A spontaneous vortex state (SVS) between 30 and 56 K was observed for the weak-ferromagnetic superconductor RuSr2GdCu2O8 with the ferromagnetic Curie temperature $T_C = 131$ K and the superconducting transition temperature $T_c = 56$ K. The low-field ($\pm 20$ G) superconducting hysteresis loop indicates a narrow Meissner state region within the average lower critical field $B_{c1}(T)/B_{0}$, with average $B_{c1}^0(0) = 12$ G and $T_0 = 30$ K. Full Meissner shielding signal in very low applied field indicates an ab plane $B_{c2}^0(0)$ $\sim 4$ G with an estimated anisotropic parameter $\gamma \sim 7$ for this layered system. The existence of a spontaneous vortex state between 30 and 56 K is the result of weak-ferromagnetic order with a net spontaneous magnetic moment of $-0.1 \mu_B$/Ru, which generates a weak magnetic dipole field around 10 G in the CuO$_2$ bilayers. The upper critical field $B_{c2}$ varies linearly as $(1-T/T_c)$ up to 7-T field. The vortex melting line $B_{m}$ varies as $(1-T/T_m)^{3.5}$ with melting transition temperature $T_m = 39$ K and a very broad vortex liquid region due to the coexistence and the interplay between superconductivity and weak-ferromagnetic order.}

I. INTRODUCTION

Recently, high-$T_c$ superconductivity with anomalous magnetic properties was reported in the weak-ferromagnetic Ru-1212 system RuSr$_2$RuCu$_2$O$_8$ ($R = $Sm, Eu, Gd, Y) with the tetragonal TiBa$_2$CaCu$_2$O$_{7-\delta}$-type structure. For the Ca-substituted system, a possible superconductivity was also reported in the weak-ferromagnetic compounds RuCa$_2$RuCu$_2$O$_8$($R=Pr$-Gd). The metallic weak-ferromagnetic (WFM) order is originated from the long-range order of Ru moments in the RuO$_6$ octahedra due to strong Ru-$4d_{xy,xy,z}$-O-$2p_{x,y,z}$ hybridization in this strongly correlated electron system. The Curie temperature $T_C \sim 130$ K observed from magnetization measurement in the prototype compound RuSr$_2$GdCu$_2$O$_8$ is probably a canted G-type antiferromagnetic order with Ru$^{5+}$ moment $\mu$ canted along the tetragonal basal plane resulting a small net spontaneous magnetic moment $\mu_s < \mu$ (Ru$^{5+}$) too small to be detected in neutron diffraction. The occurrence of high-$T_c$ superconductivity with maximum resistivity onset $T_{c}(\text{onset}) \sim 60$ K in RuSr$_2$GdCu$_2$O$_8$ is related with the quasi-two-dimensional CuO$_2$ bilayers separated by a rare-earth layer in the Ru-1212 structure. Broad resistivity transition width $\Delta T_c = T_{c}(\text{onset}) - T_{c}(\text{zero}) \sim 15 - 20$ K observed is most likely originated from the coexistence and the interplay between superconductivity and weak-ferromagnetic order. The diamagnetic $T_c$ is observed anomalously at lower temperature near $T_{c}(\text{zero})$ instead of at $T_{c}(\text{onset})$, and a reasonably large Meissner signal was reported using stationary sample magnetometer with diamagnetic $T_c \sim 30$ K in $\pm 1$ G applied field at zero-field-cooled (ZFC) mode. Lower $T_c(\text{onset})$ $\sim 40$ and 12 K were observed for RuSr$_2$EuCu$_2$O$_8$ and RuSr$_2$SmCu$_2$O$_8$, respectively. No superconductivity can be detected in RuSr$_2$RuCu$_2$O$_8$ ($R=Pr$, Nd). Superconducting RuSr$_2$YCu$_2$O$_8$ phase is stable only under the high pressure. The physics is still unclear in this system, and it will be interesting to investigate the effect of the weak-ferromagnetic order on the superconducting critical fields $B_{c2}$ and $B_{c1}$, as well as on the possible existence of a spontaneous vortex state (SVS) at a higher temperature above the Meissner state.

II. EXPERIMENTAL

The stoichiometric RuSr$_2$GdCu$_2$O$_8$ samples were synthesized by the standard solid-state reaction method. High-purity RuO$_2$ (99.99 %), SrCO$_3$ (99.99 %), Gd$_2$O$_3$ (99.99 %), CuO (99.99 %) preheated powders with the nominal composition ratio of Ru: Sr: Gd: Cu = 1: 2: 1: 2 were well mixed and calcined at 960 °C in air for 16 h. The calcined powders were then pressed into pellets and sintered in flowing N$_2$ gas at 1015 °C for 10 h to form RuSr$_2$GdO$_6$ and Cu$_2$O precursors. This step is crucial in order to avoid the formation of unwanted impurity phases. The N$_2$-sintered pellets were heated at 1060 °C in flowing O$_2$ gas for 10 h to form the Ru-1212 phase. The pellets were oxygen annealed at slightly higher 1065 °C for 5 days and slowly furnace cooled to room temperature with a rate of 15 °C per h.

The powder x-ray diffraction data were collected with a Rigaku Rotaflex 18-kW rotating anode diffractometer using graphite monochromatized Cu-K$_\alpha$ radiation with a scanning step of 0.02° (10 s counting time per step) in the 2 $\theta$ ranges of 5°–100°. The electrical resistivity and magnetoresistivity measurements were performed using the standard four-probe method with a Linear Research LR-700 ac (16 Hz) resistance bridge from 2 to 300 K with applied magnetic field up to 7 T. The magnetization, magnetic susceptibility, and magnetic hysteresis measurements from 2 to 300 K with applied fields.
from 1 G to 7 T were carried out with a Quantum Design 1-T \( \mu \)-metal shielded MPMS2 or a 7-T MPMS superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSION

The powder x-ray diffraction pattern for the oxygen-annealed RuSr\(_2\)GdCu\(_2\)O\(_8\) polycrystalline sample indicates close to a single phase with the tetragonal lattice parameters of \( a=0.5428(5)\) nm and \( c=1.5859(9)\) nm. The space group \( P4/mmbm \) is used for Rietveld refinement analysis, where neutron-diffraction data indicate that a RuO\(_6\) octahedra \( 14^\circ \) rotation around the \( c \) axis is needed to accommodate physically reasonable Ru-O bond lengths.\(^1\) The refinement with the fixed \( 14^\circ \) rotation angle gives a good residual error \( R=5.05\% \).

The temperature dependence of the electrical resistivity \( \rho(T) \) and the volume magnetic susceptibility \( \chi_v(T) \) at 1-G field-cooled (FC) and zero-field-cooled (ZFC) modes for RuSr\(_2\)GdCu\(_2\)O\(_8\) are shown collectively in Fig. 1. The high-temperature resistivity decreases monotonically from room temperature value of 9.2 m\( \Omega \) cm (not shown) to 6.4 m\( \Omega \) cm at 200 K, and extrapolated to 2.8 m\( \Omega \) cm at 0 K with a good resistivity ratio \( \rho(300 K)/\rho(0 K) \) of 3.3 for the polycrystalline sample. The high-temperature resistivity shows a non-Fermi-liquid-like linear \( T \) dependence down to a Curie temperature \( T_C \) of 131 K, then changes to a \( T^2 \) behavior below \( T_C \) due to magnetic order.

The superconducting onset temperature of 56 K is determined from the deviation from \( T^2 \) behavior, with a zero resistivity \( T_{c}(\text{zero}) \) at 39 K. The broad transition width \( \Delta T_{c} \) is estimated to be close to 10 G. No diamagnetic field-expulsion signal can be detected below 39 K due to strong flux pinning where superconductivity coexists with weak-ferromagnetic order.

The zero-field-cooled (ZFC) volume susceptibility \( \chi_v(T) \) at 1, 10, and 100 G applied fields are shown collectively in Fig. 2. All data show the same magnetic order \( T_{c}(\text{Ru}) \) of 131 K. Although the diamagnetic \( T_{c} \) of 39 K was still observed at 10-G ZFC measurement, the diamagnetic signal at 5 K is reduced to 60% of the full Meissner signal. Consider the polycrystalline nature of sample with varying microcrystallite size and orientation, the average superconducting lower critical field \( B_{c1} \) at 5 K is estimated to be close to 10 G. No net diamagnetic signal can be detected at 100-G ZFC mode where the sample is already in the vortex glass or lattice state and the small diamagnetic signal is overshadowed by a large weak-ferromagnetic background.\(^38\)

Based on this information, the low-field (\( \pm 20 \) G) isothermal superconducting hysteresis loops \( M-B_{\perp} \) are measured and collectively shown in Figs. 3(a) (5, 10, 15, and 20 K) and 3(b) (25, 30, and 35 K). The initial magnetization curve deviates from straight line in 4 G at 5 K, 3.5 G at 10 K, 3 G at 15 K, 2 G at 20 K, and 1 G at 25 K. This is the narrow region that full Meissner signals are detected and is roughly corresponding to the anisotropic lower critical field in the \( ab \) plane \( B_{c2}(T) \) with \( B_{c2}^{ab}(0) \sim 4 \) G. The average lower critical field \( B_{c2}^{ab} \) for the polycrystalline sample is determined from

![FIG. 1. Electrical resistivity \( \rho(T) \) and volume magnetic susceptibility \( \chi_v(T) \) at 1-G field-cooled (FC) and zero-field-cooled (ZFC) modes for oxygen-annealed RuSr\(_2\)GdCu\(_2\)O\(_8\).](image1)

![FIG. 2. ZFC volume susceptibility \( \chi_v(T) \) for RuSr\(_2\)GdCu\(_2\)O\(_8\) at 1, 10, and 100 G. Note that the full Meissner shielding signal was observed only at low applied field and low temperature.](image2)
RuSr₂GdCu₂O₈: $K_{1,1 Ga}$ at $10K$, $K_{1,5 Ga}$ at $15K$, and $K_{a,5}$ an $T_{c}$ value is close to a reported anisotropic Ginzburg-Landau formula $B_{c2}$.

Critical fields and the spontaneous vortex pinning is neglected. The effect on the exact peak value due to the surface barrier is the peaks of initial diamagnetic magnetization curves. The effect on the exact peak value due to the surface barrier pinning is neglected. $B_{c2}$ decreases steadily from 12 G at 5 K, 11 G at 10 K, 9 G at 15 K, 6 G at 20 K, 3 G at 25 K, and below 1 G at 30 K. A simple empirical parabolic fitting gives $B_{c2}(T) = B_{c2}(0)[1 - (T/T_{o})^{2}]$, with average $B_{c2}^{av}(0) = 12$ G and $T_{o} = 30$ K (see Fig. 4). Using the anisotropic Ginzburg-Landau formula $B_{c2}^{av} = [2B_{c1}^{dipole} + B_{c1}^{10.4 G}] / 3$, c-axis $B_{c1}^{10.4 G} \sim 28$ G and the anisotropy parameter $\gamma \sim 7$ is estimated. This value is close to a reported anisotropic $\gamma$ value for YBa₂Cu₃O₇, where the 123-type structure can be written as Cu-1212 CuBa₂YCu₂O₇. An average penetration depth $\lambda_{ave}(0) = [\Phi_{0}/2\pi\lambda_{ave}(0)]^{1/2}$ of 520 nm was derived with estimated $\lambda_{ab}(0) = 340$ nm and $\lambda_{c}(0) = 2400$ nm from $B_{c1}^{10.4 G} = \Phi_{0}/2\pi\lambda_{ab}$, and $B_{c2}^{10.4 G} = \Phi_{0}/2\pi\lambda_{c}$, where $\Phi_{0}$ is flux quantum.

Since $T_{o} = 30$ K is well below $T_{c}(\text{onset}) = 56$ K and $T_{c}(\text{zero}) = 39$ K in zero applied field, a spontaneous vortex state (SVS) indeed exists between 30 and 56 K. The low-field phase diagram $B_{c2}(T)$ for the polycrystalline sample is shown in Fig. 4, with the average $B_{c2}(T)$ separates the Meissner state from the vortex state and a smaller $B_{c2}(T)$ inside the Meissner region for reference. $T_{c}(\text{zero}) = 39$ K in the broad resistive transition is the onset of vortex depinning by a driving current. This temperature is very close to the melting transition temperature $T_{m}$ from the spontaneous vortex glass or lattice state to the spontaneous liquid state due to nonzero dipole field $B_{dipole}$ of weak-ferromagnetic order. The critical field $B_{c2}$ defined from $T_{c}(\text{onset})$ and the vortex melting field $B_{m}(T)$ defined from $T_{c}(\text{zero})$ are temperature independent for small applied fields below 20 G. The internal dipole field generated by a weak-ferromagnetic order can be estimated using a simple extrapolation $[B_{c2}(0) + B_{dip}]/B_{c2}(0) = T_{c}/T_{o} = 56$ K/30 K, which results with a dipole field $B_{dipole} = 10.4$ G on the CuO₂ bilayers. A small net spontaneous magnetic moment $\mu_{s}$ of $\sim 0.11 \mu_{B}$ per Ru is estimated using $B_{dipole} \sim 2\mu_{s}/4.79$ with $d = c/2 = 0.58$ nm which is the distance between midpoint of CuO₂ bilayers and two nearest-neighbor Ru moments. If the weak-ferromagnetic structure is a canted $G$-type antiferromagnetic order with Ru moments $\mu = 1.5 \mu_{B}$ for Ru$^{3+}$ in $t_{2g}$ states) canted along the tetragonal basal plane, the small spontaneous magnetic moment gives a canting angle of $4^\circ$ from the tetragonal c axis and is difficult to be detected in neutron diffraction with a resolution around 0.1 $\mu_{B}$.²¹

At 5 K, the shape of superconducting hysteresis loop with a large remanent molar magnetization $M_{r}$ of 83 G cm$^{-3}$/mol indicates a strong pinning as well as a good indication of bulk nature of superconductivity for the oxygen-annealed sample. The remanent $M_{r}$ decreases to 4 G cm$^{-3}$/mol at 30 K and 1 G cm$^{-3}$/mol at 35 K, where a weak-ferromagnetic background can be clearly seen. Fluctuation in the hysteresis loop is probably also related to the weak-ferromagnetic order.

To study the high-field effect on superconductivity, the magnetoresistivity $\rho(T, B_{a})$ for RuSr₂GdCu₂O₈ up to 7 T are collectively shown in Fig. 5. The broadening of the resistive transition in magnetic fields is the common features for all high-$T_{c}$ cuprate superconductors.⁴⁷ The normal-state resistivity is field independent and follows a $T^2$ dependence below $T_{c}$, with the superconducting $T_{c}(\text{onset})$ of 56 K in the zero field decreases slightly to 53 K in 7-T field. The temperature dependence of upper critical field $B_{c2}(T)$ can be fitted with a linear function $B_{c2}(0)[1 - T/T_{c}]$ with average $B_{c2}(0) = 133$ T.⁴⁷ An average coherence length $\xi_{0}^{av} = [\Phi_{0}/2\pi B_{c2}^{av}(0)]^{1/2}$ of 0.5 nm with the Ginzburg-Landau
parameter $\kappa$ of 1040 and the thermodynamic critical field $B_c(0)=(B_c(1)B_c(0))^{1/2}=0.32$ T. No anisotropic $\xi_{ab}$ and $\xi_c$ values can be estimated from present data. The $T_c$(zero) decreases from 39 K in zero applied field to 32 K in 1-kG, 28 K in 5-kG, 25 K in 1-T, 22 K in 2-T, 19 K in 3-T, 17 K in 4-T, 16 K in 5-T, 15 K in 6-T, and 14 K in 7-T field. If the zero resistivity is taken as the lower bound of the vortex melting temperature $T_{m}$, then the temperature dependence of the vortex melting transition line $B_m(T)$ can be fitted roughly by the formula $B_m(T)=B_m(0)[1−T/T_m]^{1/3}$, with $B_m(0)=35$ T and large exponent 3.5. In the lower field region, $B_m(T)$ rises as $[1−T/T_m]^{1/3}$ as predicted by the mean-field approximation for temperature near $T_m=39$ K.47 The full phase diagram $B_{a}(T)$ of RuSr$_2$GdCu$_2$O$_8$ is shown in Fig. 6 to exhibit both the high- and low-field features. The very broad vortex liquid region with $\Delta T=17$ K in zero field and $\Delta T=42$ K in 7-T field is extraordinary and is most likely originated from the coexistence and the interplay between superconductivity and weak-ferromagnetic order. This magnetic order is so weak that superconductivity can coexist with the magnetic order, but the effect of a weak spontaneous magnetic moment $\mu_s \sim 0.1 \mu_B$ is detected through the appearance of a spontaneous vortex state above 30 K with a broad spontaneous vortex liquid region above $T_m$ of 39 K.

To study the broad vortex liquid region, the isothermal field-dependent magnetoresistivity $\rho(B_a)$ for $T<T_c$ are shown in Fig. 7, where the zero resistivity gives a lower bound of the vortex melting field $B_m$. In the resistive vortex liquid region, the magnetoresistivity increases with increasing applied magnetic field and temperature. At 40 K, the magnetoresistivity is rapidly approaching a saturation value in an extrapolated saturation field $B_m−B_C$(40 K) $\sim$ 40 T.

The last issue to be addressed is the depression of $T_c$ by small spontaneous Ru magnetic moments. The weak-ferromagnetic order is actually a canted antiferromagnetic order that can coexist with superconductivity. However, the observed $T_c$ of 56 K is too low as compared with 93 K for YBa$_2$Cu$_3$O$_7$ or 103 K for TlBa$_2$CaCu$_2$O$_7$. The depression of $T_c$ by small spontaneous magnetic moment can be partially recovered by substitution of nonmagnetic Cu ions at Ru site. For example, in the Ru$_{1-x}$Cu$_x$Sr$_2$GdCu$_2$O$_8$ system, $T_c$ onset up to 65 K for $x=0.1$ and 72 K for $x=0.4$ was reported.26,29

IV. CONCLUSION

The lower critical field with $B_{c1}(0)=12$ G and $T_0=30$ K indicates the existence of a spontaneous vortex state (SVS) between 30 K and $T_c$ of 56 K. This SVS state is closely related with the weak-ferromagnetic order with a net spontaneous magnetic moment of $\sim 0.1 \mu_B$ per Ru. The broad vortex liquid region observed above vortex melting line $B_m(T)$ is also due to the coexistence and the interplay between superconductivity and weak-ferromagnetic order. Indeed, a possible spontaneous vortex state was also reported in the weak ferromagnetic superconductor Ru-1222 compound RuSr$_2$(Eu$_{1.5}$Ce$_{0.5}$)Cu$_2$O$_{10.48}$.48

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