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Shift of superconducting transition temperatures in "magnetic superconductor" $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ under influence of annealing in high pressure oxygen atmosphere

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Effect of annealing in high pressure oxygen atmosphere on superconducting transition temperatures for ceramic samples of magnetic superconductor $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ was studied. It was shown that properties of the samples are consistent with behavior of the granular superconducting system. As a result of oxygen saturation the superconducting transition temperatures become higher. Particularly, shift of the superconducting transition temperature for intergranular medium is ΔT_{ci} = 9.2 K and for the matter within the granules ΔT_{cg} = 6.8 K. This difference is due to the mechanism of oxygen diffusion along the grain boundaries. In the temperature range of 135 $<T<$ 350 K the resistance behavior obeys the Mott's law of variable range hopping for three-dimensional case.

Keywords: superconductor $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$, superconducting transition,oxygen saturation.

Исследовано влияние отжига в атмосфере кислорода на температуры сверхпроводящего перехода в керамических образцах магнитного сверхпроводника $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$. Показано, что свойства образца соответствуют поведению сверхпроводящей гранулированной системы. В результате насыщения кислородом температура сверхпроводящего перехода повышалась. Смещение температур сверхпроводящего перехода для межгранульной среды составляло ΔT_{ci} = 9.2 К, для вещества внутри гранул ΔT_{cg} = 6.8 К. Указанное различие, по-видимому, обусловлено механизмом диффузии кислорода по границам зёрен. В диапазоне температур 135 $< T <$ 350 К температурное поведение сопротивления образца соответствует механизму Мотта прыжковой проводимости с переменной длиной прыжка для трёхмерного случая.

Зсув температур надпровідного переходу у "магнітному надпровіднику" $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ під впливом відпалу в атмосфері кисню при високому тиску. *Є.Ю.Біляєв.*

Досліджено вплив відпалу в атмосфері кисню на температури надпровідного переходу в керамічних зразках магнітного надпровідника $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$. Показано, що властивості зразка відповідають поведінці надпровідної гранульованої системи. У результаті насичення киснем температура надпровідного переходу підвищується. Зсув температур надпровідного переходу для міжгранульного середовища становить ΔT_{ci} = 9.2 К, для речовини усередині гранул ΔT_{cg} = 6.8 К. Зазначена відмінність найімовірніше зумовлена механізмом дифузії кисню уздовж меж зерен. У діапазоні температур 135 $< T <$ 350 К температурна поведінка опору зразка відповідає механізму Мотта стрибкової провідності із змінною довжиною стрибка для тривимірного випадку.

1. Introduction

Continuously improving technology of the complex oxide compounds production aimed at the creation of materials that demonstrate a combination of properties that previously considered being impossible. Such materials are europium and gadolinium ruthenocuprates that combine properties of superconducting and the magnetically ordered states — the so-called "magnetic superconductors". In ruthenocuprates $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ two competing order parameters — the spontaneous magnetization, with emerging at T_M (100 ÷ 140 K) the weak ferromagnetic component in sublattice of Ru atoms, and superconducting order parameter due to hole doping of CuO_2 layers with the critical temperature T_c (30 ÷ 50 K), — coexist in one crystal lattice, experiencing mutual spatial modulation.

The possibility of coexistence of superconducting and magnetic properties in these materials is due to the fact that the weak ferromagnetic state related to the tilting of antiferromagnetically ordered magnetic moments in the Ru sublattice [1] induces on CuO_2 conducting layers the inner magnetic field of $H \approx 0.1$ T [2]. The value of this magnetic field is greater than the lower critical field H_{C1} (estimated $\approx 5 \cdot 10^{-3}$ T [3]), but it is significantly less than the upper critical field $H_{C2} \approx$ 28 ÷ 80 T [4]. Thus, the superconductivity in CuO_2 layers germinates directly in the mixed state [2].

However, being, in fact, the high-temperature superconductors based on copper oxide layers, ruthenocuprates inherit a tendency of copper oxide high-temperature superconductors to lose the stoichiometric oxygen included in their crystal lattice, which leads to degradation of their superconducting properties.

The aim of this work was to study the effect of annealing in an atmosphere of pure oxygen at high pressure on the characteristic temperatures of the inter-granular and intragranular superconducting transitions for the granular ceramic samples of magnetic superconductor $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$.

2. Experimental

Test samples were prepared in the "Rakah Institute of Physics" by solid-phase synthesis. One of the samples obtained was left in the original (as prepared) state (Sample Eu_A). Two others were annealed for 24 h at temperature T = 900°C and the high pressure of pure oxygen P = 100 atm (Sample Eu_B), and P = 50 atm (Sample Eu_C) [5]. Powder diffraction studies confirmed the purity and prevailing single-phase composition (~ 97 %) for the samples obtained. The unit cell parameters ($a = b = 3.846$ Å, c = 28.72 Å) within the experimental error coincided with the data for europium ruthenocuprates given in the works of other authors [3].

For electrical measurements the pressed ceramic tablets were cut in pieces having the form of parallelepipeds with dimensions 10×2×1 mm^3 and distance between the potential contacts was 4 mm.

Measurements of the temperature dependences of resistance were carried out in Kharkiv Institute for Low Temperature Physics and Engineering (ILTPE) in the temperature range of 3.5 ÷ 350 K by 4-probe DC technique applying the current I = 100 mkA. The samples were mounted on a copper sample holder in a vacuum chamber of cryostat. To improve the thermal contact the heat-conducting glue was used. Temperature in the cryostat was controlled by automatic stabilization system with accuracy from $\approx 10^{-4}$ K in the region of liquid helium temperatures to $\approx 10^{-1}$ K at the maximum achievable temperature of 350 K. In the test setup we used a stabilized DC power supply with alternating polarity to compensate the thermal EMF, graded Pt and RuO_2 resistive thermometers, multimeters Keithley 2000 and nanovoltmeter Keithley 2182.

3. Results and discussion

The temperature dependences of resistance for all three samples are shown in Fig. 1. Granular structure of the ceramic samples manifested itself in the typical "shouldered" form of the observed intragranular and inter-granular resistive transitions [6].

From Fig. 1 we can see that for the samples saturated with oxygen almost twofold decrease in resistance was observed in the normal state, apparently due to injection of the current carriers — holes — into the layers of CuO_2.

Fig. 2 shows the first derivatives for the temperature dependences of resistance, which allow determining, by positions of the peaks, the critical temperatures corresponding to superconducting transition both for the substance within the granules and

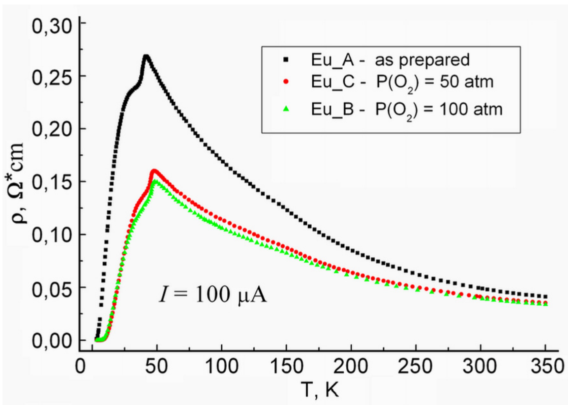

Fig. 1. Temperature dependences of resistance for three samples of $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$.

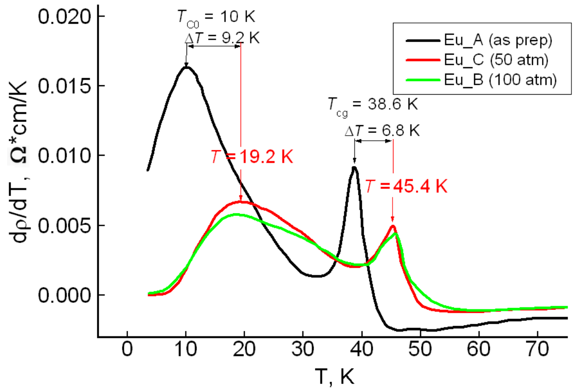

Fig. 2. Influence of annealing in oxygen on superconducting transition temperatures.

for the intergranular environment in the granular systems under study.

Due to fact that the ceramic samples studied were granular systems, the transition to the superconducting state occurred through two step process. For $T < 50$ K at first we see establishing of the superconducting state for the substance within the granules. The critical temperatures of that transition varied in the range from T_{cg} = 38.6 to 45.4 K depending on the degree of oxygen saturation. Then there follows a small "shoulder", after which we can see a further drop in resistance associated with the establishment of the Josephson weak links in the disordered intergranular medium, with the critical temperatures that vary from T_{ci} = 10 K for the "as prepared" sample Eu_A to T_{ci} = 19.2 K for the samples Eu_B and Eu_C annealed in oxygen at different pressures (see Fig. 2).

As a result of oxygen saturation (Fig. 2) we determine that the displacement of superconducting transition temperatures for intergranular medium is ΔT_{ci} = 9.2 K and for the matter within the granules — ΔT_{cg} = 6.8 K. The difference is obviously due to the mechanism of oxygen diffusion along the grain boundaries. The rate of oxygen diffusion is only slightly dependent on pressure, so the resistance curves for the samples annealed in oxygen at pressures of 50 and 100 atm are practically identical. Large width of the superconducting transition for the intergranular environment (with corresponding $d\rho/dT$ peak half-width $\approx$ 18 K in Fig. 2) can be explained by its strong heterogeneity. After annealing in oxygen, judging by the increase in the width of the intergranular superconducting transition, this heterogeneity was even intensified, which may be the evidence of further decomposition of the intergranular medium caused by partial evaporation of the most volatile component of the compound — RuO_2 [7].

For all three samples studied in the high-temperature range ($T = 135 \div 350$ K) the temperature dependence of resistance obeyed the Mott's hopping conductivity law, inherent to the mechanism of variable range hopping (VRH) for three-dimensional case,

$$\rho \approx \rho_0 \exp(T_0/T)^{1/4}, \qquad (1)$$

where $T_0 = B_0{}^4 \cdot (L_c{}^{-3}/k_B \cdot N(E_F))$ — the Mott's characteristic temperature (total sum of energy of localized states for the charge carrier expressed in the temperature units), B_0 = const = $1.7 \div 2.5$, k_B — the Boltzmann constant. This conductivity behavior corresponded to the hopping conductivity between isolated granules of ruthenocuprate which were at these temperatures in the non-superconducting state (see Fig. 3). When fitting the experimental data we obtained the values $T_0 \approx$ 150,000 K for Eu_A and $T_0 \approx$ 75,000 K for samples Eu_B and Eu_C, which are common values if you compare them with the values of the Mott's temperature obtained by other authors [8].

The lack of data on the density of electronic states at the Fermi level $N(E_F)$ for, still little-studied, europium-based ruthenocuprates does not allow to calculate precisely the radii of localization of the wave functions of charge carriers L_c.

For temperatures $T < 135$ K the resistance of ruthenocuprate samples decreases with temperature more rapidly than predicted by the Mott's law. The reason for

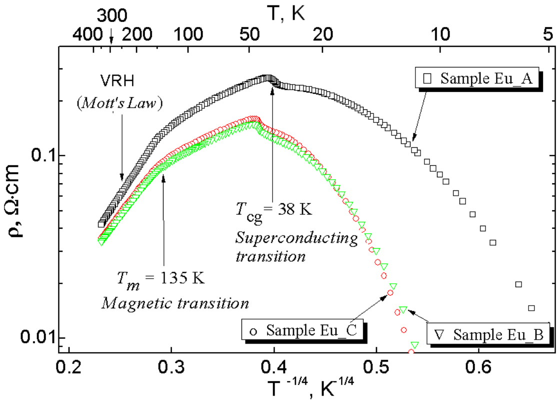

Fig. 3. VRH mechanism for temperatures $T > T_m$ in antiferromagnetic (AFM) state of ruthenocuprate samples Eu_A, Eu_B and Eu_C. For temperatures $T_{cg} < T < T_m$ after transition to the weak ferromagnetic (WFM) state deviations from the Mott's law arise.

this drop of resistance may be the ferromagnetic ordering in the samples studied. Marked by an arrow in Fig. 3 the temperature $T = 135$ K, corresponds to the temperature of kink on the temperature dependence of magnetization measured in ZFC (zero field cooling) regime for the sample Eu_C [5]. After this temperature magnetization of the sample increases and a feature on the temperature dependence of thermal conductivity was observed [5] which may also be connected with some processes of structural relaxation.

It should be noted that the mere appearance of the weak ferromagnetic state in ruthenocuprates is caused by fact that covalent bonds lengths for Cu–O and Ru–O, being almost equal at the room temperature, have different temperature dependence. With temperature lowering, the Cu–O bonds shrink more than Ru–O. This leads to coordinated rotation of adjacent oxygen octahedra which become too big to fit the lattice and in which the antiferromagnetically ordered Ru^{+5} ions are confined [9]. This rotation achieves the value of angle 14° and through the Dzyaloshinskii-Moriya interaction causes the coordinated tilting of antiferromagnetically ordered Ru^{+5} magnetic moments perpendicular to the layered structure of the compound. At $T_m \approx 135$ K in this system of uncompensated perpendicular component of the antiferromagnetically ordered magnetic moments of Ru^{+5} ions even small magnetic field (from Earth or cryostat) causes the weak ferromagnetic (actually component ferrimagnetic) state. This ferromagnetic ordering in the perpendicular

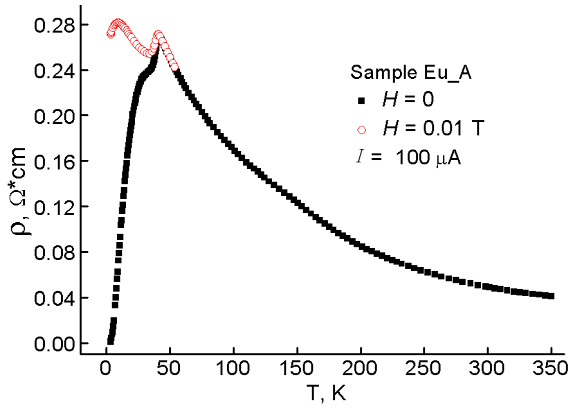

Fig. 4. Effect of a weak magnetic field on superconductivity in intergranular medium.

components of magnetization results in reduction of resistance by reducing the magnetic scattering of the conduction electrons. Apparently, this process of establishing of ferromagnetic order in ruthenocuprate samples determines the temperature behavior of the resistance in the temperature range between T_m and T_{cg} and explains the violation of the VRH Mott's low.

The influence of external magnetic field on the superconducting transition in the granulated ruthenocuprates is shown by example of the sample Eu_A (as prepared) in Fig. 4. The Figure shows that application of the weak magnetic field $H = 0.01$ T doesn't change the superconducting transition within the granules because the upper critical field in ruthenocuprates is very high ($H_{C2} \approx 28 \div 80$ T [4]) and thanks to the ferromagnetic component of the internal magnetic field the superconducting material in granules is already in the mixed state. But this small magnetic field easily destroys the weak superconductivity in disordered intergranular environment.

4. Conclusions

Thus, by studying the temperature and magnetic field dependences of resistance for ceramic samples of europium ruthenocuprate $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ we investigated the influence of annealing in high pressure oxygen atmosphere on superconducting transition temperatures both inside granules and in disordered intergranule media. The studied samples showed the temperature and magnetic field behavior pertinent to the granular superconducting system. It was shown that oxygenation rose the superconducting transition temperatures both inside the granules and in the disordered intergranular environment. Stronger shift of the superconducting transition temperature for the intergranular medium compared with the intragranular one indicates that the penetration of oxygen into the sample during annealing occurs along the grain boundaries. The rate of oxygen diffusion is only slightly dependent on pressure. It was shown that the temperature behavior of the samples' resistance above the temperature of magnetic transition $T_m = 135$ K matches the Mott's formula for variable range hopping in three-dimensional case. However, in the intermediate temperature range ($T_{cg} < T < T_m$), when the ferromagnetic order in the sample has already been established, and superconductivity has not yet occurred, there are deviations from the Mott's law, apparently related to the fact that the appearance of the weak ferromagnetic order and structural relaxation in the crystal lattice lead to reduction in the charge carriers scattering.

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