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Magnetic Studies of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ Compounds

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Effects of Ru addition on magnetic properties of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ compounds were studied. Samples of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ with x from 0.00 to 0.70 were prepared by the solid state reaction technique from Eu_2O_3, $BaCO_3$, CuO and RuO_2 precursors. Temperature dependences of the zero-field cooled (ZFC) and the field cooled (FC) DC magnetic moment at low and high applied magnetic field H_a were measured by the QD SQUID magnetometer MPMS XL-7 and AC magnetization $M_{AC}(H)$ curves at 77 K by the compensation method using the second-order SQUID gradiometer. The molar susceptibility χ of the samples was corrected to the effects of the sample holder and diamagnetism and χ^* also was corrected to the temperature independent paramagnetic/diamagnetic contribution χ^{TN} and fitted by the Curie–Weiss relation. The values of the Weiss temperature and the effective magnetic moment have been estimated at low and high value of applied magnetic field.

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1. Introduction

Already during the first years of the discovery of the high-T_C superconductors, the RE-123 type, where RE = Y and the rare earths elements, it has been reported that the magnetic susceptibility of most RE-123 compounds above the critical temperature T_C can be well described by the Curie–Weiss relation with a small negative values of the Weiss temperature Θ. The experimental values of the μ_{eff} of Re^{3+} ions are in very good agreement with the expected ones for $4f$ ions in magnetic ground state using the Hand rules [1–4]. The observed discrepancies for Sm- and Eu-123 systems have been ascribed to close proximity energy of their low-lying excited states to the ground state [5, 6]. Thus, e.g., the experimental value of μ_{eff} of Eu^{3+} ions obtained by measurements of Eu_2O_3 at 300 K is near 3.4 μ_B [7], opposite to zero predicted by the Hand rule.

2. Experimental

In the paper, we study the effects of doping by Ru ions in the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ system on magnetic properties.

We prepared three sets of samples of $EuBa_{3-x}Ru_xO_{7-\delta}$. The samples in each of the sets were prepared in one (and the same) thermal cycle. All the three sets of the samples show the same trends of change in the studied properties with a higher spread of the values, for $x \geq 0.20$, while for $x = 0.10$, e.g., the T_C and the transition width (ΔT_C) values of the corresponding sample in the first, second and third sets 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 first set of the samples.

The samples 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 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.

The $T_C(R = 0)$ was determined by the standard resistance four-point method and ΔT_C 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 obtained using PANalytical Empyrean Diffractometer (CuK_α radiation).

AC (0.1 Hz) magnetization M_{AC} at low field and 77 K was measured by a compensation method using the second-order SQUID gradiometer [8]. Temperature dependences of ZFC/FC DC magnetic moment were measured by the QD SQUID magnetometer MPMS XL-7. Molar (per formula unit) susceptibilities χ of the samples were corrected to the effect of the sample holder and to the diamagnetism using the tabulated values of diamagnetic susceptibilities of cations and anions given by Bain and Berry [9]. The corrected FC $\chi^*(T)$ curves ($\chi^* = \chi - \chi^{TN}$) were fitted by the Curie–Weiss law, $\chi = C/(T - \Theta)$. Corresponding values of the Weiss temperature Θ^* and the effective magnetic moment μ^*_{eff} were estimated.

3. Results and discussion

The results of the X-ray diffraction measurements are presented in Fig. 1. From the XRD measurement, it can be concluded that in addition to the main superconducting Eu-123 phase, the excess phase exists, whose peaks can be observed evidently starting for $x \geq 0.03$. The phase could be identified as the non-metal,

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non-superconducting $Ba_3EuRu_2O_9$phase with interesting magnetic properties [10].

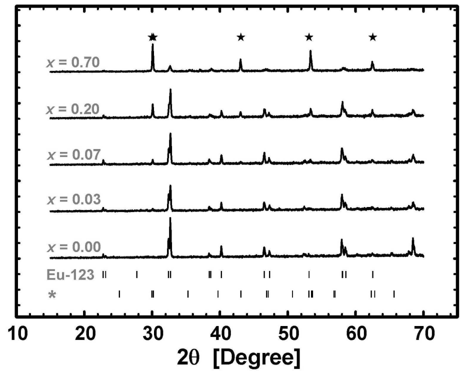

Fig. 1. XRD patterns of the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples with the shown x values and the vertical bars which indicate the peak positions of main peaks of the Eu-123 phase (ICSD #65392) and $Ba_3EuRu_2O_9$ phase (it is marked by a star (ICSD #51928)).

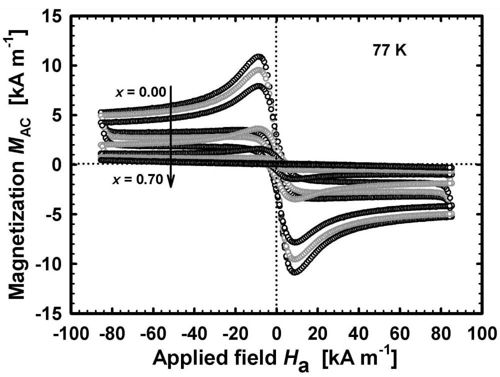

Fig. 2. M_{AC} vs. H_a dependences for the samples of the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ at 77 K.

The hysteresis curves of M_{AC} vs. H_a for the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples at 77 K are shown in Fig. 2.

All the samples show the Z-shape of magnetization curves at the low H_a typical for the superconducting polycrystalline samples except for the one with $x = 0.70$. The increasing content of Ru results in a decrease in M_{AC} and the magnetization hysteresis. For a higher H_a, the M_{AC} vs. H_a curves show an evident (para) magnetic "tail" — magnetic contribution indicated by the slope of the curves pointing to the first and third quadrants (the data are not shown here).

ZFC and FC χ vs. T dependences for the samples of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ with $x = 0.00$, 0.03, 0.07, 0.1 and 0.70 at 4 kA m^{-1} are shown in Fig. 3.

FC χ vs. T dependences of the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples at 4 MA m^{-1} with $x = 0.00$, 0.03, 0.07, 0.10 and 0.70 are shown in Fig. 4.

At 4 kA m^{-1}, all samples show positive values of χ above T_C, whereas below T_C, the negative values of χ dominate, as a result of the presence of superconducting

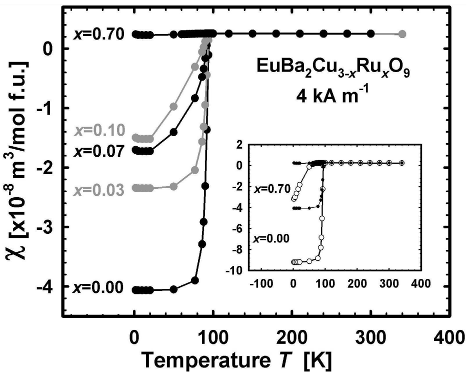

Fig. 3. FC χ vs. T dependences for the samples of the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ with given x at 4 kA m^{-1}. The insert shows the FC (•) and also ZFC (○) χ vs. T dependences for $x = 0.00$ and 0.70.

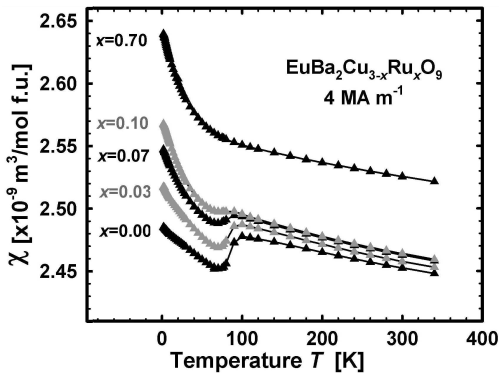

Fig. 4. FC χ vs. T dependences for the samples of the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ with given x at 4 MA m^{-1}.

Eu-123 phase, except for FC $\chi$of the sample with $x = 0.70$. However, at 4 MA m^{-1}, all the samples have a positive value of FC χ and the presence of the superconducting phase can be identified only by peaks situated at the T_C values or the negative values of their ZFC characteristic, except for the sample with $x = 0.70$, which has the highest content of the $Ba_3EuRu_2O_9$ phase. For the

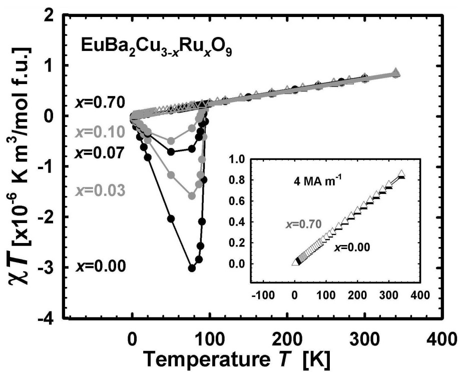

Fig. 5. The χ^*T vs. T dependences for the samples of the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ for shown x at 4 kA m^{-1}(○) and 4 MA m^{-1}(△). The insert shows dependence only for 4 MA m^{-1}.

quantitative estimate of the proportion between the superconducting Eu-123 and $Ba_3EuRu_2O_9$ phases, the Rietveld analysis using HighScore Plus v.3.0.4. software package and the ICSD database were used. The results are in Table, the last two columns.

The χ^*T vs. T dependences, ($\chi^* = \chi - \chi^{TN}$) measured in FC conditions at 4 MA m^{-1} are shown in Fig. 5.

The almost linear behaviours of χ^*T vs. T dependences of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples, measured at 4 MA m^{-1} and at 4 kA m^{-1} above 100 K, confirm a significant effect of χ^{TN}. χ^{TN} was estimated from the slope of the linear fit of the measured data. Moreover, the almost coincident behaviours χ^*T vs. T curves of $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples measured at 4 MA m^{-1} and the 4 kA m^{-1} above 100 K strongly supports the antiferro-magnetic ordering in superconducting Eu123 and $Ba_3EuRu_2O_9$ phases. The values of Θ^* and $\mu^*_{\rm eff}$ estimated based on corrected data are in Table.

TABLE

The effective magnetic moment $\mu^*_{\rm eff}$ [$\times 10^{-4}$ μ_B] per formula unit and the Weis temperature $\Theta*$ [K] estimated using fits of measured data in the temperature range of 200–300 K and 1.8–340 K at 4 kA m^{-1} and 4 MA m^{-1}, respectively. In the last two columns, the mass percentages of the Eu-123 and Ba3EuRu2O9 phase are shown.

$EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$						
T	100–300 K		1.8–340 K		Eu-123	$Ba_3EuRu_2O_9$
H_a	4 kA m^{-1}		4 MA m^{-1}			
x	$\mu^*_{\rm eff}$	Θ^*	$\mu^*_{\rm eff}$	Θ^*	[%]	[%]
0.00	1.9	32	1.9	–151	0	-
0.03	2.0	33	1.8	–58	96.6	3.4
0.07	2.1	38	1.8	–34	91.9	8.1
0.20	2.1	25	1.8	–26	76.1	23.9
0.70	1.6	49	1.9	–30	24.9	75.1

Based on the results, it can be concluded that nearly zero values of magnetic $\mu^*_{\rm eff}$, and their independence on the change of H_a from 4 kA m^{-1} to 4 MA m^{-1} strongly support conclusion that the Eu^{3+} ion is nonmagnetic with the total magnetic moment $J = 0$. At the same time, this contribution of the $Ba_3EuRu_2O_9$ phase to $\mu^*_{\rm eff}$ is small, at least in the studied conditions, including the sample with $x = 0.70$ containing 75% of the $Ba_3EuRu_2O_9$ phase. Doi et al. [10] studied crystal and magnetic properties of $Ba_2MRu_2O_9$ phase (M = Y, In, La,Sm, Eu, Lu) on polycrystalline samples prepared by the solid state reaction in air at 1100 °C. They reported for $Ba_3EuRu_2O_9$ sample the antiferromagnetic ordering between two Ru ions within Ru_2O_9 dimer, however, the effective magnetic moment over 2.5 μ_B for $T > 100$ K. The different magnetic properties of the phase in our samples could be explained e.g., by different preparation conditions. $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples were sintered in 1050 °C in flowing oxygen and, in addition, in our samples, the $Ba_3EuRu_2O_9$ phase is included in superconducting matrix unlike the single phase samples studied in [10]. Certainly, other factors can be considered, e.g., the antiferromagnetic exchange interaction between Ru_2O_9 dimers or Eu and Ru ions.

4. Conclusions

The ZFC/FC magnetic properties of the $EuBa_2Cu_{3-x}Ru_xO_{7-\delta}$ samples with x from 0.00 to 0.70 were studied using the QD SQUID magnetometer MPMS XL-7 and the AC magnetization $M_{AC}(H)$ dependences by a compensation method with the second-order SQUID gradiometer. Apart from increasing Ru content, T_C is still above 88 K and $\Delta T_C < 2.2$ K up to $x < 0.2$. X-ray diffraction data show the presence of another $Ba_3EuRu_2O_9$ phase, in addition to the superconducting phase.

The value of the magnetization M_{AC} decreases as the Ru content x increases. The molar FC susceptibilities after correction to the sample holder, diamagnetism and the temperature independent paramagnetic/diamagnetic contribution were fitted by the Curie–Weiss relation in the temperature range of 100–300 K and 1.8–340 K for 4 kA m^{-1} and 4 MA m^{-1}, respectively. The corresponding effective magnetic moment $\mu^*_{\rm eff}$ is in the order of 10^{-4} μ_B/formula unit, including the sample with $x = 0.7$ whose content of the $Ba_3EuRu_2O_9$ phase was estimated to be 75% (mass). The results suggest a strong effect of oxygen preparation conditions and/or the presence of superconducting Eu-123 matrix on the magnetic ordering of Ru_2O_9 dimers in the $Ba_3EuRu_2O_9$ phase.

Acknowledgments

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