Field dependence of the intragrain superconductive transition in $\text{RuSr}_2\text{EuCu}_2\text{O}_8$

B. Lorenz,¹ Y. Y. Xue,¹ R. L. Meng,¹ and C. W. Chu^{1,2,3}

¹*Texas Center for Superconductivity and Department of Physics, University of Houston, Houston, Texas 77204-5932*

²*Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720*

³*Hong Kong University of Science and Technology, Hong Kong, China*

(Received 28 June 2001; revised manuscript received 16 November 2001; published 12 April 2002)

A narrow intragrain phase-lock transition was observed in $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ under a magnetic field H up to a few Tesla. The corresponding transition temperature T_2 decreases rapidly (≈ 100 K/T at low fields) with H , indicating that the grains of $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ behave unlike a homogeneous bulk superconductor. Our data suggest that the bulk superconducting transition may occur on a length scale well below the grain size $2\text{--}6\text{ }\mu\text{m}$.

DOI: 10.1103/PhysRevB.65.174503

PACS number(s): 74.72.-h, 74.50.+r, 74.80.-g

I. INTRODUCTION

Interest has been high since the reported coexistence of superconductivity (SC),^{1,2} weak ferromagnetism (FM),¹ and antiferromagnetism (AFM) (Refs. 3 and 4) in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (Ru1212Gd) and $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ (Ru1212Eu). The superconducting transition in these compounds shows behavior typical of a granular superconductor. Two steps of the transition, commonly ascribed to intergrain and intragrain transitions, are well separated in magnetic-susceptibility and electrical-resistivity experiments.^{5,6} However, recent neutron-scattering experiments showed a more complex nature of the magnetic ordering, including a change of the principal axis of the magnetic moments with an applied external field.³ Therefore, the homogeneity of the intragrain magnetic and superconducting states is questioned. Extrinsic structural defects⁷ or the possible phase separation of FM and AFM regions are expected to have a major effect on the intragrain superconductivity. In such a scenario a grain of a ceramic Ru1212 sample could actually consist of nanoscale SC domains coupled through Josephson junctions below a thermodynamic transition temperature T_c . Therefore, the behavior of the intragrain SC under a magnetic field H is of particular interest. The magnetotransport properties of Ru1212 should strongly depend on the intragrain Josephson coupling strength. In the strong-coupling limit, the intragrain Josephson-junction penetration depth (λ_2) may be roughly equal to the London penetration depth (λ_L) below an intragrain phase-lock transition of T_2 , and the intragrain SC properties are similar to those of other "ordinary" cuprates. In the weak-coupling limit, however, individual grains may rather be similar to disordered Josephson-junction arrays (JJA's) with an unusually large λ_2 .⁸ In this case a severe suppression of T_2 by a comparatively small magnetic field is expected.

Another interesting observation is the recently reported field dependence of a specific-heat anomaly near 46 K in Ru1212Gd.⁵ It was suggested that the T_c increases with magnetic field H up to 4 to 5 T due to a possible p -wave superconductivity. Such an abnormal H dependence of T_c should also show up in the magnetotransport properties. In the strong (intragrain) Josephson coupling limit T_2 is expected to show a field dependence similar to that of T_c whereas in the weak-coupling limit T_2 should decrease with H , as is quali-

tatively known for Josephson-junction arrays. Previous magnetoresistance (MR) measurements below the ferromagnetic transition temperature T_F show a positive MR at low fields passing through a maximum at about 2 T, but no effect on the superconducting T_c was reported.⁹

Despite the intensive investigations of the last decade the SC properties of a disordered two-dimensional (2D) JJA under magnetic field is still a matter of debate. Depending on the nature of the disorder and the model used, different ground states have been proposed, e.g., various glass states,¹⁰ metal,¹¹ superconductors with global phase coherence,¹² a paramagnetic Meissner state,¹³ and a chirally ordered normal phase.¹⁴ Various phase transitions may appear (e.g., glass transitions). The intragrain magnetotransport of Ru1212, therefore, offers the opportunity to explore 2D JJA's if the coupling strength is moderate to weak, i.e., if the intragrain T_2 is clearly smaller than T_c and the penetration depth, λ_2 , is unusually large.

This motivated our investigation of the magnetotransport of Ru1212 ceramic samples. In order to exclude any possible magnetic contribution from the Gd moment, the measurements were preferentially done on Ru1212Eu. However, both systems have been shown to behave very similarly with respect to their FM and SC transitions, the T_c of Ru1212Eu being slightly lower than that of Ru1212Gd.⁶ The ac susceptibility χ under a dc bias field H , combined with the bulk resistivity, was used to extract the intragrain SC transition. Various powder samples were also used to identify the characteristic length scales involved.

II. EXPERIMENTAL SETUP

Ceramic samples with a nominal composition $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ were prepared by solid-state reaction techniques as described earlier.⁶ The x-ray-diffraction pattern shows that the samples are nearly single phase with a small amount of SrRuO_3 . An elemental analysis reveals a slight Ru deficiency and some extra copper with the actual cation composition of Ru:Sr:Eu:Cu=0.91(5):2.106(2):2.29(2). From structural, magnetic, and transport properties it was concluded that $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ is very similar to its extensively investigated sister compound, $\text{RuSr}_2\text{GdCu}_2\text{O}_8$. In particular,

FIG. 1. dc susceptibility of the bulk and a powder sample of $\text{RuSr}_2\text{EuCu}_2\text{O}_8$. Circles: ZFC mode. Triangles: FC mode. Upper and lower lines: powder sample in FC and ZFC modes. Inset: M vs H at 5 K.

the superconducting transition proceeds in two steps previously interpreted as intergrain and intragrain transitions of a granular superconductor.^{5,6}

dc and ac susceptibility measurements were performed using the Quantum Design superconducting quantum interference device (SQUID) magnetometer. The ac measurements were done with a field amplitude of 3 Oe in a dc bias field up to 5 T. Magnetoresistance data were measured in the same SQUID by an ac resistance bridge from Linear Research.

III. RESULTS AND DISCUSSION

The zero-field-cooled (ZFC) and the field-cooled (FC) magnetizations of a bulk piece of Ru1212Eu at 5 Oe are shown in Fig. 1. The magnetic transition temperature $T_F = 115$ K is slightly lower than the 133 K observed in Ru1212Gd , probably due to the possible Cu/Ru site mixing as suggested by the cation nonstoichiometry. The intergrain coupling seems to be rather weak so that the nonlinearity of the ZFC $M-H$ branch begins below 1 Oe, and M saturates at 4 Oe (inset, Fig. 1). Two drops of M_{ZFC} appear at 20 and 28 K, respectively. The susceptibility (M_{ZFC}/H) decreases quickly below 20 K, and reaches -0.04 emu/cm^3 (about 50% shielded-volume fraction) at 5 K. In order to explore the origin of the two diamagnetic transitions, we have conducted similar susceptibility measurements using a powdered sample with an average particle size of 3 μm , comparable with the grain size of the bulk pellet. The magnetization of a powder is also shown in Fig. 1 (solid lines). In the powder data the strong diamagnetic signal of the bulk sample at $T_1 \approx 20$ K is completely missing. This leads us to the conclusion that the 20-K transition indi-

FIG. 2. ac susceptibility of $\text{RuSr}_2\text{EuCu}_2\text{O}_8$. Open triangles and squares: real and imaginary parts of the bulk sample. Solid line: real part of the powder sample.

cates the intergrain phase-lock temperature and the 28-K diamagnetic transition is the intragrain transition at T_2 . This interpretation is further supported by the ac susceptibility data shown in Fig. 2. The peaks in the imaginary part, χ'' , and the drops in the real part, χ' , appear at around 20 and 30 K, respectively. Note that these temperatures are about 10 K lower than those of Ru1212Gd ($T_1 \approx 30$ K and $T_2 \approx 40$ K),⁸ probably due to the chemical pressure caused by the replacement of Gd by the smaller Eu. The diamagnetic drop between T_1 and T_2 , $\Delta M_{ZFC} \approx 0.002$ emu/cm^3 , in Ru1212Eu , is significantly larger than that in Ru1212Gd ,^{2,8,15} suggesting a shorter λ_2 in our Ru1212Eu sample. The larger intragrain Meissner effect, ΔM_{FC} , above T_1 observed here seems to be closely related to the shorter λ_2 but will not be discussed further since it is not essential to the topic presented here.

To provide additional support of our assumption about the origin of the T_1 and T_2 transitions, we conducted a systematic investigation of the ac susceptibility as a function of the average particle size for sorted powders of Ru1212Gd . The process of separating the powders with controlled particle sizes was described elsewhere.⁸ Figure 3 shows the real part χ' of the ac susceptibility of Ru1212Gd for powders with average particle sizes of 40, 2.3, and 0.8 μm , in comparison with χ' of the bulk material. The grain size of this sample before grinding into powder was estimated as 2–5 μm from scanning electron microscopy. It is obvious from Fig. 3 that the strong diamagnetic shielding signal below T_1 of the bulk sample appreciably weakens for the 40- μm powder, and even disappears for particle sizes of 2.3 and 0.8 μm , i.e., if the particle size drops below the grain size there is no diamagnetic transition at T_1 . However, the diamagnetic signal at T_2 does survive the reduction in particle size, although its magnitude is reduced due to a large (intragrain) penetration depth.⁸ The disappearance of the T_1 transition with decreasing particle size cannot be easily ex-

FIG. 3. ac susceptibility of sorted powders of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$. Closed squares: bulk sample. Open symbols: sorted powders with average particle size given in the legend.

plained by chemical inhomogeneities, but it indicates that the two transitions observed are linked to the typical intergrain (T_1) and intragrain (T_2) transitions of a granular superconductor. Accordingly, these two transitions are also resolved in the temperature dependence of the resistivity^{5,6} that is more sensitive to weak links across the grain boundaries. It should be noted that the diamagnetic signals at T_1 and T_2 in Fig. 3 appear on top of a magnetic background that can roughly be approximated by the susceptibility of the $0.8 \mu\text{m}$ powder.

The zero-field resistivity $\rho(0)$ and thermoelectric power S of bulk $\text{Ru1212}(\text{Eu}/\text{Gd})$ were discussed previously.⁶ For Ru1212Eu ρ reaches a maximum around $T_m = 36 \text{ K}$ and drops to zero slightly above 20 K . The thermoelectric power changes slope close to T_m , and decreases to zero slightly above the zero resistance temperature. The details of the resistive transition are shown in the derivative, $d\rho/dT$ (Fig. 4). In zero magnetic field [Fig. 4(a)] $d\rho/dT$ appears as a close superposition of two peaks corresponding to the intergrain and intragrain superconducting transitions. The two peaks are split off by a small magnetic field, and can easily be decomposed by assuming Gaussian peak shapes [dotted lines in Fig. 4(b)]. This procedure is used to separate the contributions from both transitions to the overall drop of resistivity, and to estimate the transition temperatures T_1 and T_2 , respectively. In particular, the deconvolution of the two peaks allows us to determine the temperature T_2 where the intragrain resistivity is close to zero. This temperature should roughly correspond to the T_2 identified in the magnetization measurements. In the following evaluation we define T_2 from resistivity by a 95% drop of the intragrain resistance as indicated by the double-sided arrow in Fig. 4(b). The chosen criterion may appear somewhat arbitrary, but it does not affect the main conclusions. The maximum of resistivity appears at higher temperature T_m , defined by the zero crossing of $d\rho/dT$.

The intergrain transition temperature T_1 decreases quickly in an external magnetic field. This is typical for a granular

FIG. 4. Derivative of the resistivity at the superconducting transition. (a) Zero magnetic field. (b) $H = 500 \text{ Oe}$. Part (b) shows the decomposition separating intergrain and intragrain superconducting transitions. The temperature T_2 , where the intragrain resistivity drops to 5% is indicated.

superconductor with weak intergrain coupling. The field dependence of the intragrain temperature T_2 is of special interest, and is estimated from both, magnetoresistivity data, as described above, and ac susceptibility experiments in a dc bias field. A typical ac susceptibility curve is shown in Fig. 5 for an external dc field of 1000 Oe . The intragrain transition is clearly detected by a drop in the susceptibility. The strong diamagnetic signal due to the intergrain phase lock transition appears below 20 K and is not shown in the figure. T_2 is determined from the crossing of the two extrapolated linear parts of χ' above and below the transition (Fig. 5). Surprisingly, T_2 is rapidly suppressed by small magnetic fields with

FIG. 5. ac susceptibility of $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ in a dc bias field of 1000 Oe . The intragrain transition temperature T_2 is determined from the crossing of the two straight lines.

FIG. 6. Field dependence of T_2 from resistivity (open triangles) and ac susceptibility data (closed circles). The inset shows the Ginzburg-Landau dependence for a bulk superconductor.

an initial slope of 100 K/T (Fig. 6). The T_2 's estimated from resistivity and susceptibility are shown in Fig. 6 by open triangles and closed circles, respectively. The agreement of both data sets is very good, the deviation at $H \approx 0$ is obviously due to the larger uncertainty in the deconvolution of the two peaks in $d\rho/dT$ at a very small field [Fig. 4(a)]. The overall temperature dependence of T_2 is very different from what one might expect for a bulk superconductor, e.g., from Ginzburg-Landau theory (inset in Fig. 6). Particularly, the unusually strong decrease of the intragrain T_2 of $dT_2/dH \approx 100$ K/T at low field cannot be explained by the bulk and homogeneous superconductivity inside the grains. A possible explanation for the steep field dependence of T_2 may be given if the intragrain transition is considered to be a phase-lock transition of another (intragrain) Josephson-junction array. The underlying subgrain structures could be structural or magnetic domains of typical nanometer size. The intragrain resistivity transition might than be understood as a percolative transition between domains coupled by junctions of different strength and disorders induced by H . The ac susceptibility data show a narrow phase-lock transition (width ≈ 0.7 K) between the two linear sections (Fig. 5), indicating a true phase transition. The width of this transition does not change with magnetic field. Other possible explanations for the current data may include a field dependence of the magnetic interaction between the RuO layers and the CuO layers in an otherwise homogeneous grain. This situation, however, appears unlikely because of the fact that the peak temperature of the heat capacitance in Ru1212Gd does not decrease drastically with the magnetic field.⁵ The intragrain superconducting state and its microscopic structure need further exploration. The linear decrease of χ below T_2 can be explained by the decrease of the penetration depth λ_2 . From an analysis of the intragrain superconducting transitions of powders with different particle sizes it is concluded that the penetration depth of the Ru1212Eu sample used here is $\lambda_2(0 \text{ K}) \approx 1 \text{ } \mu\text{m}$.¹⁶

FIG. 7. Magnetoresistance $\rho(50 \text{ K})$ (open circles) and temperature of resistivity maximum T_m (closed squares) as a function of the magnetic field. The inset shows the correlation between ρ and T_m .

Besides T_1 and T_2 , the maximum in resistivity (T_m) and the resistance in the ferromagnetic phase, $\rho(H)$, are relevant quantities for investigating the interplay of superconductivity and magnetic structures. At low fields, up to about 0.4 T, $\rho(H)$ and T_m are not changed by the magnetic field. For $H > 0.4$ T, however, the resistivity increases and its maximum shifts to higher temperature, saturating at about 4–5 T. As shown in Fig. 7, $\rho(H)$ above 50 K and $T_m(H)$ seem to be strongly correlated. A positive magnetoresistance similar to the present data for Ru1212Eu was also reported for Ru1212Gd below the ferromagnetic transition temperature.⁹ The anomalous increase of $T_m(H)$ and $\rho(H)$ above 0.4 T may be due to a change in the magnetic structure of Ru1212Eu, as previously proposed from neutron-scattering experiments on Ru1212Gd.³ According to the neutron-scattering data the Ru moments are ordered antiferromagnetically with a small residual ferromagnetic moment. The direction of the moments was suggested to be parallel to the tetragonal c axis. At 0.4 T the Ru moments are assumed to rotate into another antiferromagnetic structure, and a sizable ferromagnetic magnetization can be induced at higher fields. This change in the magnetic structure is obviously reflected in the positive magnetoresistivity and the increase of T_m as discussed above. As a consequence $\rho(H)$ and $T_m(H)$ should be correlated. In fact, the inset in Fig. 7 indicates a linear relation between ρ and T_m , but a change of slope possibly takes place at a field of about 1.5 T. The origin of this slope change is not clear, and needs further exploration. It should be noted that a similar field-induced shift to higher temperature was qualitatively observed in the peak of specific heat in Ru1212Gd, and was interpreted as a possible signature of p -wave superconductivity.⁵ However, since no heat-capacity data between 0 and 4 T have been reported a more detailed comparison with the present resistivity data is not possible, and it is not clear if both phenomena are of the same physical origin.

The key issue to understand the unusual field dependence of $\rho(H)$ is the magnetic structure involving antiferromagnetic ordering with a weak ferromagnetic component. The

strong-field dependence of the intragrain T_2 , observed in the present data, indicates inhomogeneities in the intragrain structure resulting in a weakly linked JJA in the superconducting state. Therefore, phase separation into nanoscale AFM and FM domains may be considered as a possible scenario.¹⁷ The field H is expected to change the intradomain magnetic order as well as the domain structure. The growth of FM domains with an increasing field H will result in enhanced carrier scattering and a positive magnetoresistance as long as the induced FM moment does not dominate the AFM order. Only at a high field (> 5 T) do the FM domains determine the transport properties and, due to reduced carrier scattering, the magnetoresistance should drop again. Percolative effects could play an essential role.

The physical origin of the observed increase of the resistivity maximum temperature T_m with the applied field is still an open question. If T_m is considered as the onset of superconductivity, the phenomenon must be related to the magnetic microstructure and its correlation to the superconducting state. It is interesting that the field effect on T_m is only observed above 0.4 T, where it was suggested that the principal axis of alignment of the AFM moments changes from a c axis to in-plane.³ This observation calls for a more detailed investigation.

IV. CONCLUSIONS

We have shown that the intragrain superconducting transition temperature of $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ decreases steeply as a function of an external magnetic field. This effect is explained by assuming that the intragrain superconductivity is due to a phase-lock transition of a nanoscale Josephson-junction array. The resistivity in the ferromagnetically ordered phase and the temperature of the resistivity maximum both increase as function of magnetic field above 0.4 T. The positive magnetoresistance and the Josephson-junction nature of the intragrain superconductivity could be explained by a phase separation into antiferromagnetic and ferromagnetic domains below the magnetic transition temperature.

ACKNOWLEDGMENTS

This work was supported in part by NSF Grant No. DMR-9804325, MRSEC/NSF Grant No. DMR-9632667, the T. L. Temple Foundation, the John and Rebecca Moores Endowment, and the State of Texas through TCSUH; and at Lawrence Berkeley Laboratory by the Director, Office of Energy Research, Office of Basic Sciences, Division of Materials Sciences of the U.S. Department of Energy under Contract No. DE-AC0376SF000098.

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