Structural inhomogeneity effects in resistive superconducting transitions of the magnetic superconductor RuSr$_2$(Gd$_{1.5}$Ce$_{0.5}$)Cu$_2$O$_{10-\delta}$

V B Krasovitsky$^1$, B I Belevtsev$^1$, E Yu Beliayev$^1$, D G Naugle$^2$, K D D Rathnayaka$^2$ and I Felner$^3$

1 B. Verkin Institute for Low Temperature Physics and Engineering, Kharkov, 61103, Ukraine
2 Department of Physics, Texas A&M University, College Station, TX 77843, USA
3 Racah Institute of Physics, The Hebrew University, Jerusalem, 91904, Israel

E-mail: belevtsev@ilt.kharkov.ua; naugle@physics.tamu.edu

Abstract. The study of granular effects in resistive superconducting transitions of ceramic ruthenocuprate RuSr$_2$(Gd$_{1.5}$Ce$_{0.5}$)Cu$_2$O$_{10-\delta}$ prepared by a solid-state reaction method is presented for samples as prepared (ASP) and annealed (12 hours at 845 °C) in pure oxygen at 62 atm. The resistive transitions for different measuring currents and applied magnetic fields (up to 8 T) bear evidence of granularity effects determined by inhomogeneous structure of the samples. This is dictated by the polycrystalline structure (with a grain size of a few µm) and oxygen deficiency in grain boundary regions. The resistive curves show clearly the intragranular and intergranular superconducting transitions, the intergranular superconductivity being determined by the Josephson coupling between the grains. This has allowed determination of intragranular ($T_c^{0}$) and intergranular ($T_{cg}$) critical temperatures, which are $\approx$ 34 K and $\approx$ 9.4 K in ASP sample, and $\approx$ 37.3 K and $\approx$ 32.8 K in the 62-atm sample in zero field. The magnetic-field dependences of these characteristic temperatures were studied and discussed. In general, the granularity effects are most pronounced in the ASP sample where great sensitivity to applied current and low magnetic field is found. These effects become, however, much weaker after oxygen annealing.

Ruthenocuprates of composition RuSr$_2$R$_{2-x}$Ce$_x$Cu$_2$O$_{10-\delta}$ (where R=Gd, Eu) have been of considerable interest in last years due to coexistence of superconductivity and magnetism [1, 2, 3]. Superconductivity is associated with CuO$_2$ planes, while magnetic order is thought to be connected with RuO$_2$ planes. It is conjectured that below 80-100 K weak-ferromagnetic order dominates. The superconducting critical temperature $T_c$ can be as high as $\approx$ 50 K for $x = 0.5 - 0.6$, so that at low temperature both superconducting and magnetic order coexist.

Thus far, only polycrystalline samples of these compounds prepared by a solid-state reaction method were studied [1, 2, 3]. In ceramic ruthenocuprates (with a grain size of a few µm), superconductivity (and magnetic properties) are affected by granularity [1, 2, 3]. The inhomogeneous distribution of oxygen enhances this effect. The grain boundary regions are usually oxygen-deficient, which causes the above-mentioned granularity effects. The degree of the oxygen deficiency is determined by conditions of preparation, post-preparation oxygen annealing and storage. Effects of granularity in ruthenocuprates manifest themselves, first of all, in the form of fairly broadened or shouldered resistive transitions to superconducting state [1, 2, 3]. This behavior of inhomogeneous systems is largely due to the suppression of
phase coherence between weakly coupled superconducting regions [4]. On the whole, granularity effects in ruthenocuprates cannot be considered as quite clear, so that additional investigations in this field are necessary. It is especially important to separate these effects from intrinsic superconducting and magnetic properties of these magnetic superconductors.

In this report, we study granularity effects in RuSr$_2$(Gd$_{1.5}$Ce$_{0.5}$)Cu$_2$O$_{10-\delta}$. The samples studied were prepared by a solid-state reaction method [1]. It is known that properties of ruthenocuprates depend essentially on oxygen content [1, 3, 5]. Samples synthesized by solid-state reaction technique are always oxygen-deficient. Oxygen distributes in a non-homogeneous way with grain-boundary regions being the most oxygen-deficient. This causes a weak connectivity between grains and granular effects in superconductivity. The oxygen non-stoichiometry can be decreased by post-preparation annealing in pure oxygen at a high pressure. This increases $T_c$ determined from resistive transitions. To prevent deoxidation of samples, they are often stored in a dessicator filled with oxygen. But this does not completely prevent the oxygen loss with time (so called ageing). If the samples are stored in open air, the ageing occurs faster. It is clear that granularity effects will be most evident in as-prepared samples. In this report we consider properties of two samples: (i) an as-prepared (ASP) sample, stored initially in a dessicator and then being taken to ambient air for considerable time; (ii) a sample annealed (12 hours at 845°C) in pure oxygen at 62 atm. Temperature and magnetic-field (up to 1.6 T) dependences of the ASP sample were measured using a standard four-point probe technique in a home-made cryostat. Others (resistive and magnetic) measurements were made with Quantum Design devices (PPMS and SQUID magnetometer) with field up to 8 T.

It was found [1, 2, 3] that resistive transitions to the superconducting state in ruthenocuprates become more broadened and shouldered with application of magnetic field which is to be generally attributed to the influence of magnetic field on Josephson coupling between grains. In the ASP sample, similar effects were found not only with field application, but with increasing measuring current as well (Figs. 1 and 2). A high enough current causes radical changes in $R(T)$ transition curves, so that quasi-reentrant behavior (with a minimum in $R(T)$) appears (Fig. 1). In general, the $R(T)$ curves of resistive transition to the superconducting state for the ASP sample can be characterized by three characteristic temperatures, $T_{C0}$, $T_{CJ}$ and $T_{cg}$. The first, $T_{C0} \approx 34$ K, indicates a transition of grains to the superconducting state that causes a kink (or noticeable turn) in $R(T)$ (Fig. 1). The temperature $T_{CJ} \approx 23.2$ K is defined as a branching

![Figure 1. Temperature dependences of resistance $R(T)$ of the as-prepared sample for different measuring currents: 0.01, 0.1, 0.2, 0.5, 0.7, 1.0, 1.5, 1.7, 2.0, 3.0, 5.0, 7.0, 10 mA. The characteristic temperatures $T_{C0} \approx 34$ K and $T_{CJ} \approx 23.2$ K are shown by arrows. The inset shows temperature behavior of the resistivity, $\rho(T)$, at current $J = 0.2$ mA in the range 4–300 K.](image-url)
point of the family of $R(T)$ curves taken for different measuring current. This coincides with the resistance maximum (Fig. 1) and indicates a temperature below which percolation chains of intergrain Josephson coupling are created and resistance starts to decrease with decreasing temperature. The third mentioned temperature, $T_{cg}$, is the intergrain critical temperature.

In general, the system studied presents a 3D Josephson junction array. Since Josephson coupling is random throughout the sample, a percolation description of the superconducting transition should be used [4, 6, 7]. With increasing measuring current, some of the weakest links of the percolating chains with the least critical currents go to a resistive state, increasing the total resistance of the system. These processes determine the increase of resistance with increasing current below $T_{cj}$ (Fig. 1). The reasons of the resistance minimum (quasi-reentrant behavior) in granular superconductors are outlined by Belevtsev [4].

The influence of magnetic field on the resistive transition of the ASP sample is shown in Fig. 2 for current $J = 0.2$ mA. It is found that low fields ($H \leq H_{cj} = 0.04$ T) exert the same effect as an increasing current: they lead to broadening of the resistive transitions (due to positive magnetoresistance (MR)) with the same branching point $T_{cj} \approx 23.2$ K (since MR is zero in the range $T_{cj} \leq T \leq T_{c0}$). In this low field range, however, a sharp decrease in the intergrain critical temperature $T_{cg}$ with increasing field takes place (inset in Fig. 2). $T_{cg}$ is defined as a temperature corresponding to a half of the normal-state resistance. This is to be attributed to suppression of intergranular Josephson junctions. For fields somewhat higher than $H_{cj}$ a considerable positive MR appears in the range $T_{cj} \leq T \leq T_{c0}$. In this case, the intragrain critical temperature $T_{c0} \approx 34$ K reveals itself as a point where MR changes sign from negative to positive with decreasing temperature. Inhomogeneous granular structure reveals itself in temperature dependence of magnetization as well (Fig. 3). It can be seen that $M(T)$ in the region of the transition to the superconducting state is shouldered with distinct features corresponding to the above-mentioned characteristic temperatures.

![Figure 2](image2.png)

**Figure 2.** Resistive transitions of the as-prepared sample at current $J = 0.2$ mA for magnetic fields in the range 0–1.6 T. The inset shows the magnetic-field variation of the intergrain critical temperature $T_{cg}$. The $T_{c0} \approx 34$ K is the intragrain critical temperature.

![Figure 3](image3.png)

**Figure 3.** Magnetization as a function of temperature at $H = 0.5$ mT for as prepared sample. The field-cooled (FC) and zero field-cooled branches are shown. Temperatures $T_{c0}, T_{cj}$ and $T_{cg}$ are defined in the main text.
The annealed at 62 atm/O₂ sample is far less resistive than the ASP sample (compare Figs. 1 and 4), but its properties are still affected by granularity. In particular, resistive transitions are shouldered, especially for high fields (Fig. 4). Derivatives $dR(T)/dT$ reveal two peaks in the region of the superconducting transition, the positions of which can be attributed to intragranular and intergranular superconducting transitions at temperatures $T_{c0}$ and $T_{cg}$. In zero field, these temperatures are $\approx 37.3$ K and $\approx 32.8$ K, respectively. At the maximum field 8 T used in this study, they reduce to 34.7 and 12.4 K, respectively. Thus, the magnetic field has a weak influence on the intragranular superconducting properties, indicating an enormous upper critical field in the ruthenocuprates. The intergranular $T_{cg}$ is far more sensitive to magnetic field, with the main variations occurring in the low-field region (Fig. 5), similar to that found for the ASP sample (inset in Fig. 2). It is seen that intragranular superconducting properties are much less affected by high-pressure oxygen annealing than the intergranular ones.

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