantum vortex is instructive [14,44]. It was proposed that a velocity mismatch between $|\uparrow\rangle$ and $|\downarrow\rangle$ condensates around a half-quantum vortex results in a shift of the chemical potential of these two condensates due to difference in their kinetic energies and leads to an additional spin polarization coupling to the magnetic field. By an analogy to this theory, we expect that consideration of kinematics of the condensates in high fields may provide a route to unveil the nontrivial coupling between the Cooper pair and magnetic field.

In summary, our MCE study of Sr$_2$RuO$_4$ revealed definitive evidence for a first-order S-N transition in the low-temperature region for fields nearly parallel to the $ab$ plane. The FOT, not attributable to conventional mechanisms, indicates a nontrivial interaction between spin-triplet superconductivity and magnetic field. This new information on the bulk superconductivity serves as a basis for investigations of the nontrivial topological nature of the SC wave function associated with the “Majorana-like” edge modes. We also anticipate that the abrupt growth of the order parameter across the FOT, accompanied by vortex formation and nontrivial symmetry breaking, should provide a new playground for investigation of novel vortex dynamics, which might be related to quantum turbulence and/or to the Kibble-Zurek mechanism.

We acknowledge Z.Q. Mao and F. Hübler for their contributions to crystal growth, T. Nakamura for his support, and K. Ishida, K. Machida, M. Sigrist, Y. Yanase, D.F. Agterberg, T. Nomura, K. Tenya, and K. Deguchi for useful discussions. We also acknowledge KOA Corporation for providing us with their products for the calorimeter. This work is supported by a Grant-in-Aid for the Global COE “The Next Generation of Physics, Spun from Universality and Emergence” and by Grants-in-Aid for Scientific Research (KAKENHI Grants No. 22103002, No. 23540407, and No. 23110715) from MEXT and JSPS.


[28] Systematic evolution of the asymmetric component with respect to the temperature and field direction supports our scenario that the asymmetric component is dominated by energy dissipation in the samples. Nevertheless, at present, we cannot deny small contributions of extrinsic origins (such as a tiny error in the temperature measurement).

[29] The thermal relaxation time is approximately 3 sec for sample #1, and the delay time of the electronics is chosen to be smaller than 1 sec. The overall delay time of our equipment is at most 5 sec for sample #1 and even shorter for sample #2.


[31] Here we linearly interpolated δM at 0.14 K (∼−0.015 emu/g) and 0.41 K (∼−0.010 emu/g) reported in Ref. [22].


[35] Here, we used the value \( \chi_{\text{ex}} = \chi_{n} \sim 0.9 \times 10^{-3} \text{ emu/mol} \) [8]. The value of \( E_{\text{cond}} \) is obtained from the relation \( E_{\text{cond}} = \frac{1}{2} \mu g H_{c}^{2} \) with the thermodynamic critical field \( \mu g H_{c} = 0.0194 T \) [19].


