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Evidence for a bulk Meissner state in the ferromagnetic superconductor $RuSr_2GdCu_2O_8$ from dc magnetization

C. Bernhard
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

J. L. Tallon
Industrial Research Limited, P.O. Box 31310, Lower Hutt, New Zealand

E. Brücher and R. K. Kremer
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

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From magnetization measurements we provide evidence that the ferromagnetic superconductor $RuSr_2GdCu_2O_8$ with $T_c \approx 45$ K and $T_M \approx 135$ K exhibits a sizeable diamagnetic signal at low temperature ($T < T^{ms} = 30$ K) and low magnetic field ($H^{ext} < 30$ Oe), corresponding to a bulk Meissner phase. We argue that a recent negative report [C. W. Chu *et al.*, cond-mat/9910056 (unpublished)] regarding the Meissner effect in Ru-1212 can be explained by impurity scattering or grain-size effects. At intermediate temperatures, $T^{ms} < T < T_c$, we observe unique thermal hysteresis effects which are characteristic of a spontaneous vortex phase.

Superconductivity (SC) and ferromagnetism (FM) are two antagonistic phenomena. The question as to whether both order parameters (OP) can coexist on a microscopic scale has attracted a great deal of ongoing interest. Experimentally, a coexistence of SC and long-range FM order was discovered in 1976 in the ternary rare-earth compounds $ErRh4B_4$ (Ref. 1) and $HoMo_6S_8$.[2] In these materials the SC state forms at higher temperature ($T_c < 10$ K) than the FM state ($T_M < 1$ K), however, both temperatures are rather low. The formation of the FM state eventually leads to the destruction of SC (reentrant behavior). Albeit, there exists a narrow intermediate temperature range where both SC and FM order can coexist. In this intermediate state the FM order exhibits a spiral modulation or a domainlike structure (depending on the magnetic anisotropy of the system). The modulation of the FM OP helps to circumvent the detrimental pairing-breaking effect due to the exchange interaction (EXI), which prevents singlet pairing (but not triplet pairing) by lifting the degeneracy of the spin-up and spin-down electrons of a Cooper-pair, and the electromagnetic interaction (EMI), which induces screening currents that suppress SC once the internal fields exceed the upper critical field H_{c2}.[3] Likewise also the SC OP may be spatially modulated as realized in a spontaneous vortex phase (in response to the EMI) or in a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) phase[5] (in response to the EXI).

Renewed interest in the interplay between FM and SC order has been stimulated by the recent discovery of coexistence of magnetism (with a sizeable ferromagnetic component) and SC order in the ruthenate-cuprate compound $RuSr_2GdCu_2O_8$ (Ru-1212) (Refs. 6–8) [and in $RuSr_2(Gd,Ce)_2Cu_2O_{10}$ (Ru-1222) (Refs. 6 and 9)]. In these materials the magnetic transition occurs at a considerably higher temperature than the SC one, i.e., in Ru-1212 $T_M = 132–138$ K and $T_c \approx 45$ K. Rather surprisingly, it was found that the onset of SC does not induce any significant modification of the magnetic order.[8] On the other hand, it is still an open question as to how the SC OP, which is thought to originate in the CuO_2 bilayers, is modified in the presence of the already developed magnetic OP, which involves the moments in the Ru-O layers. Recent proposals include the possibility of a FFLO-type state[10] or of a spontaneous vortex phase (SVP).[10,11,9] Obviously, these new materials with their extraordinary properties promise to be unique model systems for studying the complex interplay of SC and FM order.

First of all, however, one has to worry about the chemical and structural homogeneity of these complex materials. One is confronted with three major concerns: (1) are the magnetic and the SC phases intrinsic to the Ru-1212 compound, or is one of them related to a minor impurity phase; (2) does the magnetic OP persist throughout the entire volume of the sample; and (3) is the same true for the SC OP? Already there exists ample evidence that the answer to the first two questions is positive. High-resolution synchrotron x-ray diffraction[12] and neutron-diffraction measurements[13,14] indicate a high structural and chemical homogeneity of our Ru-1212 samples with no detectable impurity phases. Secondly, muon-spin rotation (μSR) measurements[8] and later electron-spin resonance (ESR) measurements[15] have shown that the magnetic order is a uniform bulk effect. The remaining unresolved third question thus concerns the homogeneity of the SC phase. Evidence in favor of a bulk SC state has been obtained for Ru-1212 from specific-heat measurements where a sizeable peak in the specific-heat coefficient γ was observed at T_c, comparable to that for nonmagnetic underdoped Y-123 or Bi-2212 cuprates with a similar $T_c \sim 40–50$ K.[16] On the other hand, Chu *et al.* recently casted doubts as to whether Ru-1212 is a bulk SC.[11] They find that a bulk Meissner effect, generally considered as the key indicator for bulk SC, does not exist in Ru-1212. They argue that the SC signal might be due to an impurity phase which is not even detectable by x-ray or neutron-diffraction experiments. Alternatively, they suggest that the absence of a Meissner

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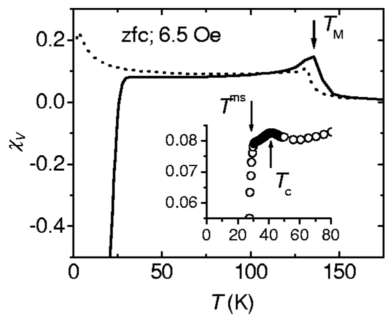

FIG. 1. Zero-field-cooled (zfc) volume susceptibility, χ_V, at 6.5 Oe of the pure sample A (solid line) and the Zn-substituted sample C (dotted line). Inset: Susceptibility of sample A around the SC transition, $T_c \approx 45$ K, shown on an enlarged scale.

effect could be attributed to the creation of a SVP. Such a SVP can be expected to form in a FM superconductor if the spontaneous magnetization, $4\pi M$, exceeds the lower critical field H_{c1} (as defined in the absence of the spontaneous magnetization), i.e., if $4\pi M > H_{c1}(T=0)$.[4,10,11] Otherwise, if $H_{c1}(T=0) > 4\pi M$, the Meissner state will be stable at low temperature. Moreover, since $4\pi M$ is only weakly T dependent below $T_c \ll T_M$ while H_{c1}(T) falls to zero at T_c, a transition to an intermediate SVP will occur at the temperature T^{ms}, where $H_{c1}(T^{ms}) = 4\pi M$.

We present low-field dc magnetization measurements on polycrystalline Ru-1212 samples, which provide evidence that a bulk Meissner state develops in the pure compound at low temperature, with $T^{ms} \leqslant 30$ K varying from sample to sample. We argue that the absence of a Meissner phase as reported in Ref. 11 can be explained in terms of a moderate reduction of H_{c1} due to impurity scattering or grain size effects. In addition, we show that the vortex state at intermediate temperatures, $T^{ms} < T < T_c$, exhibits unique thermal hysteresis effects which are characteristic of a SVP.

Two polycrystalline, pure (SC) $RuSr_2GdCu_2O_8$ samples (A and B), and one Zn-substituted (non-SC) $RuSr_2GdCu_{2.94}Zn_{0.06}O_8$ sample (C) have been prepared as described previously.[7,8] The duration and the temperature of the final sintering step have been slightly varied: 96 h at 1060 °C in flowing O_2 for A and C; and 20 h at 1055 °C for B. It was previously shown that prolonged sintering at 1060 °C helps to remove 90° [100] rotation twins, antiphase boundaries of the rotation of the RuO octahedra and also a minor degree of intermixing of Ru↔Cu and Sr↔Gd.[7,12] Apart from these differences, high-resolution x-ray-diffraction (XRD) (Ref. 12) and neutron-diffraction measurements[13,14] have confirmed that our samples contain no impurity phases above the limits of sensitivity (~1%). The electronic properties have been characterized by resistivity and thermoelectric power (TEP) measurements. The onset of the drop in resistivity and the temperature where the TEP becomes zero indicate $T_c \approx 45$ K for samples A and B and $T_c < 4$ K for the Zn-substituted sample C.[7,8,16] All samples have been further investigated by μSR measurements which confirm that the magnetic ordering of the Ru-moments is hardly affected by the thermal treatment or by Zn substitution.[17]

dc magnetization measurements have been performed with a Quantum Design MPMS7 magnetometer. Figure 1 shows the volume susceptibility, χ_V, of samples A and C obtained after zero-field cooling (zfc) to 2 K before applying an external field $H^{ext} = 6.5$ Oe. A value of ~95% of the ideal density $\rho = 6.7$ g/cm^3 of stoichiometric $RuSr_2GdCu_2O_8$ with $a = 3.84$ Å and $c = 11.57$ Å (Refs. 7 and 12) has been determined for samples A and C and was used to calculate the susceptibility. We have not corrected for the demagnetization factor which should be small since the samples have a bar-shaped form and H^{ext} is parallel to the long axis. The magnetic ordering of the Ru-moments is marked for both samples by a cusp in χ_V at $T_M = 137$ (A) and 132 K (C). In sample C, χ_V exhibits a pronounced increase below 50 K due to the paramagnetic contribution of the Gd moments which order antiferromagnetically (AF) at 2.5 K [as indicated by a cusp in χ_V and as seen in μSR (Refs. 8 and 17) and neutron diffraction[14]]. For the SC sample A, however, a sizeable diamagnetic shift occurs at $T^{ms} = 30$ K. This is not the thermodynamic SC transition, which occurs at $T_c \approx 45$ K (Ref. 16) and is marked by a weak diamagnetic shift as shown in the enlargement in the inset to Fig. 1.

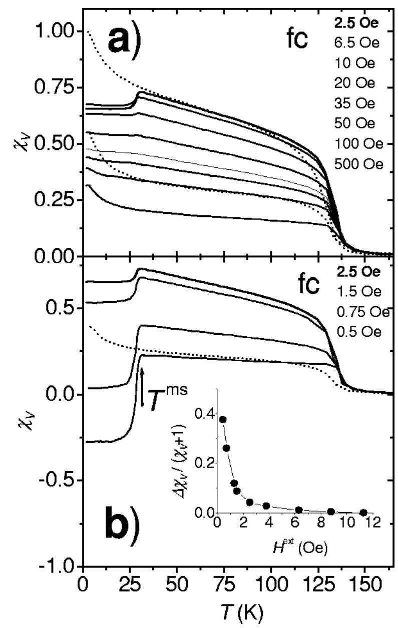

FIG. 2. Field-cooled (fc) volume susceptibility, χ_V, (a) of the pure sample A at 2.5, 6.5, 10, 20, 35, 50, 100, and 500 Oe (solid lines) and the Zn-substituted sample C at 2.5 and 100 Oe (dotted lines); (b) of sample A at 2.5, 1.5, 0.75, and 0.5 Oe (solid lines) and sample C at 0.5 Oe (dotted line).

Figure 2 shows the field-cooled (fc) volume susceptibility, χ_V, of sample A (solid lines) at $0.5 \leqslant H_{ext} \leqslant 500$ Oe and of sample C (dotted lines) at 0.5, 2.5, and 100 Oe. The external field was changed at 200 K with the sample in the paramagnetic state. The low fields were measured by a comparison of the respective paramagnetic signals at 200 K with the signals measured at $50 \leqslant H_{ext} \leqslant 500$ Oe. For both samples a spontaneous magnetization develops at similar temperatures of $T_M = 137$ K (A) and $T_M = 132$ K (C) and below ~100 K it rises almost linearly with decreasing temperature. A clear difference appears only below 30 K where the susceptibility of the SC sample is strongly reduced as compared to the Zn-substituted one. For the Zn-substituted sample χ_V increases at low T due to the paramagnetic contribution of the Gd moments. In marked contrast, for the SC sample χ_V decreases suddenly below $T^{ms}=30$ K (corresponding to a sizeable diamagnetic shielding) and remains almost T independent below T^{ms}. Evidently, in the SC sample the paramagnetic Gd moments are screened against the external field and also the internal spontaneous magnetization. In other words, the SC sample is in a bulk Meissner state at $T<T^{ms}$. Apparently, the paramagnetic Gd moments provide a very useful probe for the Meissner effect. Below we argue that the observed behavior is indicative of a transition from a Meissner phase at $T<T^{ms}=30$ K to a SVP at $T^{ms}=30$ K $<T<T_c\approx 45$ K. The volume fraction of the Meissner phase as estimated from the size of the diamagnetic shift, $(\chi_V(T\rightarrow 0)-\chi_V(T^{ms}))/(\chi_V(T^{ms})+1)$, is shown in the inset of Fig. 2(b) as a function of H^{ext}. Apparently the Meissner fraction is almost 40% at 0.5 Oe but falls very steeply as a function of H^{ext}. Our estimate gives only a lower limit for the Meissner fraction. The diamagnetic shielding tends to be reduced by vortex pinning and also by the small average grain size of around 2–10 μm (which tends to be further reduced due to 90° [100] rotation twins[12]) which is almost comparable to the magnetic penetration depth λ. Assuming an average grain radius $r=3$ μm and an effective magnetic penetration depth $\lambda_{eff}=\sqrt[3]{\lambda_{ab}^2\lambda_c}\sim 500$ nm, we obtain from the Shoenberg formula $\chi/\chi_0=1-(3\lambda/r)\coth(r/\lambda)+3\lambda^2/r^2\approx 0.5$,[18] i.e., a two times larger Meissner fraction. Note that $\lambda_{eff}\approx 500$ nm is quite a reasonable assumption since the unique dependence of T_c on λ in underdoped cuprate SC (Ref. 19) implies $\lambda_{ab}\approx 300$ nm for $T_c\approx 45$ K, whereas λ_c typically exceeds 2000 nm.[18] Based on these considerations we conclude that sample A exhibits a bulk Meissner state with the volume fraction exceeding 40%.

This brings us to the interesting question as to why no evidence of a bulk Meissner phase has been obtained in a recent study on seemingly similar Ru-1212 samples.[11] A straightforward explanation is that $H_{c1}(T=0)$ is moderately reduced in these samples. As was noted above, if $H_{c1}(T=0)<4\pi M$, a SVP will be energetically more favorable than the Meissner phase even at zero applied field and at zero temperature. H_{c1} may be reduced by pair breaking due to magnetic (or nonmagnetic) defects causing a reduction of the SC condensate density and a commensurate enhancement of λ (which is particularly strong in case of a SC OP with d-wave symmetry[20]). Such defects may arise due to some intermixing between Cu and Ru or to the antiphase boundaries of the rotation of the RuO_6 octahedra.[7,12] Also, since the effective value of H_{c1} depends on the ratio of λ/r, the morphology of a given Ru-1212 sample (for example the amount of [100] rotation twins[7]) may actually determine whether or not it exhibits a Meissner effect. The data in Fig. 2 imply that $H_{c1}(T=0)$ in our sample A exceeds $4\pi M$ by less than 30 Oe since the diamagnetic shift at T^{ms} diminishes very rapidly as H^{ext} increases. At 35 Oe the susceptibility already starts to exhibit a slight paramagnetic T dependence due to the Gd moments that are no longer screened against the local fields. From the remanent magnetization found after high-field saturation measurements[8] we estimate that $4\pi M$ is of the order of 50–70 Oe. Note that $4\pi M$ is about ten times smaller than the internal field of ~ 700 Oe as obtained

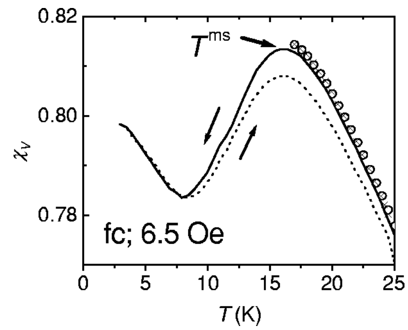

FIG. 3. Low temperature fc curve at 6.5 Oe for the pure sample B which has the same T_c as sample A but has been prepared under slightly different conditions as noted in the text. The Meissner phase forms at significantly lower temperature $T^{ms}=16$ K. Note the thermal hysteresis of χ_V around T^{ms} which is absent if the sample is only cooled to $T=17$ K (crosses) and subsequently warmed (open circles).

from μSR measurements[8] or deduced for the case that the Ru moments of size $1\mu_B$ exhibit purely ferromagnetic order. This difference indicates that the Ru moments exhibit a canted antiferromagnetic order with a $\sim 10\%$ ferromagnetic component[14] possibly related to the tilting of the RuO_6 octahedra.[12] Under the assumption that $4\pi M$ is only weakly T dependent below $T_c\ll T_M$ and using $H_{c1}(T^{ms})=H_{c1}(T=0)\times(1-(T^{ms}/T_c)^2)=4\pi M$ with $T^{ms}/T_c=30/45$, we then obtain $H_{c1}(T=0)$ of the order of 80–120 Oe. In turn this gives $\lambda=\sqrt{\Phi_0/H_{c1}}\sim 400$–500 nm in reasonable agreement with our above estimates.

The finding that T^{ms} appears to decrease only slightly from 30 K at 0.5 Oe to 27 K at 10 Oe can be understood due to the random orientation of the spontaneous magnetization of the individual domains with respect to H^{ext}. For very small fields the domains will not be aligned and in most domains the effective internal field will be only marginally increased or even be decreased. However, once these domains become aligned by a sufficiently large field H^{ext}, the internal field will suddenly be increased to a value $4\pi M+H^{ext}>H_{c1}(T=0)$. For the individual domains the alignment thus will trigger a sudden transition from a state with a Meissner phase below $T^{ms}\simeq 30$ K to one where the SVP persists to the lowest temperatures.

In the following we show that the transition temperature of the Meissner phase T^{ms} varies considerably even among samples that have been prepared under similar conditions. Figure 3 shows the fc data at 6.5 Oe for sample B which has been sintered at slightly lower temperature and for a shorter period as described above. Sample B has a similar critical temperature $T_c\approx 45$ K like sample A (as confirmed by transport and thermodynamic measurements[7,16]), but a Meissner phase forms only at significantly lower temperature $T^{ms}=16$ K. Another interesting feature is the strong thermal hysteresis of χ_V at the transition from the vortex phase to the Meissner phase. Upon cooling (solid line) the transition occurs at a distinctively lower temperature (of about 1 K) than upon warming (dotted line). Notably, the hysteresis occurs only after the sample has been cooled below T^{ms}. It is absent if the sample is only cooled to $T=17$ K (crosses) and subsequently warmed (open circles). This kind of hysteresis, in particular the undercooling effect, is indicative of a first-

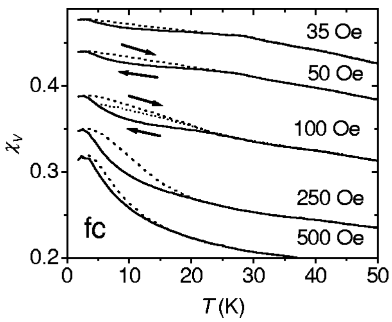

FIG. 4. Thermal hysteresis of the fc data of sample A at 35, 50, 100, 250, and 500 Oe. The solid lines (dotted lines) show χ_V upon cooling (warming). The arrows indicate the direction of the temperature change. At 100 Oe two hysteresis curves for cooling to 2 and 4 K are shown by the thick and thin dotted lines, respectively.

order transition such as from a SVP to a Meissner state where the magnetization exhibits a discontinuous change. In the SVP flux lines are formed which penetrate the sample volume completely. Below T^{ms}, as the Meissner state develops, the flux lines are expelled from the interior of the grains. However, pinning of the vortices by any kind of defects will lead to an incomplete expulsion of the vortices and thus will reduce the diamagnetic shift. On warming the sample again above T^{ms}, the flux lines have to reenter the individual grains. Pinning will hinder the vortices from reentering the superconducting grains. This leads to hysteresis as shown in Fig. 3, where the magnetization upon cooling is higher than that upon subsequent warming.

In sample A the signature of the hysteretic transition at T^{ms} is less pronounced, probably because it contains fewer defects that act as pinning centers and its transition temperature, $T^{ms}=30$ K, is almost twice as high. However, yet another kind of thermal hysteresis related to the magnetization of the Gd moments occurs for $H^{ext}\geqslant 35$ Oe, once the SVP persists to low T. As noted above, the paramagnetic Gd moments eventually become partially aligned in the local field at low T and therefore give rise to a sizeable enhancement of the spontaneous magnetization. Note, that in the SVP the density of the vortices is not only determined by H^{ext} but, in addition, by the spontaneous magnetization. Therefore, even though H^{ext} is constant for a fc curve, the vortex density tends to increase upon decreasing the temperature as the Gd moments become aligned by the local field. Any vortex pinning thus will lead to thermal hysteresis such as shown in Fig. 4, where χ_V is lower upon cooling (solid lines) than upon warming (dotted lines). We have confirmed that such hysteretic behavior of the magnetization does not occur for the Zn-substituted (non-SC) sample C (not shown here). The observed unique hysteretic behavior therefore demonstrates the direct interaction between SC and FM order in the SVP and thus their microscopic coexistence.

In summary, we have presented dc magnetization measurements which provide evidence that the FM superconductor $RuSr_2GdCu_2O_8$ develops a bulk Meissner state. In addition, we show that the state at intermediate temperatures, $T^{ms}<T<T_c$, exhibits unique thermal hysteresis effects which are characteristic of a spontaneous vortex phase. We outline that the absence of a Meissner phase in Ru-1212 as reported in Ref. 11 can be explained in terms of a moderate reduction of H_{c1} due to impurity scattering or grain-size effects.

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