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Effects of Ru Addition on the Superconducting Properties of the Eu-123 System

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Effects of the Ru addition on the structural and superconducting properties of the Eu-123 system were studied. Samples of the nominal composition $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ with x ranging from 0.0 to 0.7 were prepared by the solid state reaction technique from Eu_2O_3, $BaCO_3$, CuO and RuO_2 precursors at the temperature of 1050 °C for 72 h in flowing oxygen and oxygen-annealed at 580 °C for 24 h. X-ray diffraction data show the presence of another Ba–Eu–Ru–O phase, for $x \geq 0.03$, in addition to the main superconducting phase. AC and DC magnetization characteristics were measured by the compensation method using the second-order SQUID gradiometer at ≈ 77 K and the QD SQUID magnetometer MPMS XL-7 at 20 K. The superconducting properties, T_c, ΔT_c, change only weakly up to $x = 0.2$, and magnetization $M(H)$ deteriorates with an increasing Ru content.

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1. Introduction

The chemical doping is a useful tool for the study of the mechanism of the high-T_c superconductivity in RE-123 superconductors, where RE is Y or lanthanide. With regard to the role of Cu–O_2 planes, special attention has been paid to substitutions by M = Fe, Co, Ni, Mg, Sc, Ti, Ge, Sn, Pb, Au, Ag, etc., into copper positions. Mostly, it has been reported that with an increasing content of M-doping atoms x, T_c decreases, namely for a higher substitution content. However, it has been observed that changes of T_c depend not only on the doping level but also on the way of the sample preparation.

Among RE-123 systems, particular attention has been paid to Y-123 and relatively small attention has been paid to M = Ru. In addition, some inconsistent results were reported for the case of nonmagnetic, e.g., Y-cations or magnetic Gd-cations in RE-123. Shulga et al. in [1] for $YBa_2Cu_{3-x}Ru_xO_{7-\delta}$ reported that the presence of a platinum group metal did not decrease T_c. For $x =$ 0.4, they reported the critical temperature $T_c(R) = 94$ K and for $x = 0.5$ still $T_c(R) = 89$ K. On the other hand, for the $GdBa_2Cu_{3-x}Ru_xO_{7-\delta}$ system, Award et al. [2] reported that the superconductivity had been completely destroyed for $x = 0.3$.

2. Experimental

We have studied effects of doping of the Ru ions in the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ compound. Samples with the nominal composition deflection $x =$ 0.0, 0.01, 0.03, 0.07, 0.1, 0.2, and 0.7 were prepared by a standard solid-state reaction method using commercial 99.99% purity oxide powders of Eu_2O_3, CuO, and $BaCO_3$. Thereafter, the powders were carefully weighed in appropriate weight amounts and homogenized in air in an agate mortar for 5 min and calcined at 930 °C for 40 h in air. The obtained precursors were again homogenized, pressed into pellets (with the diameter of 12 mm) and sintered in a horizontal tube furnace in flowing oxygen of 20 ml/min) at about 1050 °C for 72 h, then cooled to 580 °C and held at this temperature for 24 h and thereafter cooled in the furnace to room temperature.

We prepared three sets of $EuBa_{3-x}Ru_xO_{7-\delta}$ samples. The samples in each set were prepared in one (and the same) thermal cycle. All three sets of the samples show almost identical properties. For example, for $x = 0.1$, the values of the critical temperature and (ΔT_c) of the corresponding sample in the first, second, and third set represent 88.4 K (1.5 K), 90.6 K (2.0 K), 90.7 K (1.9 K), respectively. In the paper, we reported results of the second set of the samples, except for the magnetization vs. applied magnetic field dependences, at 20 K, in Fig. 1, which were measured on the samples of the first set only. The results of the detailed study of magnetic properties of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ compounds will be published in another paper.

$T_c(R = 0)$ was determined by the standard resistance four-point method and the transition width ΔT_c was characterized by the 10–90% criterion. The inaccuracy of temperature measurements was less than 0.2 K. The phase composition was studied by X-ray diffraction measurements (Cu K_α radiation). AC low field magnetization M_{AC} at 77 K was measured by a compensation method using the second-order SQUID gradiometer [3] and DC magnetization M_{DC} at higher field and lower temperature by the Quantum Design SQUID magnetometer MPMS XL-7.

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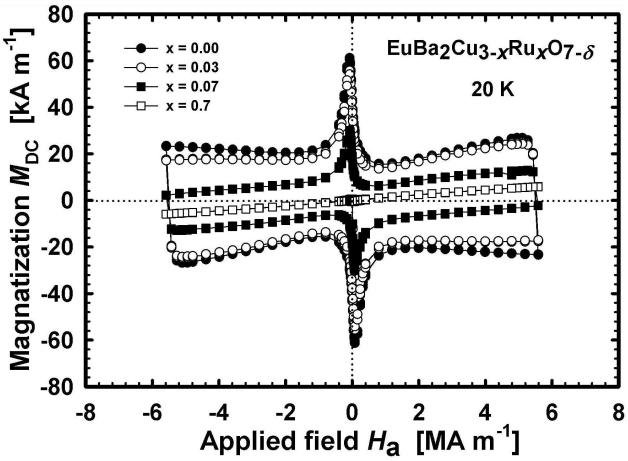

Fig. 1. M_{DC} vs. H_a dependences at 20 K and for higher values of H_a of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples.

3. Results and discussion

From X-ray diffraction data, it can be concluded that besides the main superconducting Eu-123 phase, the presence of the excess phase starts evidently for $x \geq 0.03$. The phase could be identified as the non-metal, non-superconducting $Ba_3EuRu_2O_9$ phase with interesting magnetic properties [4]. Figure 2 and its inset show the effect of the Ru addition on T_c and ΔT_c, respectively.

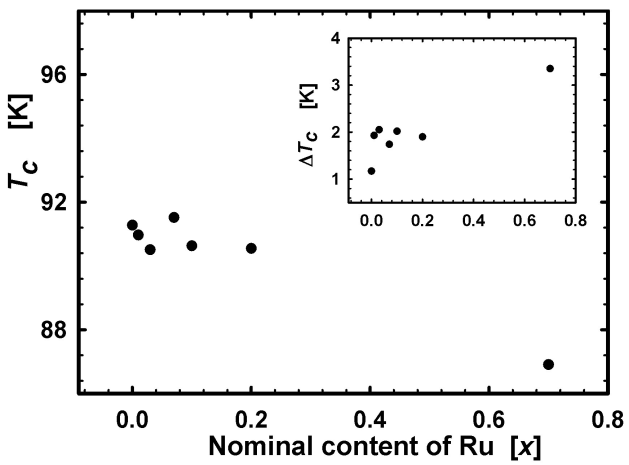

Fig. 2. T_c vs. x of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples. The insert shows ΔT_c vs. x.

In Fig. 3 the hysteresis curves of the volume magnetization M_{AC} vs. the applied field H_a for the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples at 77 K and relatively low applied field H_a are shown.

The increasing content of Ru results in decreasing of M_{AC} and magnetization hysteresis. However, the magnetization curves of the sample with $x = 0.7$ show an evident (para)magnetic "tail"- magnetic contribution indicated by the slope of the curve pointing to the first and third quadrants. The hysteresis of the curve could

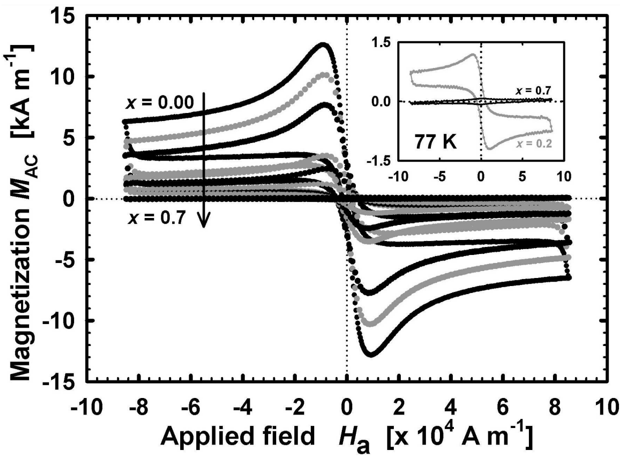

Fig. 3. M_{AC} vs. H_a of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples at 77 K and low magnetic field. Inset is selected view of the hysteresis loops for the samples with $x = 0.2$ and 0.7.

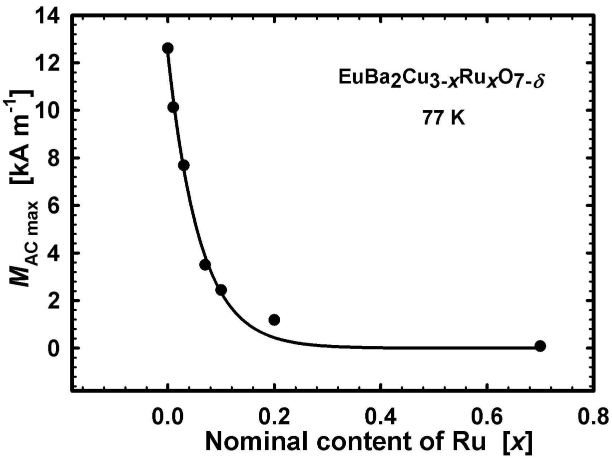

Fig. 4. $M_{AC\,max}$ vs. the nominal content of Ru(x) for $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples at 77 K.

be ascribed to the superconducting phase. In Fig. 4, a decreasing trend of the maximal value of M_{AC}, ($M_{AC\,max}$) with an increase of the Ru content at 77 K is documented. The solid line in Fig. 4 is a fit of the measured data by the $y = 12.4\exp(-16.7x)$ function.

In Fig. 1 the effects of the Ru addition in $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples at 20 K and the applied field H_a up to ≈ 5.6 MA m^{-1} are shown. The magnetization loops with the Ru content $x \leq 0.03$ indicate the so-called second peak effect, while the loops for $x = 0.7$ show the magnetic "tail".

The sample with the highest Ru content shows a strong magnetic contribution that can be ascribed to the $Ba_3EuRu_2O_9$ phase, which competes with the superconducting phase that becomes visible at lower H_a only (see inset of Fig. 5).

The results of the magnetization vs. the applied magnetic field dependences in Fig . 1, 3–5 can be interpreted as a composition of two contributions of the su-

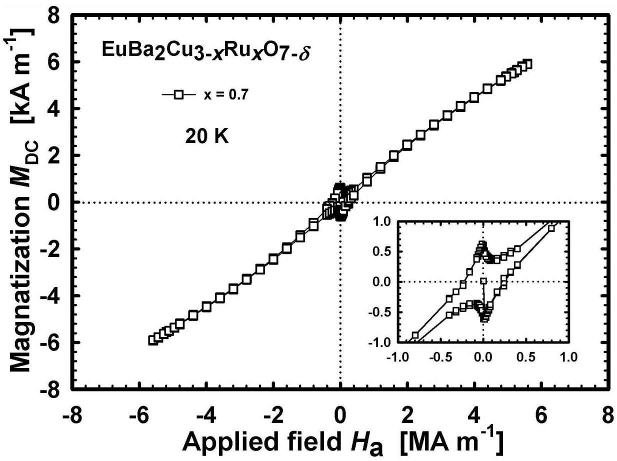

Fig. 5. M_{DC} vs. H_a of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ sample with $x = 0.7$ at 20 K. The inset is an enlargement and shows the low-field part where the superconducting contribution dominates in this part of the magnetization curve.

perconducting and paramagnetic components of the Eu-123 main phase and magnetic contribution of the excess $Ba_3EuRu_2O_9$ phase. In the first paramagnetic contribution, the Van Vleck paramagnetic contribution of Eu^{3+} ions must be considered. The magnetic properties of the samples with the high Ru content strongly affect the secondary $Ba_3EuRu_2O_9$ phase. The indicated effect of the secondary magnetization peak effect could be ascribed to Eu^{2+} ions that substitute Ba^{2+} sites in Eu-123, which is in agreement with [5]; and by doing the syntheses of our samples in the oxygen atmosphere.

3. Conclusions

The samples with nominal compositions $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ where x is ranging from 0.0 to 0.7 were prepared by the solid state reaction technique from Eu_2O_3, $BaCO_3$, CuO, and RuO_2 precursors at the temperature of 1050 °C for 72 h in flowing oxygen and oxygen-annealed at 580 °C for 24 h. When increasing the Ru content, the critical temperature T_c changes slightly only, while still being higher than 90.5 K, and ΔT_c is still about 2 K up to $x \leq 0.07$. X-ray diffraction data show the presence of another non-metal $Ba_3EuRu_2O_9$ phase in addition to the main superconducting phase starting from $x = 0.03$. Based on that, the T_c, ΔT_c remain almost unaffected up to $x = 0.2$, the magnetization $M(H)$ deteriorates with an increasing Ru content and the excess $Ba_3EuRu_2O_9$ phase starting from $x = 0.03$ suggest that the solution of Ru in the Eu-123 phase is very limited, if at all.

AC magnetization characteristics, M_{AC}, were measured by a compensation method using the second-order SQUID gradiometer at $\approx$ 77 K and DC magnetization characteristics, M_{DC}, by the QD SQUID magnetometer MPMS XL-7 at 20 K. The magnetization loops with the Ru content $x \leq 0.03$ indicate the so-called second peak effect and the loops for $x > 0.03$ show the magnetization (para)magnetic "tail" at 20 K. The maximum value of the volume magnetization of the samples at 77 K decreases as the exponential function of the Ru-content x.

Acknowledgments

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