Coexistence of ferromagnetism and superconductivity in the hybrid ruthenate-cuprate compound $RuSr_2GdCu_2O_8$ studied by muon spin rotation and dc magnetization

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

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

Ch. Niedermayer and Th. Blasius
Universität Konstanz, Fakultät für Physik, D-78434, Konstanz, Germany

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

D. R. Noakes and C. E. Stronach
Department of Physics, Virginia State University, Petersburg, Virginia 23806

E. J. Ansaldo†
University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0
(Received 7 December 1998)

We have investigated the magnetic and the superconducting properties of the hybrid ruthenate-cuprate compound $RuSr_2GdCu_2O_8$ by means of zero-field muon-spin rotation (ZF-μSR) and dc magnetization measurements. The dc-magnetization data established that this material exhibits ferromagnetic order of the Ru moments [$\mu(\mathrm{Ru}) \approx 1\ \mu_B$] below $T_C = 133$ K and becomes superconducting at a much lower temperature $T_c = 16$ K. The ZF-μSR experiments indicate that the ferromagnetic phase is homogeneous on a microscopic scale and accounts for most of the sample volume. They also suggest that the magnetic order is not significantly modified at the onset of superconductivity. [S0163-1829(99)07321-X]

I. INTRODUCTION

Since the discovery of superconductivity in the cuprate system $La_{2-x}Ba_xCuO_4$ in 1986,[1] an ever growing variety of high-T_c superconducting cuprate compounds has been synthesized all of which contain CuO_2 planes (some also contain CuO chains) as their essential structural elements which host the superconducting charge carriers.[2] Between the CuO_2 planes are various kinds of layers, typically NaCl-type, which are insulating and act merely as a charge reservoir. To date, the ruthenate compound Sr_2RuO_4 is the only known layered perovskitelike system which becomes superconducting even though it does not contain any CuO_2 planes or CuO chains.[3] Despite its rather low transition temperature $T_c = 1.5$ K, the study of its electronic and magnetic properties has become a very rich and active field of research.[4] In parallel, the electronic and magnetic properties of the related ruthenate compounds, such as, for example, the $SrRuO_3$ system which is an itinerant $4d$-band ferromagnet with $T_C \approx 165$ K, have attracted a great deal of interest.[5]

Another potentially promising and exciting direction of research has been prompted by the circumstance that the RuO_2 layers share the same square-planar coordination and a rather similar bond length with their CuO_2 counterparts. A whole new family of hybrid ruthenate-cuprate compounds may therefore be constructed whose members consist of different sequences of alternating RuO_2 and CuO_2 layers. Recently, one such a hybrid ruthenate-cuprate compound, the 1212-type $RuSr_2GdCu_2O_8$ system comprising CuO_2 bilayers and RuO_2 monolayers, has been synthesized as a single-phase material.[6] A subsequent study of its electronic and magnetic properties has revealed that this material exhibits electronic ferromagnetic order at a rather high Curie temperature $T_C = 133-136$ K and becomes superconducting at a significantly lower critical temperature $T_c = 15-40$ K (depending on the condition of preparation and annealing).[6–8] The most surprising observation, however, is that the ferromagnetic order does not vanish when superconductivity sets in at T_c. Instead, it appears that the ferromagnetic state remains largely unchanged and coexists with superconductivity. This finding implies that the interaction between the superconducting and the ferromagnetic order parameters is very weak and it raises the question of whether both order parameters coexist on a truly microscopic scale. Since the early investigations of Ginzburg in 1957,[9] the prevailing view is that the coexistence of a superconducting- (with singlet Cooper pairs) and a ferromagnetic order parameter is not possible on a microscopic scale since the electromagnetic interaction and the exchange coupling lift the degeneracy of the spin-up and the spin-down partners of the Cooper pair and cause strong pair breaking. Indeed, merely based on magnetization and transport measurements one cannot exclude the possibility that the $RuSr_2GdCu_2O_8$ samples may be

spatially inhomogeneous with some domains exhibiting ferromagnetic order and others superconducting order.[6] We note that unambiguous evidence for the occurrence of bulk superconductivity in $RuSr_2GdCu_2O_8$ has recently been obtained from specific-heat measurements which reveal a sizeable jump at T_c of $\Delta\gamma \equiv C_p/T \approx 0.35$ mJ/g at K^2, characteristic of a strongly underdoped cuprate superconductor.[10] In the following we report on muon-spin rotation (μSR) measurements which establish that the ferromagnetic order is uniform and homogeneous even on a microscopic scale.

The μSR technique is ideally suited for such a purpose since it provides an extremely sensitive local magnetic probe and, furthermore, allows one to reliably obtain the volume fraction of the magnetically ordered phase.[11] Here we present the result of a zero-field muon-spin rotation (ZF-μSR) study of a $RuSr_2GdCu_2O_8$ sample with $T_c = 16$ K and $T_C = 133$ K which provides evidence that the magnetic order parameter is spatially homogeneous and accounts for most of the sample volume. Furthermore, the ZF-μSR data establish that the ferromagnetic order is hardly affected by the onset of superconductivity and persists to the lowest available temperature of the experiment $T = 2.2$ K. The ZF-μSR data can be complemented by dc-magnetization measurements which establish the presence of ferromagnetic order from the observation of a spontaneous magnetization at $T_C = 133$ K and of hysteretic isothermal magnetic behavior with a remanent magnetization. It is shown that the ferromagnetic ordering involves the Ru magnetic moments with $\mu(\mathrm{Ru}) \approx 1.05(5)\mu_B$, while the larger Gd moments with $\mu\ (\mathrm{Gd}^{3+}) \approx 7.4(1)\mu_B$ remain paramagnetic down to very low temperatures. In addition, the magnetization measurements indicate an almost complete diamagnetic shielding effect below T_c.

II. EXPERIMENT

A. Sample preparation and characterization

Polycrystalline samples of the 1212-type system $RuSr_2GaCu_2O_8$ have been synthesized as previously described[8] by solid-state reaction of RuO_2, $SrCO_3$, Gd_2O_3, and CuO powders. The mixture was first decomposed at 960 °C in air. It was then ground, milled, and die-pressed into pellets. The first sintering step took place in flowing nitrogen atmosphere at 1010 °C. This step results in the formation of a mixture of the precursor material Sr_2GdRuO_6 and Cu_2O and is directed towards minimizing the formation of $SrRuO_3$.[6] The material was then reground before it was reacted in flowing oxygen for 10 h at 1050 °C. This sintering step was repeated twice with intermediate grinding and milling. Each reaction step was carried out on a MgO single-crystal substrate to prevent reaction with the alumina crucible. Finally the samples were cooled slowly to room temperature in flowing oxygen. Following this procedure we have also made a Zn-substituted $RuSr_2GdCu_{1.94}Zn_{0.06}O_8$ sample and a Y↔Gd cosubstituted sample $RuSr_2Gd_{0.9}Y_{0.1}Cu_2O_8$. X-ray-diffraction (XRD) measurements indicate that all samples are single phase 1212-type material and give no indication for traces of the ferromagnetic phase $SrRuO_3$. Figure 1(b) displays a representative XRD spectrum of $RuSr_2GdCu_2O_8$, the plus signs show the raw data and the solid line shows the result of the Rietveld refinement. The related structure of $RuSr_2GdCu_2O_8$ is shown in Fig. 1(a).

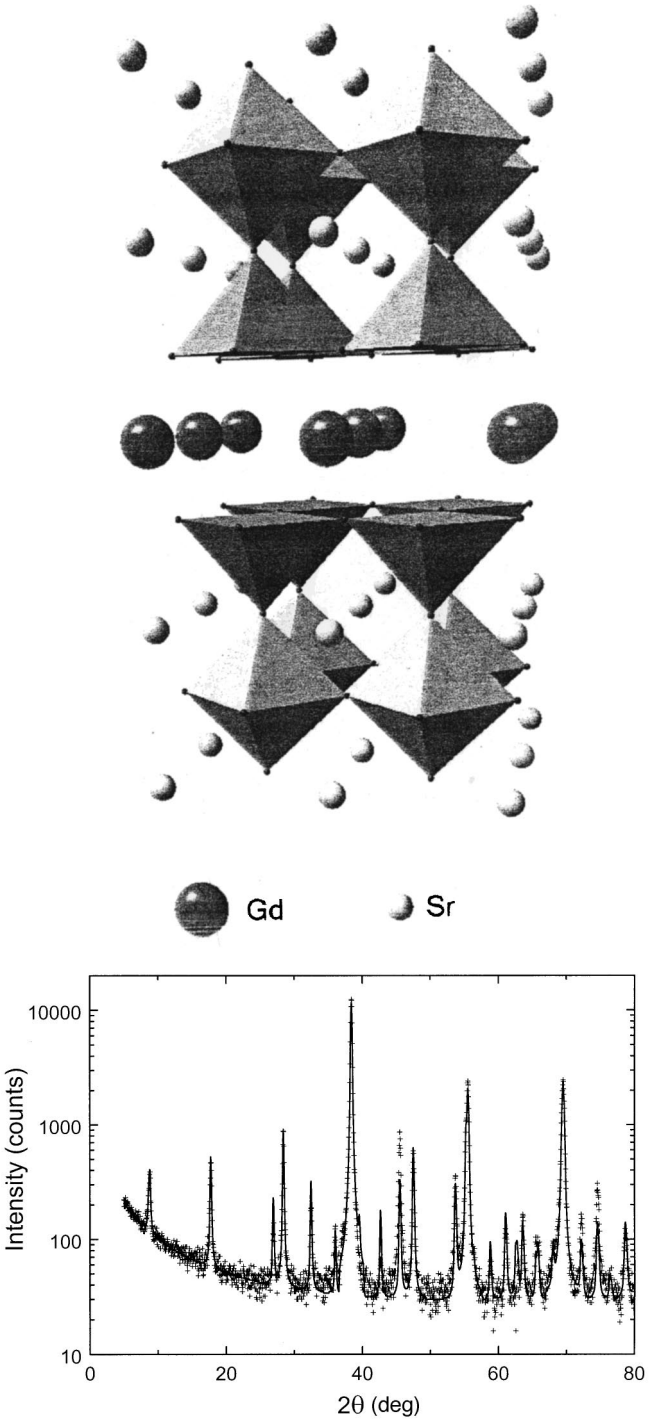

FIG. 1. (a) The structure of $RuSr_2GdCu_2O_8$ with the Cu atoms sited at the center of the base of the square pyramids and the Ru atoms at the center of the octahedra. (b) The x-ray-diffraction (XRD) spectrum for a $RuSr_2GdCu_2O_8$ sample (Co $K\alpha$ source). The plus signs (+) are the raw x-ray data and the solid line is the calculated Rietveld refinement profile for tetragonal (space group *P4*/mmm) $RuSr_2GdCu_2O_8$.

The electronic properties of $RuSr_2GdCu_2O_8$ have been characterized by measurements of the temperature-dependent resistivity and thermoelectric power. Representative results

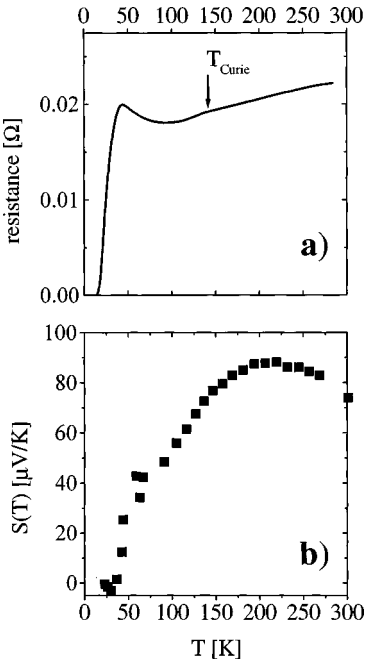

FIG. 2. (a) Temperature dependence of the resistivity ρ of $RuSr_2GdCu_2O_8$. (b) The temperature-dependent thermoelectric power $S(T)$.

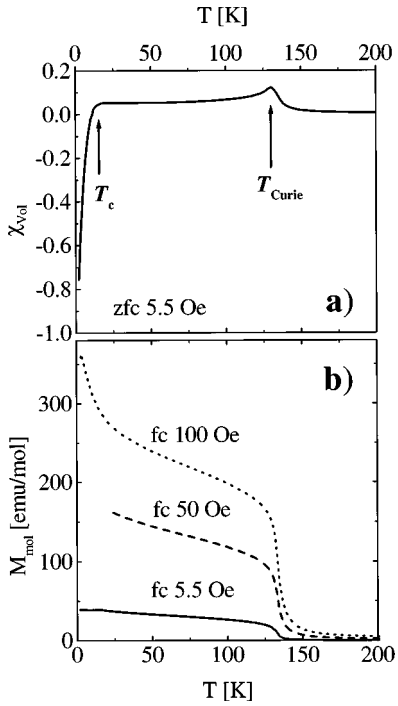

FIG. 3. (a) Temperature dependence of the zero-field-cooled dc volume magnetization χ_V of $RuSr_2GdCu_2O_8$. The arrows show the superconducting and the ferromagnetic transition at $T_c=16$ K and $T_C=133$ K, respectively. (b) The field-cooled molar magnetization $M_{\rm mol}$ for applied fields of $H=5.5$, 10, 100 Oe.

are shown in Figs. 2(a) and 2(b), respectively (see also Ref. 8). The temperature dependence of the thermoelectric power $S(T)$ and, in particular, its normal-state value of $S(300\ \text{K})\approx 75\ \mu\text{V/K}$ is rather typical for a strongly underdoped cuprate superconductor with $T_c \ll T_{c,\max}$, consistent with a hole content of $p\approx 0.07$ holes per CuO_2 planes and a value of $T_{c,\max}$ of the order of 100 K.[8,12] The resistivity measurements indicate that the $RuSr_2GdCu_2O_8$ sample exhibits zero resistivity at a critical temperature of $T_c=16$ K. The precise value of T_c varies between 12 and 24 K, depending on synthesis conditions, and may be raised to 40 K by long-term annealing. The temperature dependence of the normal-state resistivity is again characteristic of a strongly underdoped superconducting cuprate compound. The ferromagnetic transition at $T_C=133$ K causes only a small yet noticeable drop in the resistivity indicating that the RuO_2 layer is almost insulating above T_C, while being poorly conducting in the ferromagnetic state.[5]

B. The technique of muon-spin rotation

The muon-spin rotation (μSR) experiments have been performed at the M15 beamline of TRIUMF in Vancouver, Canada, which provides 100% spin-polarized muons. The μSR technique is especially suited for the study of magnetic materials and allows one to study the homogeneity of the magnetic state on a microscopic scale and also to access its volume fraction.[11] The μSR technique typically covers a time window of 10^{-6}–10^{-9} s and allows one to detect internal magnetic fields over a wide range of 0.1 G to several Tesla. The 100% spin-polarized surface muons ($E_\mu\approx 4.2$ MeV) are implanted into the bulk of the sample where they thermalize very rapidly ($\sim 10^{-12}$ s) without any noticeable loss in their initial spin polarization. Each muon stops at a well-defined interstitial lattice site and, for the perovskite compounds, forms a muoxyl bond with one of the oxygen atoms.[13] The whole ensemble of muons is randomly distributed throughout a layer of 100–200 μm thickness and therefore probes a representative part of the sample volume. Each muon spin precesses in its local magnetic field B_μ with a precession frequency of, $\nu_\mu=(\gamma_\mu/2\pi)\cdot B_\mu$, where $\gamma_\mu/2\pi=135.5$ MHz/T is the gyromagnetic ratio of the positive muon. The muon decays with a mean lifetime of $\tau_{\mu^+}\approx 2.2\ \mu\text{s}^{-1}$ into two neutrinos and a positron which is preferentially emitted along the direction of the muon spin at the instant of decay. The time evolution of the spin polarization $P(t)$ of the muon ensemble can therefore be obtained via the time-resolved detection of the spatial asymmetry of the decay positron emission rate. More details regarding the zero-field (ZF) μSR technique are given below.

III. EXPERIMENTAL RESULTS

A. dc magnetization

Before we discuss the result of the μSR experiments, we first present some dc-magnetization data which establish that the $RuSr_2GdCu_2O_8$ sample exhibits a spontaneous magnetization at a ferromagnetic transition of $T_C=133$ K and becomes superconducting at a much lower temperature $T_c=16$ K. Figure 3(a) shows the temperature dependence of the volume susceptibility χ_V, which has been obtained after zero-field cooling the sample to $T=2$ K, then applying an external field of $H^{\rm ext}=5.5$ Oe, and subsequently warming up to $T=200$ K. The density of the sample has been assumed to be $\rho=6.7\ \text{g/cm}^3$ corresponding to stoichiometric $RuSr_2GdCu_2O_8$ with lattice parameters of $a=3.84$ Å and

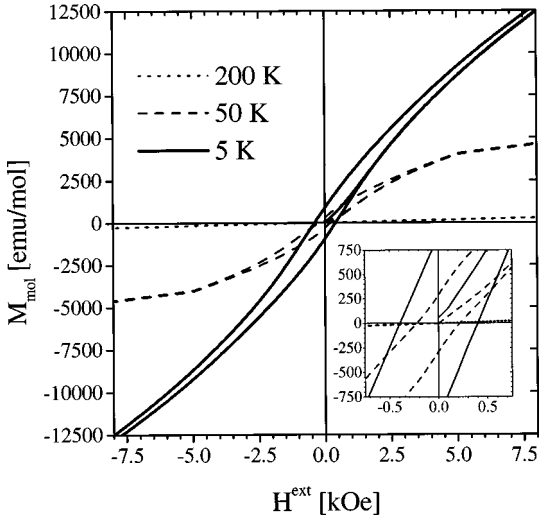

FIG. 4. The isothermal magnetization loops of $RuSr_2GdCu_2O_8$ at $T=5$, 50, and 200 K. The inset shows a magnification of the low-field region.

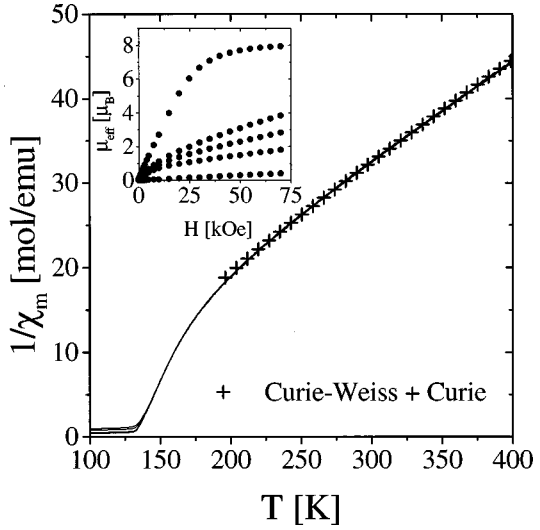

FIG. 5. The temperature-dependent inverse molar susceptibility $1/\chi_m$ for the high-temperature range of 400 K$>T>$100 K. The plus signs show the best fit using a two component Curie-Weiss + Curie function. Shown in the inset is the saturation magnetization in units of effective Bohr magnetons per unit volume as a function of applied field at temperatures of $T=2$, 30, 50, 100, 200 K.

$c=11.57$ Å.[8] The superconducting transition is evident in Fig. 3(a) from the onset of a pronounced diamagnetic shift below $T_c=16$ K. The diamagnetic shift at the lowest available temperature of $T=2$ K corresponds to an almost complete diamagnetic shielding of the sample volume, implying that at least the surface region of the sample is homogeneously superconducting. In fact, all pieces that have been cut from the pellet exhibit a similarly large diamagnetic shielding effect (small differences can be attributed to different demagnetization factors). Nevertheless, the dc-magnetization measurements cannot give unambiguous evidence for the presence of bulk superconductivity since an almost complete diamagnetic shielding may also be caused by a filamentary structure of superconducting material in a small fraction of the otherwise nonsuperconducting material. We note however, that unequivocal evidence for the occurrence of bulk superconductivity in $RuSr_2GdCu_2O_8$ has recently been obtained from specific-heat measurements which reveal a sizeable jump of $\Delta\gamma\equiv C_p/T\approx 0.35$ mJ/g at K^2 at T_c, comparable to or greater than that seen in other underdoped cuprates.[10] For comparison in strongly underdoped $YBa_2Cu_3O_{7-\delta}$ it is found that $\Delta\gamma\approx 0.2-0.3$ mJ/g at K^2.[14] We also note that the specific-heat measurements have been performed on the same samples which have been studied by μSR- and dc-magnetization measurements. Figure 3(b) displays the (low) field-cooled molar magnetization M_m for applied fields of $H^{\rm ext}=5.5$, 50, and 100 Oe. The ferromagnetic transition at $T_C=133$ K is evident from the sudden onset of a spontaneous magnetization. Evidently, the magnetic order parameter has at least a sizeable ferromagnetic component and it persists almost unchanged to the lowest measured temperature $T=2$ K. In particular, it does not appear to weaken as superconductivity sets in at $T_c=16$K. Additional evidence for the presence of ferromagnetic order is presented in Fig. 4, which shows that the isothermal magnetization loops at $T=5$ and 50 K exhibit hysteretic magnetic behavior with a remanent magnetization $M_{\rm rem}\approx 400$ Oe at 5 K and 200 Oe at 50 K.

Having established the existence of ferromagnetic order, the question arises of whether it involves the Ru moments or the Gd moments. In the following we present high-temperature susceptibility data which indicate that the ferromagnetic order involves only the Ru moments, whereas the Gd moments remain in the paramagnetic state below T_C. Figure 5 shows the inverse molar susceptibility, $1/\chi_m \approx (M_m/H^{\rm ext})^{-1}$ obtained for different external fields in the range $5.5\leqslant H^{\rm ext}\leqslant 1000$ Oe (solid lines) in the temperature region 200 K$<T<$400 K. Shown by the plus signs (+) is the best fit to the experimental data using a two-component Curie-Weiss+Curie function, $\chi=C_1/(T-\Theta)+C_2/T$, with $\Theta=T_C=133$ K kept fixed. This function describes the experimental data rather well and it gives us very reasonable values for the magnetic moments, with $\mu_1=1.05(5)\mu_B$ for the moments that order at T_C and $\mu_2=7.4(1)\mu_B$ for the moments that remain paramagnetic below T_C. The magnetic moment of the paramagnetic component agrees reasonably well with the expected magnetic moment of Gd^{3+} which for a free Gd^{3+} ion[15] is $\mu(Gd^{3+})=7.94\mu_B$ and $\mu(Gd^{3+})=7.4\mu_B$ for the structurally similar $GdBa_2Cu_3O_{7-\delta}$ compound.[16] On the other hand, the value of the Ru moments with $\mu(\mathrm{Ru})=1.05(5)\mu_B$ also appears to be reasonable. For Ru^{5+} the number of $4d$ electrons is 3 and the free-ion value of the magnetic moment is $3\mu_B$ for the high-spin state and $1\mu_B$ for the low-spin state. The experimentally observed value of $\mu(\mathrm{Ru})=1.05(5)\mu_B$ therefore seems to imply that Ru^{5+} is in the low-spin state. Shown in the inset of Fig. 5 is the field-dependent magnetization for the temperatures $T=2$, 30, 50, 100, and 300 K. The low-temperature magnetization can be seen to saturate at a value of $\mu_{\rm sat}\approx 8\mu_B$, as may be expected for a system that contains one Gd moment per formula unit with $\mu(\mathrm{Gd})=7\mu_B$ plus one Ru moment with $\mu(\mathrm{Ru})=1\mu_B$.

The idea that the Gd moments do not participate in the ferromagnetic transition at $T_C=133$ K is supported by the result of dc-magnetization measurements on the 10% Y↔Gd cosubstituted $RuSr_2Gd_{0.9}Y_{0.1}Cu_2O_8$. Figures 6(a) and 6(b)

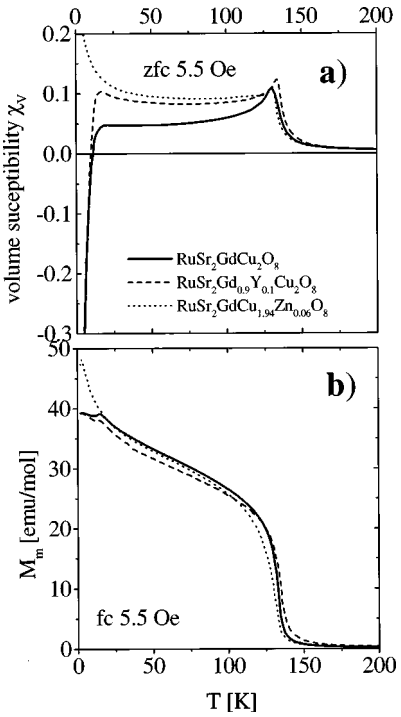

FIG. 6. (a) The temperature-dependent volume susceptibility χ_V of $RuSr_2GdCu_2O_8$ (solid line), for Zn-substituted $RuSr_2GdCu_{1.94}Zn_{0.06}O_8$ (dotted line) and for Y↔Gd cosubstituted $RuSr_2Gd_{0.9}Y_{0.1}Cu_2O_8$ (dashed line). (b) The temperature-dependent molar magnetization M_m, shown by the same symbols as in (a).

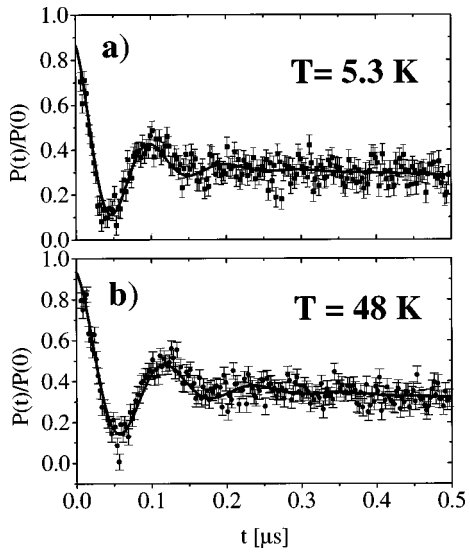

FIG. 7. The time-resolved normalized muon-spin polarization, $P(t)/P(t=0)$, at temperatures of (a) $T=5.3$ K$<T_c$ and (b) $T_c<T=48$ K$<T_C=133$ K. The large oscillatory component gives clear evidence for the presence of a magnetically ordered state.

display the zero-field-cooled,- and the field-cooled susceptibilities (dashed lines) and compare them with the corresponding data on the pure $RuSr_2GdCu_2O_8$ sample (solid line). It is evident that the ferromagnetic transition is not significantly affected by the partial substitution of nonmagnetic Y^{3+} for magnetic Gd^{3+}. Also shown in Figs. 6(a) and 6(b) by the dotted lines are the results for the Zn-substituted $RuSr_2Cu_{1.94}Zn_{0.06}O_8$ sample. The circumstance that the ferromagnetic order is not affected by the Zn substitution supports our view that the majority of the Zn impurities has been introduced into the CuO_2 layers while hardly any of them reside within the RuO_2 layers. Moreover, we infer from the rapid T_c suppression upon Zn substitution that only the CuO_2 layers host the superconducting charge carrier in $RuSr_2GdCu_2O_8$.

B. Zero-field muon-spin-rotation (ZF-μSR)

Next we discuss the result of the zero-field (ZF) μSR experiments. Figures 7(a) and 7(b) show representative ZF-μSR spectra for the evolution of the normalized time-resolved muon-spin polarization $P(t)/P(0)$ at temperatures of $T=5$ and 48 K. The value of the initial muon-spin polarization $P(0)$ has been determined by a transverse field (TF) μSR experiment performed on the same sample at a temperature above T_C. In the ferromagnetic state below $T_C=133$ K we find that the spectra are well described by the relaxation function:

$$P(t)/P(t=0)=A_1\exp(-\lambda t)\cos(2\pi\langle\nu_\mu\rangle t)+A_2\exp(-\Lambda t), \quad (1)$$

where $\langle\nu_\mu\rangle$ is the average muon-spin precession frequency which corresponds to the average value of the spontaneous internal magnetic field at the muons sites, $\langle\nu_\mu\rangle=\gamma_\mu/2\pi\langle B_\mu\rangle$, with $\gamma_\mu=835.4$ MHz/T being the gyromagnetic ratio. The damping rate of the nonoscillating (longitudinal) component Λ is proportional to the dynamic spin-lattice relaxation rate $\Lambda\sim 1/T_1$, whereas the relaxation rate of the oscillating (transverse) component, λ is dominated by the static distribution of the local magnetic field, i.e., $\lambda\approx\gamma_\mu\langle\Delta B_\mu\rangle$. Figure 8 shows the temperature dependence of (a) the precession frequency $\langle\nu_\mu\rangle(T)$, (b) the transverse relaxation rate $\lambda(T)$, and (c) the longitudinal relaxation rate $\Lambda(T)$.

Before we discuss the ZF-μSR data in more detail, we first emphasize the most important implications, which are evident from Figs. 7 and 8. Firstly, the presence of an oscillating component in the ZF-μSR spectra for $T<T_C=133$ K gives unambiguous evidence for an ordered magnetic state which is homogeneous on a microscope length scale (of typically 20 Å). Secondly, from the amplitude of the oscillating component ($A_1\approx 2/3$) we can deduce that the magnetically ordered state accounts for more or less the entire volume of the sample. And thirdly, from the temperature dependence of the μSR signal it becomes clear that the magnetic order persists almost unchanged in the superconducting state.

1. The volume fraction of the magnetic phase

In the following we outline how the volume fraction of the magnetically ordered phase is obtained from the amplitude of the oscillating component of the ZF-μSR spectra. For a polycrystalline sample with randomly orientated grains in zero external field the local magnetic field, on average, is parallel (perpendicular) to the direction of the muon-spin direction with probability 1/3 (2/3). For a homogeneous magnetically ordered sample, one therefore expects that 2/3 of the amplitude of the ZF-μSR signal (the transverse compo-

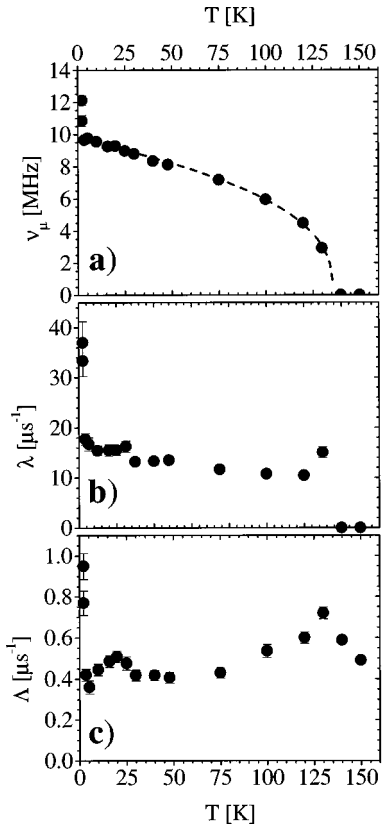

FIG. 8. The temperature dependence of the μSR signal of $RuSr_2GdCu_2O_8$. (a) The muon-spin precession frequency, $\nu_\mu(T)$ (MHz)$=135.5$ (MHz/T) $\langle B_\mu \rangle$. Shown by the dashed line is the best fit using the scaling function $\nu_\mu(T)=\nu_0(1-T/T_C)^\beta$, with $\beta=0.333(5)$, $T_C=133(1)$ K, and $\nu_0=9.70(5)$ MHz $[B_\mu=720(1)\mathrm{G}]$. (b) The relaxation rate of the precessing component, $\lambda(T)$. (c) The relaxation rate of the nonprecessing component, $\Lambda(T)\sim 1/T_1$.

nent) exhibit an oscillatory behavior, while 1/3 of the signal (the longitudinal component) is nonoscillating and is only slowly damped due to spin-flip excitations. On the other hand, for a sample with inhomogeneous magnetic order, for example containing nonmagnetic regions, the amplitude of the oscillating signal will be accordingly reduced and a second nonoscillating transverse component will appear. If the nonmagnetic regions are microscopically small, this nonoscillating component is likely to have a rather large damping rate of the order of $\lambda\sim\gamma_\mu\langle B_\mu\rangle$ due to stray fields which are imposed by the neighboring magnetic domains. From Figs. 7(a) and 7(b) it can be seen that the ZF-μSR data on $RuSr_2GdCu_2O_8$ give no indication for such an inhomogeneous magnetic state. As was mentioned above, the amplitude of the initial muon-spin polarization $P(t=0)$ has been determined from a transverse-field (TF)-μSR measurement. From the size of the amplitude of the oscillatory component we deduce that more than 80% of the sample is magnetically ordered below $T_C=133$ K. Based on this analysis we estimate that the volume fraction of any disordered magnetic or nonmagnetic phase must be well below 20%. Note that some of the muons (typically 10–20 %) do not stop inside the sample but somewhere in the cryostate walls. In the ZF-μSR experiment these muons give rise to a missing fraction since their spin-polarization is much more slowly damped than for the rest of the signal. In the TF-μSR experiment, however, this very slowly damped component can be detected via its precession in the external field and it contributes to the total muon-spin polarization $P(0)$. The 80% fraction of the magnetically ordered phase therefore has to be regarded as a lower bound. In fact, it is rather likely that the entire sample volume is magnetically ordered. Finally, we note that the muons apparently occupy only one muon site, since only one precession frequency is seen in the ZF-μSR spectra. Also it is clear from the ZF-μSR data that muon diffusion effects are negligibly small below $T_C=133$ K, similar to the other cuprate superconductors where muon diffusion is observed only at significantly higher temperatures of $T\geqslant 250$ K.[13]

2. Local magnetic field at the muon site

It is evident from Fig. 8(a) that the muon-spin precession frequency (the local field at the muon site) does not exhibit any strong anomaly at the superconducting transition temperature T_c. Instead, as shown by the dashed line, the temperature dependence of the muon-spin precession frequency $\langle \nu_\mu \rangle(T)$ (and thus of the magnetic order parameter) is well described by the function $\nu_\mu(T)=\nu_0(1-T/T_c)^\beta$, with $\nu_0=9.7(1)$ MHz [corresponding to $\langle B_\mu\rangle(T\rightarrow 0)\approx 720(10)\mathrm{G}$], $T_c=133(1)$ K, and $\beta=0.333(5)$. This functional form is strictly valid only in the critical regime close to T_C but it can be seen to provide a reasonable description of the magnetic order parameter over a fairly wide temperature range of $T_C\geqslant T\geqslant 5$ K. The anomaly at very low temperature arises most likely from the magnetic ordering transition of the Gd moments at $T_N\approx 2.6$ K. Note that for the structurally related compound $GdBa_2Cu_3O_{7-\delta}$ (Gd-123) the antiferromagnetic ordering transition of the Gd moment occurs at a very similar temperature of $T_N=2.3$ K.[16,17] The value of the critical exponent $\beta=0.333$ is close to the theoretical value 0.345 in the 3D *XY* model.[18] We cannot determine with certainty the number of components in the spin system with these data and, in particular, distinguish between the two-component *XY* ($\beta=0.345$) and the three-component Heisenberg ($\beta=0.365$) models. The contribution of ferromagnetic fluctuations above T_C to the susceptibility provides better discrimination as will be discussed later.

The oscillating transverse component exhibits a damping rate of the order of $\lambda\approx 10-15\ \mu s^{-1}$ corresponding to a spread in the local magnetic field of $\langle \Delta B_\mu\rangle/\langle B_\mu\rangle\approx 0.2$. This 20% spread of the local magnetic field does not seem to agree with a scenario where the ferromagnetic order is assumed to exhibit a spiral modulation (with a wavelength shorter than the superconducting coherence length of typically 20 Å in the cuprates) and/or to be spatially inhomogeneous as in $ErRh_4B_4$,[19] $HoMo_6S_8$,[20] and Y_9Co_7.[21] Instead, we emphasize that the observed spread in the local magnetic field can be accounted for by the grain-boundary effects and by the differences in the demagnetization factors of the individual grains which naturally arise for a polycrystalline sample that has a very small average grain size of about 1 μm.[8] Also, we point out that recent transmission-electron-microscopy studies have revealed that our present Ru-1212 sample contains [100] rotation twins and also exhibits some cationic disorder due to the intermixing of Sr↔Gd and to a lesser extent of Ru↔Cu.[8] These kinds of structural imperfections certainly tend to further increase the transverse relaxation rate λ of the

ZF-μSR spectra. Meanwhile, we have prepared Ru-1212 samples which are structurally more perfect (by sintering at slightly higher temperature and for longer periods).[8] Recent dc-magnetization measurements have shown that these crystallographic defects do not affect the fundamental magnetic and superconducting behavior. In fact, both the superconducting and the ferromagnetic transitions become somewhat sharper and T_c and T_C are slightly increased for these structurally more perfect samples.[8] Additional μSR measurements on these samples are presently under way.

3. Longitudinal relaxation rate, $\Lambda \sim 1/T_1$

The temperature dependence of the relaxation rate of the nonoscillating component of the ZF-μSR signal, $\Lambda(T) \sim 1/T$, is shown in Fig. 8(c). As a function of decreasing temperature $\Lambda(T)$ can be seen to exhibit a cusplike feature at the ferromagnetic transition of the Ru moments at $T_C = 133$ K and a steplike increase at very low temperature which most likely is related to the ordering of the Gd moments. The cusp feature at $T_C = 133$ K characterizes the slowing down of the spin dynamics of the Ru moments as the ferromagnetic transition is approached. The cusp maximum occurs when the spin-fluctuation rate τ_c equals the typical μSR time scale for $\tau_c \sim 10^{-6}$.[11] Note, that in the ferromagnetically ordered state that longitudinal relaxation rate remains unusually large with values of $\Lambda(T \ll T_C) \approx 0.3-0.4\ \mu s^{-1}$ that are at least an order of magnitude larger than expected for a classical ferromagnet[22] (where two-magnon excitations provide the major contribution to spin dynamics). We have confirmed by a μSR measurements in a longitudinal field of $H^{LF} = 6$ kOe that this large relaxation rate is indeed characteristic for the longitudinal component of the μSR signal. At present we cannot provide a definite explanation of the origin of the unusually large value of Λ. However, we emphasize that the $RuSr_2GdCu_2O_8$ system can be expected to exhibit a rather complex magnetic behavior since, besides the ferromagnetically ordered Ru moments, it also contains the larger Gd moments with $\mu(Gd^{3+}) \approx 7.4 \mu_B$ which remain paramagnetic below T_C. The magnetic ordering transition of the Gd moments at $T \approx 2.6$ K is evident in the ZF-μSR data in Figs. 8(a)–8(c) from the sudden increase in the local magnetic field (or the μSR precession frequency, $\langle \nu_\mu \rangle$) and a corresponding increase in both relaxation rates, λ and Λ. In addition, we note that recently it has been shown by μSR measurements that in strongly underdoped high-$T_c$cuprate superconductors (like the present $RuSr_2GdCu_2O_8$ compound) also the Cu moments exhibit a spin-glass-type freezing transition at low temperature.[23] Finally, it appears that the longitudinal relaxation rate Λ exhibits an additional weak anomaly at a temperature of $T \approx 20$ K, i.e., in the vicinity of the superconducting transition at $T_c = 16$ K. At present we are not sure whether this effect is related to the onset of superconductivity. From Fig. 8(b) it appears that the transverse relaxation rate also exhibits a steplike increase in the same temperature range. The local magnetic field at the muon site, however, [see Fig. 8(a)] does not seem to exhibit any anomaly in the vicinity of T_c. We expect that further μSR measurements on rare-earth substituted $RuSr_2Gd_{1-x}R_xCu_2O_8$ samples, as well as on less strongly underdoped samples with higher critical temperatures of T_c up to 40 K, should shed more light on the complex magnetic behavior and its interplay with superconductivity in the Ru-1212 system.

TABLE I. The local magnetic field at the muon site $\langle B_\mu \rangle$, obtained from the dipolar-field calculation. The results are shown for two different muon sites and for three different orientations with the Ru moments [$\mu(Ru^{5+}) = 1 \mu_B$] ferromagnetically ordered along the Ru-O bond [100], along the diagonal [110], or perpendicular to the RuO_2 planes [001]. Note that for the [110] orientation there exist two magnetically inequivalent muon sites.

Muon site	[100]	[110]	[001]
(0.13,0.225,0.16)	960 G	1068/805 G	1471 G
(0.128,0.222,0.175)	740 G	824/665 G	1231 G

C. Dipolar field calculation

While the ZF-μSR data give clear evidence for the presence of a homogeneous magnetically ordered state, they do not provide any direct information about the origin of the magnetic moments, the type of the magnetic order, and its direction. Based on dipolar-field calculations of the local magnetic field at the muon site, however, one can test the consistency with an assumed magnetic structure. The result of these calculations depends on the location of the interstitial muon site and also on the orientation of the Ru moments. Unfortunately, for the Ru-1212 system neither of these is accurately known at present. Nevertheless, it seems plausible that the muon site is similar to that in $YBa_2Cu_3O_{7-\delta}$ (and other related cuprate compounds) where the positive muon forms a hydroxyl bond with the apex oxygen and is located at the so-called ''apical site'' near the point $(0.12a, 0.225b, 0.14c)$.[13] Indeed, as is summarized in Table I, we obtain rather good agreement with the experimental value of $\langle B_\mu \rangle (T \rightarrow 0) = 720$ G if we take a similar apical site near the point $(0.13a,\ 0.22b,\ 0.16-0.17c)$ and assume that the ferromagnetically ordered Ru moments [$\mu(Ru) = 1 \mu_B$]are oriented along the RuO_2 plane either along the Ru-O bond, [100], or along the diagonal [110] (see Table I). For the [110] orientation, however, there exist two magnetically inequivalent muon sites which should give rise to two distinctive precession frequencies in the μSR spectra (which are not observed experimentally). For the Ru moments oriented perpendicular to the RuO_2 layer along [001] the resulting local magnetic field at the apex site is significantly larger than the experimental value. In order to obtain reasonable agreement with experiment for the [001] orientation, one has to assume that the muon site is located much closer to the CuO_2 planes. Such a muon site, however, is not very realistic (simply speaking the positive muon is repelled by the positively charged CuO_2 planes) and has not been observed in any of the related cuprate compounds. We thus tentatively conclude that the moments align in-plane consistent with the two-component *XY* scenario. While this result is rather convenient in terms of the coexistence of the ferromagnetic order of the Ru moments and the superconductivity which resides within the CuO_2 layers as discussed below, one has to keep in mind that the underlying assumptions are rather crude. For more detailed and decisive information on the structure and

the orientation of the Ru spin order we must await the result of neutron-scattering experiments.

IV. A POSSIBLE SCENARIO FOR COEXISTENCE OF FERROMAGNETIC AND SUPERCONDUCTING ORDER

Having established that the ferromagnetic and the superconducting order parameter coexist on a microscopic scale, we arrive at the important question as to how this system manages to avoid strong pair-breaking effects. We suspect that the answer is closely related to the layered structure of the hybrid ruthenate-cuprate compound and, in particular, to the purely two-dimensional coherent charge transport in the strongly underdoped CuO_2 planes. We envisage a scenario where the ferromagnetically ordered Ru spins are aligned in the RuO_2 plane having a very large out-of-plane anisotropy while the charge dynamics of the superconducting CuO_2 planes is purely two-dimensional, i.e., coherent charge transport occurs only along the direction of the CuO_2 planes. For such a configuration the principal pair-breaking effect due to the electromagnetic interaction can be minimized, since the dot product of the magnetic vector potential (which then is normal to the planes) and the momentum of the Cooper pair (which is parallel to the planes) vanishes. An additional requirement is that the direct hyperfine interaction between the superconducting electrons of the CuO_2 planes and the ordered Ru spins has to be extremely small. Both requirements may be fulfilled in the present Ru-1212 system due to the confinement of the superconducting electrons of the strongly underdoped CuO_2 planes. The absence of magnetic pair breaking is suggested by the fact that the $T_c$value is fully consistent with the underdoped state indicated by the thermoelectric power.[12] So far we have been unable to significantly increase the doping state (by, e.g., Ca substitution) so as to explore these implications. Furthermore, we have not yet succeeded in crystallographically aligning powders or growing single crystals which would allow one to investigate the magnetic anisotropy. However, further information can be obtained by examining the ferromagnetic fluctuations above T_C as seen in the divergence of the susceptibility. Figure 9 shows d_χ/dT plotted versus (T/T_C-1) for the zero-field-cooled susceptibility for $T>T_C$. The slope of $-2.30(3)$ indicates a critical exponent of $\gamma=1.30(3)$ consistent with 3D *XY* fluctuations for which $\gamma=1.32$ (Ref. 18) and again consistent with orientation of the Ru moments within the *a-b* plane.

Finally, we note that an alternative (and highly speculative) explanation for the coexistence of high-T_c superconductivity and ferromagnetic order in the present Ru 1212 superconductor could be that the superconducting order parameter has a nonzero angular momentum which itself breaks time-reversal symmetry. Such an unconventional order parameter symmetry has been discussed also in the context of the Sr_2RuO_4 superconductor. We point out, however, that at present we have no evidence in favor of such a scenario.

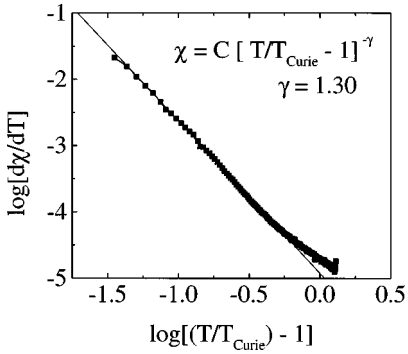

FIG. 9. d_χ/dT plotted versus (T/T_C-1) for the zero-field-cooled susceptibility in the temperature range of $T>T_C$. The slope of $-2.30(3)$ indicates a critical exponent of $\gamma=1.30(3)$ consistent with 3D *XY* fluctuations for which $\gamma=1.32$ (Ref. 18) and consistent with orientation of the Ru moments within the *a-b* plane.

V. CONCLUSIONS

In summary, we have performed dc-magnetization and zero-field muon-spin rotation (ZF-μSR) measurements which characterize the superconducting and the magnetic properties of the hybrid cuprate-ruthenate compound $RuSr_2GdCu_2O_8$. The dc-magnetization data establish that this material exhibits ferromagnetic order (or at least magnetic order with a sizeable ferromagnetic component) below $T_C=133$ K and becomes superconducting at a much lower temperature of $T_c=16$ K. We obtain evidence that superconducting charge carriers originate from the CuO_2 planes, while the ferromagnetic order is associated with the Ru moments with $\mu(\mathrm{Ru})\approx 1\mu_B$. The larger Gd moments with $\mu(\mathrm{Gd})\approx 7.4\mu_B$ do not appear to participate in the ferromagnetic transition but remain paramagnetic to very low temperature and undergo most likely an antiferromagnetic transition at $T_N=2.6$ K. The ZF-μSR experiments provide evidence that the ferromagnetic phase is homogeneous on a microscope scale and accounts for most of the sample volume. Furthermore, they indicate that the magnetically ordered state is not significantly modified by the onset of superconductivity. This rather surprising result raises the question as to how ferromagnetic and superconducting order can coexist on a microscopic scale while avoiding strong pair-breaking effects that tend to destroy superconductivity. We have outlined a possible scenario which relies on the two-dimensional charge dynamics of the CuO_2 planes and the assumption that the ferromagnetic order parameter of the Ru moments is confined to the RuO_2 layers.

ACKNOWLEDGMENTS

We would like to acknowledge S. Kreitzman and B. Hitti for the technical support during the μSR experiments at TRIUMF. J.L.T. thanks the Royal Society of New Zealand for financial support. Ch.N. and Th.B. thank the German BMBF for financial support. C.E.S. and D.R.N. were supported by U.S. Air Force Office of Scientific Research Grant No. F49620-97-1-0297.

*Permanent address: Institute of Experimental Physics, Warsaw University, Hoża 69, 00-681 Warsaw, Poland.
†Present address: 1318 Tenth St., Sakatoon, Saskatchewan, Canada S7H OJ3.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2] R. J. Cava, Science **247**, 656 (1990).
[3] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994).
[4] See, for example, Y. Maeno, S. Nishizaki, K. Yoshida, S. Ikeda, and T. Fujita, J. Low Temp. Phys. **105**, 1577 (1996).
[5] See, for example, L. Klein, J. S. Dodge, C. H. Ahn, J. W. Reiner, L. Mieville, T. H. Geballe, M. R. Beasley, and A. Kapitulnik, J. Phys.: Condens. Matter **8**, 10 111 (1996); G. Cao, S. McCall, M. Shepard, J. E. Crow, and R. P. Guertin, Phys. Rev. B **56**, 321 (1997); I. I. Mazin and D. J. Singh, Phys. Rev. B **56**, 2556 (1997).
[6] L. Bauernfeind, W. Widder, and H. F. Braun, Physica C **254**, 151 (1995); L. Bauernfeind, W. Widder, and H. F. Braun, J. Low Temp. Phys. **105**, 1605 (1996); L. Bauernfeind, W. Widder, and H. F. Braun, in *Proceedings of the Fourth Euro Ceramics*, edited by A. Barone, D. Fiorani, and A. Tampieri (Gruppo Editorale Faenza Editrice, Italy, 1995), Vol. 6, p. 329.
[7] I. Felner, U. Asaf, Y. Levi, and O. Millo, Phys. Rev. B **55**, R3374 (1997).
[8] J. L. Tallon, C. Bernhard, M. E. Bowden, T. M. Stoto, B. Walker, P. W. Gilbert, G. V. M. Williams, D. M. Pooke, and M. R. Presland (unpublished).
[9] V. L. Ginsburg, Sov. Phys. JETP **4**, 153 (1957).
[10] J. L. Tallon, J. W. Loram, G. V. M. Williams, and C. Bernhard (unpublished).
[11] See, for example, A. Schenck, *Muon Spin Rotation: Principles and Applications in Solid State Physics* (Adam Hilger, Bristol, 1986).
[12] S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14 928 (1992).
[13] M. Weber, P. Birrer, F. N. Gygax, B. Hitti, E. Lippelt, H. Maletta, and A. Schenck, Hyperfine Interact. **63**, 207 (1990); N. Nishida and H. Miyatake *ibid.* **63**, 183 (1990).
[14] J. W. Loram, K. A. Mirza, J. R. Cooper, and W. Y. Liang, Phys. Rev. Lett. **71**, 1740 (1993).
[15] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, Philadelphia, 1976).
[16] J. O. Willis, Z. Fisk, J. D. Thompson, S.-W. Cheong, R. A. Aiken, J. L. Smith, and E. Zirngiebl, J. Magn. Magn. Mater. **67**, L139 (1987); D. McK. Paul, H. A. Mook, A. W. Hewat, B. C. Sales, L. A. Boatner, R. J. Thompson, and M. Mostoller, Phys. Rev. B **37**, 2341 (1988).
[17] See, for example, A. Golnik, Ch. Niedermayer, E. Recknagel, M. Rossmanith, A. Weidinger, J. I. Budnick, B. Chamberland, M. Filipkowsky, Y. Zhang, D. P. Yang, L. L. Lynds, F. A. Otter, and C. Baines, Phys. Lett. A **125**, 71 (1987); Ch. Niedermayer, H. Glückler, A. Golnik, U. Binninger, M. Rauer, E. Recknagel, J. I. Budnick, and A. Weidinger, Phys. Rev. B **47**, 3427 (1993).
[18] J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980).
[19] W. A. Fertig, D. C. Johnston, L. E. DeLong, R. W. McCallum, M. B. Maple, and B. T. Mattias, Phys. Rev. Lett. **38**, 987 (1977); D. E. Moncton, D. B. McWhan, P. H. Schmidt, G. Shirane, W. Thomlinson, M. B. Maple, H. B. MacKay, L. D. Woolf, Z. Fisk, and D. C. Johnston, *ibid.* **45**, 2060 (1980).
[20] M. Ishikawa and O. Fischer, Solid State Commun. **23**, 37 (1977); P. Burlet, J. Flouquet, J. L. Genicon, R. Horyn, O. Pena, and M. Sergent, Physica C **215**, 127 (1995); J. W. Lynn, G. Shirane, W. Thomlinson, R. N. Shelton, and D. E. Moncton, Phys. Rev. B **24**, 3817 (1981).
[21] B. V. Sarkissian, J. Appl. Phys. **53**, 8070 (1982); E. J. Ansaldo, D. R. Noakes, J. H. Brewer, R. Keitel, D. R. Harshman, M. Semba, C. Y. Huang, and B. V. B. Sarkissian, Solid State Commun. **55**, 193 (1985).
[22] See, for example, A. Yaouanc and P. Dalmas de Reotier, J. Phys.: Condens. Matter **3**, 6195 (1991); P. C. M. Gubbens *et al.*, Hyperfine Interact. **85**, 239 (1994).
[23] See, for example, Ch. Niedermayer, C. Bernhard, T. Blasius, A. Golnik, A. Moodenbaugh, and J. I. Budnick, Phys. Rev. Lett. **80**, 3843 (1998).