Quenched metastable vortex states in Sr$_2$RuO$_4$

D. Shibata,$^1$ H. Tanaka,$^2$ S. Yonezawa,$^1$ T. Nojima,$^3$ and Y. Maeno$^1$

$^1$Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
$^2$Faculty of Science, Kyoto University, Kyoto 606-8502, Japan
$^3$Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

(Dated: November 25, 2014)

Sr$_2$RuO$_4$, a leading-candidate spin-triplet superconductor and a highly anisotropic quasi-two-dimensional type-II superconductor, provides unique opportunity to study unconventional as well as conventional vortex phases. To investigate its vortex-matter phases, we studied the ac susceptibility of Sr$_2$RuO$_4$ for fields parallel to the RuO$_2$ plane by adapting two different thermal processes: In addition to the ordinary field sweep (FS) process, we newly employed the “each-point field cooling (EPFC)” process, in which the superconductivity is once thermally destroyed before collecting the data. We find that the ac susceptibility signal substantially changes with the EPFC process. This result indicates that we succeed in inducing new metastable vortex states by the EPFC process. We also find a new field scale $H^\ast$, below which the FS and EPFC processes provide the same value of the ac susceptibility. This new field scale suggests a liquid-like vortex state in the low-field region.

I. INTRODUCTION

In a large part of the field-temperature superconducting phase diagram of a type-II superconductor below its critical temperature $T_c$, magnetic quantum vortices penetrating the superconductor exhibit a number of vortex-matter phases depending on strengths of vortex-vortex interaction, thermal fluctuation, pinning energies by lattice defects, etc. Although such vortex-matter phases have been extensively studied in high-$T_c$ cuprate superconductors, superconductors with lower $T_c$ (e.g. NbSe$_2$, CeRu$_2$, etc.) also exhibit vortex phase transitions. In such low-$T_c$ superconductors, vortices at low fields form a quasi-long-range-ordered lattice, which is called as the vortex Blagg glass (VGB). This is because the arrangement of vortices is mostly governed by the repulsive vortex-vortex interaction. As the magnetic field is increased, vortex lattice becomes softer, because the vortex-vortex interaction becomes weaker. Then, near the upper critical field $H_{c2}$, other interactions can become dominant. As a result, the VBG state changes into the vortex glass (VG) state, in which vortices form a glassy structure without long-range ordering due to a dominance of vortex pinning. As the field is further increased, thermal fluctuation then becomes dominant and the VG melts into the vortex liquid (VL), where vortices can move individually.

It is now widely known that the measurement of the ac susceptibility $\chi_{ac} \equiv \chi = i\chi''$ is a powerful technique to explore the vortex matter phases. One example is the peak effect, which is the occurrence of an anomalous maximum in the shielding signal $\chi$ near $H_{c2}$. In weakly pinned superconductors, the onset of the peak effect corresponds to the VBG-VL transition and the peak top corresponds to VG-VL transition. Another example is hysteretic behavior in $\chi_{ac}$. It is often observed that the field cooling (FC) process and the zero field cooling (ZFC) process lead to different values of $\chi_{ac}$. Such differences originate from hysteretic vortex configurations mainly caused by vortex pinning. In typical cases, an ordered vortex lattice state and a disordered vortex amorphous/glass-like state are achieved by the ZFC and FC processes, respectively.

Sr$_2$RuO$_4$, a layered perovskite superconductor with $T_c$ = 1.5 K, has been extensively studied due to its unconventional pairing state. Spin susceptibility measurements with the nuclear magnetic resonance (NMR) and with the polarized neutron scattering indicate the spin part of the Cooper pair is in the spin-triplet state. Muon-spin rotation and optical Kerr effect studies have revealed that the superconducting state of Sr$_2$RuO$_4$ is of chiral-$p$-wave, in which two degenerate order parameters form a complex linear combination, breaking the time reversal symmetry. Recently, a non-trivial topological nature of the chiral-$p$-wave superconducting wave function has been attracting wide attention. Such a chiral-$p$-wave spin-triplet superconductor has spins and orbital degrees of freedom in its superconducting order parameter. Thus, it is expected that magnetic field affects such degrees of freedom and leads to emergence of new superconducting phases. Indeed, such multiple phases have been observed in UPt$_3$. In case of Sr$_2$RuO$_4$, a previous specific-heat study reported possible existence of new phases in the vicinity of $H_{c2}$. However, more recent studies with a smaller crystal did not reproduce the result. Thus, it is still an open question whether the superconducting multiphase exists in Sr$_2$RuO$_4$ or not.

Sr$_2$RuO$_4$ has another interesting aspect as a highly anisotropic quasi-two-dimensional superconductor, reflecting its layered crystal structure. The anisotropy in the upper critical field $H_{c2}$, $\Gamma_H = H_{c2||ab}/H_{c2||c}$, is 20 for $T \to 0$. On the other hand, recent studies indicate that the intrinsic superconducting anisotropy $\Gamma_1 = \xi_{ab}/\xi_c$ is as large as 60. This large anisotropy may lead to interesting vortex phase formation in this material.
that, however, its coherence length along the c axis is estimated to be \( \xi_c(0) \sim \xi_c(0)/60 \sim 13 \text{ Å} \), being still larger than the interlayer spacing \( c/2 \sim 6 \text{ Å} \). Thus, interlayer coherence should be maintained in \( \text{Sr}_2\text{RuO}_4 \), in clear contrast to high-\( T_c \) cuprates, whose interlayer coherence can be vanishingly small.

Considering these situations, investigation of the vortex phase diagram in \( \text{Sr}_2\text{RuO}_4 \) is quite interesting and important. Firstly, to distinguish between the ordinary vortex-matter phases and unconventional superconducting multiphases originating from the spin-triplet order parameter, it is important to understand the vortex phase diagram in detail. Secondly, this oxide provides an unique opportunity to study vortex phases in highly anisotropic low-\( T_c \) superconductivity. Previously, the small-angle neutron scattering (SANS) measurement revealed vortex lattices in some regions of the \( H-T \) phase diagram both for \( H \parallel a \) and \( H \parallel c \).\(^{29,31} \) However, details of the vortex phase diagram has not been explored. In addition, although \( \chi_{ac} \) of \( \text{Sr}_2\text{RuO}_4 \) has been reported,\(^{32-34} \) effects of different thermal/field treatments have not been investigated.

In this paper, we report \( \chi_{ac} \) of \( \text{Sr}_2\text{RuO}_4 \) for \( H \parallel ab \) measured with a newly developed thermal/field process as well as with a conventional field-sweep process. With the new process, we succeed in systematically inducing metastable vortex states. By comparing \( \chi_{ac} \) results with different thermal treatments, we obtain a vortex phase diagram with a new phase boundary at low fields.

II. EXPERIMENTAL

We used single crystalline \( \text{Sr}_2\text{RuO}_4 \) grown by a floating-zone method.\(^{25} \) The sample used in this study has the size of \( 1.5 \times 6.0 \times 0.1 \text{ mm}^3 \), and was cut from the crystal boule used for the SANS measurements.\(^{29} \) Zero-field \( \chi_{ac} \) measurements revealed the transition at \( T_c = 1.45 \text{ K} \), which is defined as the mid-point temperature of the real part \( \chi' \). The directions of the tetragonal crystalline axes of the sample were determined from X-ray Laue pictures. After cut, we glued two strain gauges with a resistance of 120 Ω (Kyowa Dengyo, KFRS-02-120-C1-13 L1M3R) as heaters onto the \( ab \)-surfaces of the sample directly. We heat-treated the sample at up to \( 150^\circ \text{C} \) for several hours in order to glue heaters. This heat treatment may have served as a gentle annealing process.

The sample together with the heaters was glued to a sapphire rod with varnish (GE7031) and placed in a mutual-inductance coil, consisting of a counter-wound pick-up coil with 3300 turns and an excitation coil with 860 turns. A string of gold wire (\( \phi = 25 \mu\text{m} \) is also attached between the sample and the thermal bath to achieve faster thermal equilibrium. Measurements of \( \chi_{ac} \) were performed with an ac field of 0.66 \( \mu\text{T-rms} \) at the frequency of 3011 Hz. The direction of the ac field is within the \( ab \) plane and about 10 degrees away from the [100] axis. The configuration of the sample assembly and magnetic field directions is schematically shown in Fig. 1(a). The sample assembly was cooled down to below 0.1 K with a \( ^3\text{He}-^4\text{He} \) dilution refrigerator (Oxford Instruments, Kelvinox-25). The dc magnetic field \( H_{dc} \) was applied using a vector magnet system.\(^{35} \) Based on the strong anisotropy of \( H_{c2} \) of \( \text{Sr}_2\text{RuO}_4 \), the field directions were determined with accuracies within 0.01° with respect to the \( ab \) plane and within 1° with respect to the direction within the plane.

![FIG. 1. (a) Schematic of the sample mounted in an ac susceptometer coils. The sample, shown in black, is placed in one part of the pick-up coil. Two different thermal processes, (b) field sweep (FS) process and (c) each-point field cooling (EPFC) process, were used in this study.](image)

In this paper, we measured \( \chi_{ac} \) in two different thermal processes, as depicted in Figs. 1(b) and (c). The first process is an ordinary field sweep (FS): the sample was cooled down to each target temperature in zero field and, kept at that temperature, the data was collected at each field on a field up-sweep sequence, followed by a field down-sweep sequence. The second process is the “each-point field cooling (EPFC)”. In this process, the sample at each field \( H_{dc} \) was once quickly heated up to above \( T_c(H_{dc}) \) using the sample heaters and cooled back to the target temperature before collecting the data as described in Fig. 1(c). We confirmed by the \( \chi_{ac} \) signal that the sample is indeed heated up to above \( T_c(H_{dc}) \) to become the normal state. After collecting the data, \( H_{dc} \) was changed before the next sequence of the heating, cooling, and data collection. As shown below, metastable vortex states can be induced with this latter process. Although we measured both the real and imaginary parts of \( \chi_{ac} \), the imaginary part was too small. Thus, in this paper, we only discuss the real part. In order to subtract \( \chi' \) contribution from normal state and background, we adopt \( \chi_{SC} = \chi'(T, H) - \chi'(2.0 \text{ K}, H) \) as already done in Ref. 34. We furthermore scaled \( \chi_{SC} \) so that \( \chi_{SC} = -1 \) at \( H_{dc} = 0 \) and \( T = 0.1 \text{ K} \).
III. RESULTS

In Fig. 2(a), we present $\chi_{\text{SC}}'(H_{dc})$ obtained with the FS and EPFC processes for $H_{dc} \parallel [110]$ at several temperatures. First, we focus on results of the ordinary FS process. The $\chi_{\text{SC}}'(H_{dc})$ curve of the FS process has a characteristic peak/dip structure near $H_{c2}$. This behavior resembles the peak effect observed in many ordinary type-II superconductors and is consistent with previous reports on Sr$_2$RuO$_4$. The origin of this behavior will be discussed later. Note that the curves contain data of field-up and down sweeps; We didn’t observe any hysteresis between field-up and down sweeps except for near $H_{c2}$ at low temperatures where the superconducting transition is of first order. This absence of hysteresis in the FS branch in the superconducting state implies that the pinning effects are rather weak in this material so that one cannot achieve metastable vortex phases with the ordinary FS process.

Next, we focus on the $\chi_{\text{SC}}'$ data of the EPFC process for $H_{dc} \parallel [110]$ in Fig. 2(a). Interestingly, the $\chi_{\text{SC}}'(H_{dc})$ curves for the EPFC process are very different from those for the FS process. Thus, we succeeded in inducing new vortex states by the EPFC process. The shielding signal $|\chi_{\text{SC}}'(H_{dc})|$ in the FS branch is smaller than that in the EPFC branch in all investigated field and temperature conditions. This behavior indicates that the vortices in the EPFC branch are harder to move than those in the FS branch.

In order to investigate the stability of the EPFC-induced state, we tried other field/thermal processes. Firstly, we applied a small dc-field cycling with the amplitude $\delta H_{dc}$ to the EPFC branch just before collecting data as schematically explained in the inset of Fig. 3(a). As shown in Fig. 3(a), the EPFC branch changes toward the FS branch with increasing $\delta H_{dc}$. A field cycling of as small as 0.001 T is sufficient for the EPFC branch to merge into the FS branch. Larger field-cycling amplitude does not change the FS branch to other branches. Secondly, we performed ordinary FS after a EPFC process at $\mu_0 H_{dc} = 1.263$ T as presented in Fig. 3(b). We found that $\chi_{\text{SC}}'$ rapidly changes once the FS process started. Then $\chi_{\text{SC}}'$ becomes constant at a value very close to that of the FS branch when we swept by more than 0.001 T. These two results are consistent each other and indicate that the vortex state in the EPFC branch is metastable. Our observation also agrees with the general tendencies that the field-cooled vortex states are metastable, and that magnetic field cycling recovers more stable vortex states.

To compare the FS and EPFC branches in more detail, we evaluate the difference $\Delta \chi_{\text{SC}}' = \chi_{\text{SC}}'(\text{FS}) - \chi_{\text{SC}}'(\text{EPFC})$. Note that $\Delta \chi_{\text{SC}}'$ provides a measure of how sensitive the vortex configuration is against field/thermal processes. From the $\Delta \chi_{\text{SC}}'$ data in Fig. 2(c), we can identify several field regions with different responses against field/thermal processes. Firstly, in the lowest field region below a field that we denote by $H^{*1}$, $\Delta \chi_{\text{SC}}'$ is almost zero, indicating that the FS and EPFC branches exhibit the same value. Thus, the vortex configurations achieved by the FS and EPFC processes are nearly the same for fields below $H^{*1}$. We emphasize that this field scale $H^{*1}$ in Sr$_2$RuO$_4$ has not been reported before to our knowledge and is newly revealed owing to the EPFC process employed in the present work. Secondly, above $H^{*1}$, $\Delta \chi_{\text{SC}}'$ becomes larger with increasing field. On further increase of the field, $\Delta \chi_{\text{SC}}'$ starts to decrease beyond an onset field $H^{*2}$. In this region, the FS branch shows a peak-effect-like feature as already explained. Above a field which we denote by $H^{*3}$, $\Delta \chi_{\text{SC}}'$ becomes zero again and both processes yield the same vortex state, probably due to small pinning effect.
χ fields decrease with increasing temperature but remain intersect each other, and $H_{c2}$ extrapolation of the region $H_{FS}$ linear extrapolation in the region $H_{EPFC}$ toward the $FS$ branch by a evolution of the EPFC branch toward the $FS$ branch. We define $\chi_{SC}^{*}$ and $c_{2}$ for the field scales: We adopt the following definitions for the phase diagram, we adopt the following definitions for the field scales: We define $H^{*1}$ as the field where the linear extrapolation in the region $H_{dc} > H^{*1}$ intersects the $\Delta \chi_{SC}^{*} = 0$ line, $H^{*2}$ as the field where the linear extrapolations of $\Delta \chi_{SC}$ increasing and decreasing regions intersects each other, and $H^{*3}$ as the field where the linear extrapolation of the region $H_{dc} < H^{*3}$ intersects the $\Delta \chi_{SC}^{*} = 0$ line, respectively. These three characteristic fields decrease with increasing temperature but remain finite up to the zero-field $T_{c}$. The narrow region between $H_{c2}$ and $H^{*3}$ become a little wider at low temperature. The separation between $H_{c2}$ and $H^{*2}$ is nearly independent of temperature below about 1 K. We note that the metastable state can be induced by the EPFC process in the wide region of the superconducting state surrounded by the $H^{*1}$ and $H^{*3}$ curves.

We performed similar measurements and analyses for $H_{dc} \parallel [100]$ to investigate the in-plane anisotropy. As shown in Fig. 2(b), $\chi_{SC}$ curves for $H_{dc} \parallel [100]$ are similar to those for $H_{dc} \parallel [110]$: The FS curves exhibit peak/dip structure near $H_{c2}$ and the shielding signal in the FS branches is smaller than that in the EPFC branches. However there are some differences. For example, although the $\chi_{SC}$ curves for $H_{dc} \parallel [110]$ at 0.1 K and 0.2 K show a clear peak/dip structure, such structure is rather vague in $\chi_{SC}^{*}(H_{dc})$ for $H_{dc} \parallel [100]$. In addition, the temperature dependence of $H^{*1}$ appears different: $H^{*1}$ for $H_{dc} \parallel [110]$ monotonically decreases as the temperature is increased toward $T_{c}$, whereas $H^{*1}$ for $H_{dc} \parallel [100]$ exhibits a plateau in the range $0.5 K < T < 1.2 K$. As a result, above 0.8 K, $H^{*1}$ for [100] is much larger than that for [110]. We comment here that this difference may be attributed to the difference in the vortex-lattice stability due to the in-plane anisotropy in the superconducting order parameter. Although previous $\chi_{ac}$ study reported additional peak structure near $H_{c2}$ only in the [110] direction, we did not observe such additional peaks in this study possibly because the number of data points was not enough.

### IV. DISCUSSION

First, we briefly summarize our experimental observations. The ordinary FS branch of Sr$_2$RuO$_4$ exhibits peak/dip structure in $\chi_{SC}$ in the field region $H^{*2} < H_{dc} < H^{*3}$, similar to the peak effect in ordinary type-II superconductors such as NbSe$_2$. The peak effect is at-

---

**FIG. 3.** Stability of the EPFC branch against a small cycling of the dc field. (a) Changes of the EPFC state toward the FS state after a small dc-field cycling $\delta H_{dc}$ to a state on the EPFC branch. (b) Results of FS measurements after a EPFC process at $\mu_{0}H_{dc} = 1.263$ T, revealing detailed evolution of the EPFC branch toward the FS branch by a field cycling. The directions of the FS are indicated with arrows. The values of $\chi_{SC}$ in the FS and EPFC processes at 1.265 T are indicated with the broken lines. The insets explain field/thermal treatments in these measurements.

**FIG. 4.** (a)-(b) Field-temperature phase diagrams of Sr$_2$RuO$_4$ for the dc field along the [110] and [100] directions. The black squares indicate $H_{c2}$. The red circles, green triangles, and blue triangles indicate $H^{*1}$, $H^{*2}$, and $H^{*3}$, respectively, derived from the comparison between FS and EPFC branches (see text).
tributed to changes in the vortex phases: the low-field on-
set of the peak effect correspond to the transition between
the ordered VBG state in low fields and the disordered
VG state, and the peak top corresponds to the transition
between the VG and VL states. Therefore, in the ordi-

cinary type-II superconductor, $H^{*2}$ and $H^{*3}$ should corre-
spond to VBG-VG and VG-VL transition lines. Similar
situation is probably realized in Sr$_2$RuO$_4$, although con-
sideration of the first-order superconducting transition is
needed as described below. Indeed, previous SANS
experiments have revealed that the vortices exhibit

clear Bragg reflections in wide regions of the phase dia-
gram for both $H_{dc} \parallel a$ and $H_{dc} \parallel c$, with thermal/field
processes corresponding to our FS process. These results
indicate that the bulk VBG state is formed in such re-
gions. We achieved new metastable vortex phases by
the EPFC process in the region $H^{*1} < H_{dc} < H^{*3}$. By
examining the difference between the EPFC and FS
branches, we are able to determine the accurate value
of the onset $H^{*2}$ of the peak-effect-like feature up to a
high-temperature region, where the peak in $\chi'_{SC}(H_{dc})$ it-
self becomes rather vague. Furthermore, we can get the
new characteristic field $H^{*1}$ signaling disappearance of
metastability in the low-field region.

For $H^{*1} < H < H^{*2}$, we revealed that vortex states in
the EPFC process is metastable and should differ from
the VBG state. There are several possible scenarios ex-
plaining the vortex state in the EPFC process. The first
scenario is that a strongly pinned glassy state is induced
by the EPFC process. Such a glassy state has been in-
deed reported in ordinary type-II superconductors. The
second scenario is that a cleaner lattice is formed after a
EPFC process. This scenario is based on the fact that the
inter-vortex distance only depends on field and cooling
process in EPFC should not change the distance. How-
ever, to the best of our knowledge, such a cleaner lattice
has not been reported in other superconductors. In the
third scenario, a metastable vortex state with vortices
pinned at the surface is realized in the EPFC branch.
Such a surface pinning is called the Bean-Livingston sur-
face barrier and has been indeed observed in high-TC
superconductors and granular superconductors. The
vortices pinned by the surface pinning potential are easily
moved by a small field cycling and are rearranged back
to a more stable bulk VBG configuration.

Let us now discuss the origin of the state for $H < H^{*1}$. Since
the field scale $H^{*1}$ has previously not been known, the
VBG state in the bulk was expected to occupy the whole
region below $H^{*2}$ down to the lower critical field $H_{c1}$, which is approximately 1 mT at $T \sim 0.8$ K. Our obser-
vation of $H^{*1}$, however, forces us to reconsider this naive
expectation. In this region, due to a large inter-vortex
distance, the vortex-vortex interaction may become too
weak to sustain a stable VBG state in the bulk. For such
a region, some theories predict existence of liquid-like
vortex state near $H_{c1}$ originating from such vanishingly
small vortex interactions. Indeed, such a liquid-like state
has been observed in high-TC cuprates near $T_c$. We propose that a similar liquid-like state is realized in
Sr$_2$RuO$_4$ below $H^{*1}$. Note that the first and third sce-
narios for the stable VBG state for $H^{*1} < H < H^{*2}$
are compatible with the formation of the liquid-like state
below $H^{*1}$. In the first scenario, it is naturally expected
that the glassy metastable state becomes difficult to form
when a liquid-like state is stable. In the third scenario,
the Bean-Livingston surface barrier is also known to dis-
appear once a liquid-like state is formed.

Before closing the discussion, we comment on the re-
lation between our result and the first-order supercon-
ducting transition. It has been recently revealed that
the superconducting to normal transition of Sr$_2$RuO$_4$ be-
low 0.8 K under in-plane field is of first-order. In or-
dinary type-II superconductors, continuous suppression
of the superconducting order parameter toward zero as
$H \rightarrow H_{c2}$ is the main source of the formation of the glass
and liquid phases near $H_{c2}$. In contrast, the order pa-

gram abruptly disappears from a finite value at the
first order transition. Thus, it is actually surprising that
the vortex phase diagrams of Sr$_2$RuO$_4$ for $H_{dc} \parallel ab$ re-
semble those of ordinary type-II superconductors. Note
that this sample exhibits weak but clear hysteretic behav-
ior at $H_{c2}$, although not clear in the scale of Fig. 2(b).
It is still an open question whether vortex phase tran-
sitions can occur near the first-order transition, which
should not be accompanied by strong fluctuations. Fur-
ther studies with cleaner samples are needed to resolve
this interesting issue.

V. CONCLUSION

The EPFC process, in which the sample was once
quickly heated up to above $T_c$ and cooled back to the
target temperature before collecting the data, enables
us to realize new metastable vortex states. Precise vor-
tex phase diagrams having a liquid-like state in the low-
field region are revealed by comparison between the FS
and EPFC branches. These vortex phase diagrams of
Sr$_2$RuO$_4$ provide important bases for further studies of
searching for superconducting multiphases originating
from the anticipated chiral-$\rho$-wave spin-triplet order pa-

Finally, we emphasize that the newly employed EPFC
process can be adapted not only to ac susceptibility mea-
surements but also to other techniques such as magneti-
ization measurements and neutron diffractions. It is also
applicable to study vortex phase diagrams of other con-

ventional and unconventional type-II superconductors.
Thus, it is envisaged that the EPFC method becomes
a general and powerful technique to investigate vortex
physics.


ACKNOWLEDGEMENTS

We acknowledge H. Takatsu for his contributions in crystal growth and R. Ikeda for helpful discussion. This work was supported by the "Topological Quantum Phenomena" (Nos. 22103002 & 22103004) Grant-in Aid for Scientific Research on Innovative Areas from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and by Grant-in-Aid for Scientific Research (KAKENHI 26287078) from the Japan Society for Promotion of Science (JPSJ)