Superconductivity in $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ compounds

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We report on the properties of new ruthenocuprates $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ ($x=0$, 0.1, 0.2, 0.3, 0.4, and 0.75) that extend the superconductivity found previously in $RuSr_2GdCu_2O_8$($T_c=45$ K) to the solid solution with varied Ru/Cu ratios. The compounds have been synthesized in a high-pressure oxygen atmosphere. The maximum temperature of the superconducting transition is 72 K for the $x=0.3$ and 0.4 compositions. The reported behavior of magnetization at low temperatures can be qualitatively explained assuming a quasi-two-dimensional character of the superconducting regions in the compounds studied.

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I. INTRODUCTION

Recent reports of the coexistence of superconductivity and ferromagnetism in ruthenocuprates $RuSr_2GdCu_2O_8$ (Ru-1212) (Refs. 1 and 2) and $RuSr_2(R_{1-x}Ce_x)_2Cu_2O_{10}$, $R=$Gd, Eu (Ru-1222) (Ref. 3) have raised considerable interest in understanding the intrinsic properties of these layered materials. The crystal structure of ruthenocuprates can be described based on its similarity to $RBa_2Cu_3O_{7-y}$ (R123) superconductors. For both Ru-1212 and -1222 the structure contains double CuO_2 planes separated by a single oxygen-less Gd layer for Ru-1212 or a double fluorite $(R_{1-x}Ce_x)_2$ block for Ru-1222. The Ru atoms, coordinating with a full octahedra of oxygens, form the RuO_2 planes that replace the Cu-O chains present in *R*123. The arrangement of Ru atoms resembles that in the $SrRuO_3$ itinerant ferromagnet ($T_c=160$ K) (Ref. 4) or the Sr_2RuO_4 superconductor ($T_c=1.5$ K) for which the possible *p* pairing of superconducting carriers was proposed.[5] Ferromagnetism with a transition temperature of 132 K that originates in the Ru sublattice was postulated for superconducting ($T_c\approx 30$ K) Ru-1212 samples based on magnetization and muon-spin rotation experiments.[2] This observation raises the long-standing issue of the conditions required for the coexistence of the two phenomena now in the class of high-temperature (HT) superconducting compounds. Recent neutron-diffraction experiments show that the dominant magnetic interactions present in $RuSr_2RCu_2O_8$ are of the antiferromagnetic (AFM) type with the Ru moments forming the *G*-type antiferromagnetic structure.[6,7] The ferromagnetism observed in these compounds was proposed to originate from the canting of Ru moments that give a net moment perpendicular to the *c* axis.[6,7] This description is similar to that suggested for Gd_2CuO_4, a nonsuperconducting weak ferromagnet, where the distortions present in the CuO_2 plane permit the presence of the antisymmetric Dzialoshinski-Moriya superexchange interactions in the system of Cu magnetic moments.[8] The presence of both CuO_2 and RuO_2 planes in the structure of ruthenocuprates indicates the need for consideration of a model where the superconductivity is strictly constrained to the CuO_2 planes, whereas the magnetic properties originate in RuO_2 planes. Picket, Went, and Shick[9] reported that strictly layered superconducting and ferromagnetic (FM) subsystems in Ru-1212 should be thin enough to allow three-dimensional ordering through coupling perpendicular to the layers but interact weakly enough to permit superconductivity. To explain the absence of the apparent bulk Meissner state for Ru-1212 a model was proposed in which the superconducting order is modified into a fine structure in order to conform to the presence of a ferromagnetic state.[10] Recently, we have reported that the partial substitution of trivalent Gd by Ce^{4+} in $RuSr_2Gd_{1-x}Ce_xCu_2O_8$ rapidly lowers T_c and simultaneously raises T_N to 145 K for the nonsuperconducting $x=0.05$ composition.[11] This decrease of T_c is consistent with the doping effect observed for underdoped HT superconductors. Partial substitution of Nb^{5+} into the Ru sublattice was found to lower both T_c and T_N for Ru-1212.[12]

Addressing the question of how superconducting properties of ruthenocuprates can be affected by the dilution of the magnetic sublattice of Ru, we attempted to partially substitute Ru with Cu ions. Previously, similar kinds of substitutions were studied in $M_{1-x}YSr_2Cu_{2+x}O_{8-\delta}$ for several elements $M=$Ga, Fe, Co, Ti, W, Mo, and Re and lead to superconducting materials synthesized in air.[13] For Ru substitution we have found that the layered Ru-1212-type structure is stable only during synthesis at high-pressure oxygen conditions. Here we report the properties of a series of superconductors with the formula $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$. The series shows a systematic change of the superconducting and magnetic properties and should also promote a better understanding of the properties of the $RuSr_2GdCu_2O_8$ parent material. For the $x=0.3$ and 0.4 compositions the maximum critical temperatures were raised to 72 K. The reentrant behavior of the magnetization in the superconducting state at low temperatures suggests a quasi-two-dimensional character of superconductivity.

II. SYNTHESIS AND CHARACTERIZATION

Polycrystalline samples of $Ru_{1-x}Sr_2GdCu_{2+y}O_{8-y}$ ($x=0$, 0.1, 0.2, 0.3, 0.4, and 0.75) were prepared by solid-state reaction of stoichiometric RuO_2, $SrCO_3$, Gd_2O_3, and CuO. After calcination in air at 920 °C the samples were ground, pressed into pellets, and annealed at 970 °C in flowing oxygen. The samples were sintered at 1060 °C for 10 h in a high-pressure oxygen atmosphere (600 bar). The crystal structure was examined by the x-ray powder-diffraction method using a Rigaku x-ray diffractometer (CuKα radiation). The diffraction patterns showed that the Ru-1212-type structure formed for all compositions with traces of other

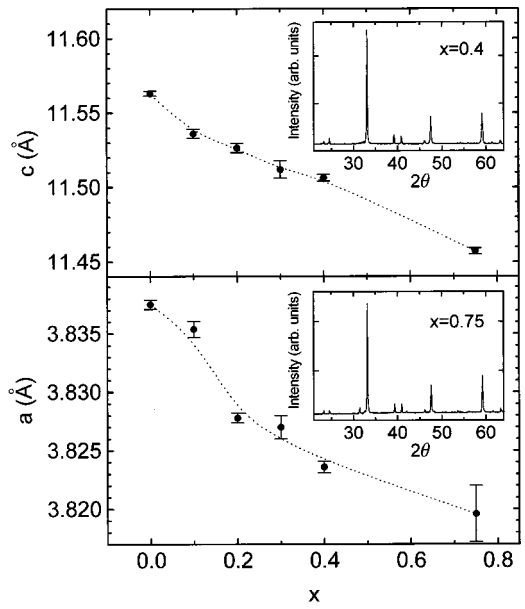

FIG. 1. Lattice constants for the series of $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ with $x=0$, 0.1, 0.2, 0.3, 0.4, and 0.75 (lines are guides to an eye). Insets present the x-ray-diffraction patterns for $x=0.4$ and 0.75 samples.

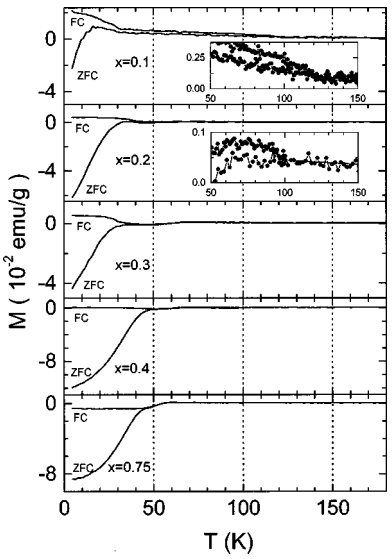

FIG. 2. Temperature dependencies of the zero-field-cooled (ZFC) and field-cooled (FC) dc magnetization (H_{dc}=approximately15 Oe) for the $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ series. For $x=0.1$ and 0.2 samples the corresponding insets show the onset of the irreversibility behavior in the normal state.

impurity phases present (presumably related to $SrRuO_8$). However, no signatures of the magnetic response that could be associated with that phase were observed for any of the samples. Thus, we conclude that this impurity formed at a high pressure of oxygen in distorted or partially substituted form with modified properties. The samples were ground, pressed into pellets, and annealed again in 600 bar of oxygen at 1085 °C for 10 h. Repeated annealing improved the phase purity of the material but did not change the temperatures of the superconducting transitions as verified by ac susceptibility measurements. The structure of all the samples were indexed in the tetragonal 4/mmm symmetry. Changes of the lattice parameters with x are presented in Fig. 1. Both a and c decrease with the substitution of Cu for Ru in the Ru-O planes. This can indicate increased hole doping with x. The insets to Fig. 1 show the x-ray-diffraction patterns for the $x=0.4$ and 0.75 compositions. An additional annealing of the $x=0.4$ sample in 200 bar of oxygen at 550 °C did not change the temperature of the superconducting transition while annealing at 800 °C in flowing air and in 1% of oxygen decreased T_c^{on} from 72 to 55 and 43 K, respectively. The effect of oxygen content on the properties of $x\neq 0$ materials qualitatively resembles the properties of $YBa_2Cu_3O_{7-y}$ and is currently under investigation. The ac susceptibility, dc magnetization, and resistivity data reported here were obtained for high-pressure oxygen synthesized $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ samples. The data was collected using a Quantum Design Physical Properties Measurement System.

III. RESULTS AND DISCUSSION

Figure 2 presents the temperature dependencies of the field-cooled (FC) and zero-field-cooled (ZFC) magnetization measured at approximately 15 Oe for the $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ series. These compounds are superconducting at low temperatures, but FC magnetization at 4.2 K remains positive for all compositions except for $x=0.75$. The details of the superconducting transitions are discussed later in this text. The irreversibility of FC and ZFC branches observed below ~120 and 100 K for $x=0.1$ and 0.2 samples, respectively (see insets in Fig. 2), resembles the behavior of the magnetization observed below $T_N\approx 132$ K for $RuSr_2GdCu_2O_8$ (Ref. 2) and thus should be attributed to the response of the Ru sublattice. However, the magnetization below these temperatures remains remarkably lower than for the $x=0$ parent material. Muon-spin rotation experiments performed for the $x=0.1$ sample indicated that the increase of the relaxation rate observed below ~120 K should not be attributed to the bulk response of the material, contrary to what was observed for parent Ru-1212.[14] It is not clear at present if the ZFC-FC irreversibility of magnetization curves found for $x=0.1$ and 0.2 arises from compositional inhomogeneity (for example, the formation of Ru-rich clusters in the Ru/Cu-O planes) or reflects the magnetic response of diluted RuO_2 planes. For the $x=0.3$, 0.4, and 0.75 compositions we did not observe any irreversibility of the magnetization in the normal state. This indicates the absence of long-range weak ferromagnetic order for the Ru sublattice. However, we should note that the AFM order, if it is not accompanied by the FM component, would not be detected in this experiment.

Figure 3 shows an expanded view of dc magnetization and ac susceptibility at low temperatures. The unusual increase of the FC magnetization below the superconducting transition, which was already observed for $RuSr_2GdCu_2O_8$,[15] shows systematic behavior with increasing x. In Fig. 3 we denote with T_{c2} the onset temperature for the increase (x

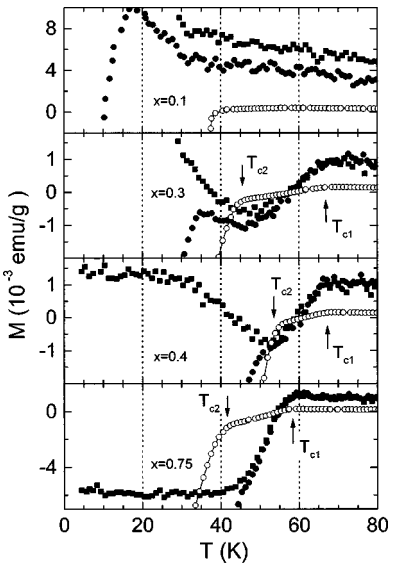

FIG. 3. Temperature dependencies of the zero-field-cooled (closed circles) and field-cooled (closed squares) dc magnetization (H_{dc}= approximately15 Oe) and ac susceptibility (open circles, H_{ac}=1 Oe,200 Hz) for the $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ series. With an expanded scale for the superconducting region, the spread of the data points within $M(T)$ dependencies reflects the limitation of the measurement's sensitivity. For the description of T_{c2} and T_{c1}, see text.

=0.3 and 0.4) and flat behavior (x=0.75) of FC magnetization below the temperature of its initial drop at T_{c1}. The T_{c2} coincides with the temperature at which the ac susceptibility changes slope, reflecting the increase of the bulk screening currents. Figure 4 compares the real parts of ac susceptibility measured for solid chunks and ground powder for the x =0.4 and 0.75 samples. Diamagnetic screening of the bulk samples increases considerably below T_{c2} indicating the onset of superconducting intergrain coupling and shows a complete shielding effect at 4.5 K. The much smaller diamagnetism measured for powder would usually indicate a small amount of the superconducting phase or that the grain size (approx. 1 μm) is comparable to the penetration depth for this material. However, in the following discussion we present arguments that the quasi-two-dimensional character of the superconducting regions can also account for this difference. By combining the ac susceptibility and dc magnetization results one can conclude that the increase of FC magnetization below T_{c2} occurs when the shielding currents start to flow through the boundaries between superconducting regions.

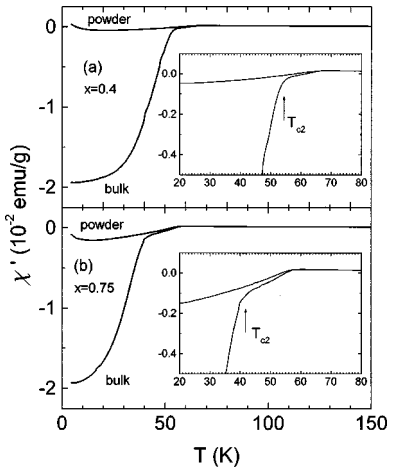

FIG. 4. Temperature dependencies of the ac susceptibility for powder and bulk samples for x=0.4 (a) and 0.75 (b). Insets present the onset of the transitions in the expanded scale. H_{ac}=1 Oe, f =200 Hz.

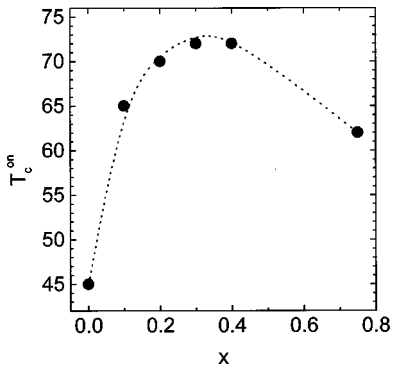

FIG. 5. T_c^{on} versus x for $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ series.

The onsets of resistive transitions were found at T_c^{on} =45, 65, 70, 72, 72, and 62 K for x=0, 0.1, 0.2, 0.3, 0.4, and 0.75, respectively (see Fig. 5). Figure 6 presents the superconducting resistive transitions for the x=0.4 and 0.75 samples measured in magnetic fields of 0, 0.01, 0.05, and 0.1 T (solid lines) and 6.5 T (open circles). The resistivity develops a shoulderlike feature below T_c, the width of which remains very sensitive to small magnetic fields. With increasing x the width as well as the height of this shoulder decreases. If one correlates this behavior with a smaller increase in FC magnetization below T_{c2} for compositions with higher x (see Fig. 3) it can be concluded that the interfaces

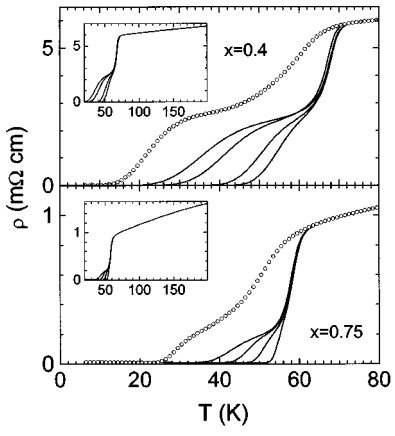

FIG. 6. Resistivity transitions for x=0.4 and 0.75 samples measured at 0, 100, 500, and 1000 Oe (solid lines, the resistivity in the transition increases with field) and at 6.5 T (open circles). Insets show the normal-state behavior. The data were collected on heating.

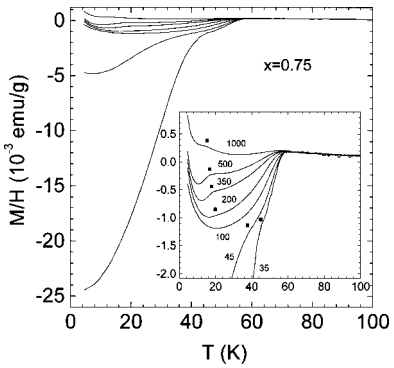

FIG. 7. Temperature dependencies of ZFC dc susceptibility measured for $x=0.75$ sample at 35, 45, 100, 200, 350, 500, and 1000 Oe. Inset shows the behavior in the expanded scale. Closed squares mark temperatures for the onset of bulk superconducting screening (see text).

between superconducting regions less efficiently affect the properties of compounds containing less Ru in the crystal structure. This pattern also seems to hold for the parent Ru-1212 for which the increase of FC magnetization is considerably more pronounced than for $x\neq 0$ compounds and its T_{c2} also correlates with the temperature of the onset of bulk diamagnetism (compare with Ref. 15).

The temperature dependencies of ZFC dc susceptibility at 35, 45, 100, 200, 350, 500, and 1000 Oe for the bulk $x=0.75$ sample are presented in Fig. 7. The susceptibility decreases at the superconducting transition and then increases at lower temperatures for $H_{dc}\geqslant 50$ Oe. In spite of the zero resistance preserved in high magnetic fields at low temperatures [see Fig. 6 for $\rho(T)$ at $H_{dc}=6.5$ T] the ZFC magnetization at 4.5 K remains negative only for magnetic fields lower than approximately 350 Oe. For intermediate values of the magnetic field the additional decrease of the magnetization in the superconducting state is observed (denoted by dots in Fig. 7). By comparing the FC and ZFC magnetization at 500 Oe measured for a chunk of the $x=0.75$ sample [Fig. 8(a), open squares] with the magnetization measured for powder [Fig. 8(a), closed squares] one can correlate this decrease to the effect of enhanced diamagnetic response below the onset temperature for bulk superconducting screening. Interestingly, below this temperature the FC branch remains higher than the magnetization measured for powder. Similar behavior of FC magnetization was also observed for samples with smaller x at lower dc fields. Figure 8(b) shows the ZFC magnetization measured at $H_{dc}=500$ Oe for powder samples of $x=0.4$ and 0.75 and for nonsuperconducting $GdBa_2Cu_3O_{7-y}$ ($y\approx 0.8$). By comparing these dependencies two contributions to the signal can be separated for $x=0.4$ and 0.75: a diamagnetism related to superconductivity and the paramagnetic response of Gd^{+3} ions. Paramagnetic behavior in the presence of superconductivity can be qualitatively understood assuming a quasi-two-dimensional character of superconducting layers separated by nonsuperconducting regions. For polycrystalline samples with randomly oriented crystallines, the paramagnetic response would arise from the crystallines for which superconducting layers are oriented parallel to the external field that

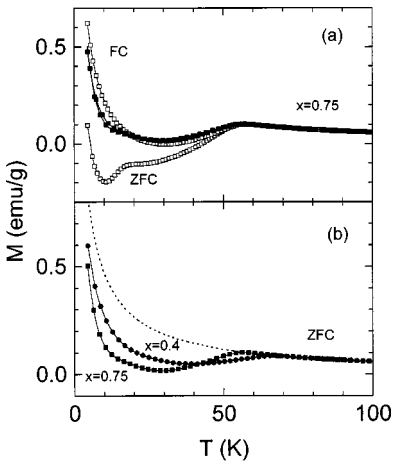

FIG. 8. Temperature dependencies of ZFC and FC dc magnetization for powder (closed squares) and bulk (open squares) $x=0.75$ sample (a); ZFC dc magnetization for $x=0.4$ (circles) and 0.75 (squares) powder samples (b). Dotted line shows the corresponding dependence for nonsuperconducting $GdBa_2Cu_3O_{6.2}$ compound. $H_{dc}=500$ Oe.

can penetrate the space between them. A similar effect was recently proposed to explain the anisotropy of magnetic susceptibility (for $H\perp ab$ and $H\|ab$) observed for high oxygen deficient (i.e., strongly underdoped) superconducting $GdBa_2Cu_3O_{7-y}$ single crystals.[16]

Figure 9 presents the $M(H)$ dependencies for the $x=0.75$ sample measured at 4.5, 20, and 50 K and magnetic fields changed between -500 and 500 Oe. The first critical field at 4.5 K is estimated to be approximately 10 Oe [Fig. 9(a)]. The hysteresis loops can be interpreted as the superposition of the magnetic and superconducting components. The magnetic response at low temperatures arises from the paramagnetism of Gd^{3+} ions. As this magnetic contribution decreases with increasing temperature, the magnetization remains negative for higher fields and presents complex hysteretic behavior [see Fig. 9(b)]. Above the temperature of

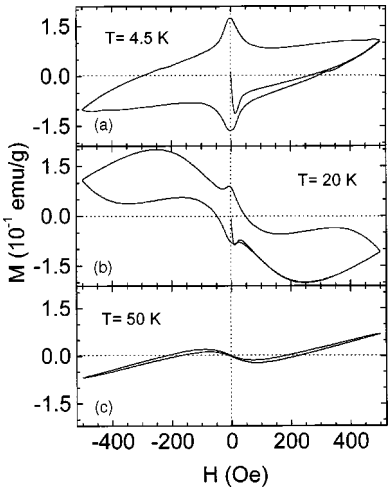

FIG. 9. The magnetic-field dependencies of the magnetization measured at (a) 4.5, (b) 20, and (c) 50 K for $x=0.75$ sample. The field was cycled between -500 and 500 Oe.

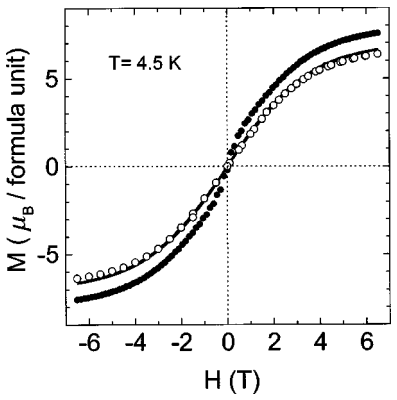

FIG. 10. The magnetic-field dependencies of the magnetization measured at 4.5 K for $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ samples (solid lines converge to one curve). Closed circles show the behavior of superconducting $RuSr_2GdCu_2O_8$, open circles of nonsuperconducting $GdBa_2Cu_3O_{6.2}$.

the superconducting transition the $M(H)$ dependence reflects only the paramagnetism of Gd^{3+} ions (not shown). A detailed discussion of the low-field magnetization behavior for $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ will be presented separately.

The high magnetic-field magnetization dependencies collected at 4.5 K for the whole series of $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ are presented in Fig. 10. In this experiment the magnetic field was changed between -6.5 and 6.5 T in 1000-Oe steps, so the data does not delineate the complicated $M(T)$ behavior below 1000 Oe shown in Fig. 9(a). The magnetizations for $x \neq 0$ samples are presented with solid lines that appear to converge to the curve obtained for nonsuperconducting $GdBa_2Cu_3O_{6.2}$ (open circles). The closed circles in Fig. 10 represent the magnetization of the $RuSr_2GdCu_2O_8$ parent compound. By comparing parent and $x \neq 0$ samples it can be concluded that no additional contribution from the Ru sublattice to the measured signal is observed for the diluted Ru sublattice, i.e., magnetic response is characteristic for the paramagnetic Gd^{3+} ions as seen in $GdBa_2Cu_3O_{6.2}$. Larger magnetization values measured for $RuSr_2GdCu_2O_8$ indicate that only for this compound the long-range weak ferromagnetism of the Ru sublattice contributes to the high-field magnetization by increasing its value by about $1\mu_B$. We should note that this contribution suggests the considerable ferromagnetic alignment of the Ru moments at high magnetic fields. However, the main magnetic contribution to the magnetization of $RuSr_2GdCu_2O_8$ arises from the paramagnetic system of Gd^{3+} ions. This can also indicate the constrained dimensionality of the superconducting regions in this material.

In conclusion, we report that the series of superconducting compounds with the formula $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ can be successfully synthesized at a high pressure of oxygen. The maximum $T_c^{on} = 72$ K ($x = 0.3$ and 0.4) remarkably exceeds the superconducting transition temperature reported for $RuSr_2GdCu_2O_8$ ($T_c^{on} = 45$ K). The signatures of the magnetic ordering of the Ru sublattice above the superconducting T_c are present only for the $x = 0.1$ and 0.2 samples. However, this feature cannot be unambiguously attributed to the bulk of the material, and detailed muon-spin rotation and neutron-diffraction experiments are necessary to resolve the magnetic behavior of the Ru sublattice diluted with Cu ions. The observed reentrant behavior of magnetization below T_c as well as its magnetic-field dependence indicate that at low temperatures the magnetization becomes dominated by the paramagnetic response of the sublattice of Gd^{3+} ions. This observation was qualitatively explained assuming a strong quasi-two-dimensional character of superconducting regions. Further studies of the nanosized characteristics of these compounds are required to investigate the suggested inhomogeneity of the superconducting phase.

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