On the magnetic and superconducting properties of $\text{Ru}_{1-x}\text{Sr}_2\text{RECu}_{2+x}\text{O}_{8-d}$, RE=Gd, Eu, compounds

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The temperature of the superconducting transition of $\text{Ru}_{1-x}\text{Sr}_2\text{RECu}_{2+x}\text{O}_{8-d}$ (RE=Gd, Eu) compounds was raised up to 72 K (for $x=0.4$; compare to $T_C=45$ K observed for $\text{RuSr}_2\text{GdCu}_2\text{O}_8$) by changing the ratio between Ru and Cu. Magnetization experiments performed under external pressure for RE=Gd: $x=0.1, 0.2, 0.3$, and 0.4 , and RE=Eu: $x=0.4$ samples reveal that T_C increases at a rate of 5–6 K/GPa. The hole doping achieved along the series has been probed in Hall effect, thermopower, and XANES experiments and is found to increase with x . Muon spin rotation spectroscopy experiments reveal the presence of a low temperature magnetic transition for $\text{Ru}_{0.6}\text{Sr}_2\text{EuCu}_{2.4}\text{O}_{8-d}$ ($T_m \approx 5$ K), similar to that recently observed in the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8-d}$ system [P. W. Klamut, *et al.*, *Physica C* **364**, 313 (2001)]. Low temperature magnetization data suggest the constrained dimensionality of the superconducting phase in both RE=Gd and Eu based compounds. © 2002 American Institute of Physics. [DOI: 10.1063/1.1452702]

The possibility of microscopic coexistence of superconductivity ($T_C=45$ K) and ferromagnetism in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, as proposed in Ref. 1 based on the results of muon spin rotation spectroscopy, has created substantial interest in the properties of this compound that, by its structural features,² should be classified in the family of high temperature superconductors (HTSC). The neutron diffraction experiments that followed^{3–5} suggest that the weak ferromagnetic component, observed for this system below $T_N=132$ K, should originate from the canting of the antiferromagnetic (AFM) lattice of Ru moments, which give a net moment parallel to the CuO_2 planes in the crystal structure. Recently, by utilizing high-pressure oxygen synthesis, we have synthesized a series of compounds with the formula $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8-d}$. In this series, T_C has been raised to 72 K ($x=0.4$) by the substitution of Cu into the Ru positions in the parent structure of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$.⁶ Whereas the bulk magnetic transitions at temperature above T_C are no longer observed for the $\text{Cu} \rightarrow \text{Ru}$ substituted samples, our recent results from zero-field muon spin rotation spectroscopy (ZF-

μSR) revealed the presence of magnetic transitions (T_m) at low temperatures well below T_C ($2 < T_m < 13$ K for $0.1 < x < 0.4$).⁷

In this article, we present the results of further studies performed on the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8-d}$ series. We also report on the superconductivity in isostructural compounds based on Eu. All samples were synthesized at high-pressure conditions of 600 bars of oxygen at 1080 °C. Details of the samples synthesis are presented in Ref. 6.

Figure 1 presents the charge carrier density at 293 K for the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8-d}$ series, as calculated from Hall effect measurements using the simplified formula $n_H = 1/(R_H \cdot e \cdot c)$. Figure 2 shows the values of room tempera-

FIG. 1. The charge carrier density vs Cu content estimated from Hall effect measurements for $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8-d}$. $T=293$ K.

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FIG. 2. Thermopower at room temperature vs Cu content for $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8-d}$. Inset presents temperature dependence of thermopower for $x=0.4$.

ture thermopower for the $x=0, 0.1, 0.3$, and 0.4 samples in this series. The inset from this figure presents the temperature dependence of thermopower measured for the $x=0.4$ sample. Positive values in the normal state suggest the underdoped nature of this superconductor. Figure 3 presents the values of characteristic Cu K -edge energy obtained in x-ray absorption near edge spectroscopy (XANES) measurements for the same set of samples. All three experiments reveal that the Cu doping into the Ru positions results in enhanced effective hole doping with its possible saturation occurring for $x \approx 0.4$. This composition has the highest T_C in the series (onset at 72 K versus 45 K for $x=0$ and 52 K for $x=0.6$).⁶ We should note that since all samples were prepared at the same oxidizing conditions, one can expect the oxygen content per formula unit could decrease with x and become closer to 7 for composition with larger x . This effect, through its probable influence on the effective charge doping achieved, could contribute to the underdoped characteristic of the $x=0.4$ sample. Measurements of temperature dependences of dc magnetization performed at external pressures up to 1.2 GPa reveal that T_C increases at a rate of approx. 5.5 K/GPa for all investigated samples. This also suggests the underdoped character of the compounds. Figure 4 shows the temperature dependences of resistivity and ac susceptibility (insets, $H_{ac}=1$ Oe, $f=200$ Hz) for Fig. 4(a) $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_{8-d}$ and Fig. 4(b) $\text{Ru}_{0.6}\text{Sr}_2\text{EuCu}_{2.4}\text{O}_{8-d}$. The onsets of the resistive transitions are 72 K for Gd- and

FIG. 3. Characteristic XANES Cu K -edge energy vs Cu content for $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8-d}$ series. $T=293$ K.

FIG. 4. Temperature dependencies of resistivity and real and imaginary components of ac susceptibility (insets) for: (a) $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_{8-d}$ and (b) $\text{Ru}_{0.6}\text{Sr}_2\text{EuCu}_{2.4}\text{O}_{8-d}$.

70 K for Eu-containing sample. Comparison with the ac susceptibility data reveals that the intergranular transition, indicated by a change in slope of the real component of ac susceptibility and the maximum of its imaginary component, occurs at a temperature several degrees lower than the transition onset temperature (a more pronounced difference is

FIG. 5. The magnetic field dependencies of dc magnetization at 4.5 K for: (a) $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_{8-d}$ and (b) $\text{Ru}_{0.6}\text{Sr}_2\text{EuCu}_{2.4}\text{O}_{8-d}$. Insets show low field behavior at expanded scale.

FIG. 6. The asymmetry of zero-field time resolved muon spin polarization for $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_{8-d}$ at 1.8 K. Fit with an equation: $A = 2/3B \cos(\gamma_\mu B_\mu t + \phi)$ for the time evolution of the muon spin polarization described by: $P(t) = A \exp(-1/2(\gamma_\mu \Delta B_\mu t)^2) + 1/3B \exp(-\lambda t)$; B —the initial asymmetry measured in the external field in the normal state, $\gamma_\mu = 851.4 \text{ MHz/T}$, B_μ —the average internal field at the muon site.

observed for $\text{Ru}_{0.6}\text{Sr}_2\text{EuCu}_{2.4}\text{O}_{8-d}$). Figure 5 presents the comparison of $M(H)$ dependencies for both samples measured at 4.5 K. Insets show the low field part of the hysteresis loops. As has been discussed in detail in Ref. 6 for the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8-d}$ series, the positive values of magnetization measured in the superconducting state at magnetic field well below H_{c2} should originate from the paramagnetic response of Gd ions. A similar effect, although considerably smaller because of the negligible contribution of the Eu moments, is also observed for $\text{Ru}_{0.6}\text{Sr}_2\text{EuCu}_{2.4}\text{O}_{8-d}$ [Fig. 5(b)] and suggests the constrain dimensionality of the superconducting phase in these compounds. The hysteresis of the $M(H)$ dependences (insets from Fig. 5) can be explained by flux pinning in the mixed state of the superconductor.

The ZF- μSR experiment revealed the presence of low temperature magnetism for superconducting $\text{Ru}_{0.6}\text{Sr}_2\text{EuCu}_{2.4}\text{O}_{8-d}$, which is similar to the behavior found for $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_{8-d}$.⁷ Figure 6 presents the asymmetry of the muon decay spectrum registered at 1.8 K for this sample. Observed behavior is indicative of fast damped oscillations due to the precession of muons spin in the inhomogeneous internal magnetic field. The initial value of the observed asymmetry indicates that the measured response is a characteristic of the bulk of the sample. The temperature dependence of the muon spin relaxation rate (σ ; measures the rate of muon spin depolarization due to the field distribution in the specimen) measured in a transverse field experiment (TF- μSR) is presented in Fig. 7. In this experiment the sample was cooled down in an external field of 2000 Oe with an orientation perpendicular to the spins of the incoming muons. The initial increase of σ at 60 K, due to the distribution of the magnetic field penetrating the superconducting volume in the form of vortices, is followed by a steep increase observed at low temperatures that can be attributed to internal magnetism in the sample. Assuming that the superconducting contribution to σ should flatten out at low temperatures, its value at 0 K can be extrapolated to $\sigma_0 = 1.6 \mu\text{s}^{-1}$ (solid line in Fig. 7) that matches well with the prediction from universal Uemura line⁸ for $T_c \approx 60$ K underdoped HTSC superconductor. The inset from Fig. 7

FIG. 7. Temperature dependence of muon spin relaxation rate σ calculated from the TF- μSR spectra for $\text{Ru}_{0.6}\text{Sr}_2\text{EuCu}_{2.4}\text{O}_{8-d}$ sample. Inset shows the temperature dependence of the internal magnetic field. The external transverse field (TF) equal to 2000 Oe.

presents the temperature dependence of the internal magnetic field as calculated from the frequency of asymmetry oscillations at different temperatures. The field decreases at the superconducting transition (Meissner effect) and then increases at low temperatures in the magnetically ordered state that sets in below $T_m \approx 5$ K. The observed low temperature internal magnetic field can be attributed to the magnetic response of the Ru/Cu-diluted sublattice or Cu moments in the CuO_2 planes. Then, the μSR data could be interpreted as indicative of a coexistence of the magnetic and superconducting order parameter as has been observed in other underdoped systems: see Ref. 9 for the antiferromagnetic correlations observed for underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_6$ for which the microscopic inhomogeneity of the charge distribution in the CuO_2 planes and associated stripes formation have been proposed.¹⁰ Further experiments aimed at understanding the microscopic nature of the low temperature magnetism observed for $\text{Ru}_{0.6}\text{Sr}_2\text{EuCu}_{2.4}\text{O}_{8-d}$ and $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8-d}$ (Ref. 7) are in progress.

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