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Granular superconductivity in polycrystalline ruthenocuprate $RuSr_2(Gd_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$: magnetoresistive and magnetization studies

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Abstract
Granular superconductivity effects in polycrystalline samples of $RuSr_2(Gd_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$, as prepared (by a solid-state reaction method) and annealed (12 h at 845 °C) in pure oxygen at 30 atm, are presented. The resistive transition to the superconducting state of the as-prepared sample is found to be considerably affected by granularity. In particular, an evident kink in the temperature dependence of the resistance $R(T)$ is seen at the temperature, $T_{c0} \approx 34$ K, at which grains become superconducting. The resistive transition depends strongly on the applied current. The family of $R(T)$ curves taken for different transport currents is branched with a branching point at $T_{cJ} \approx 23.2$ K. Below this temperature the intergrain Josephson coupling starts to develop. For low current, R decreases with decreasing temperature below T_{cJ} as expected for the transition to the superconducting state, whereas $R(T)$ curves for higher current form a minimum at $T \approx 17.3$ K, showing a quasi-reentrant behaviour. The influence of the granular structure of the as-prepared sample shows itself also in the temperature behaviour of the magnetization, $M(T)$, in low field. Application of low magnetic field (below 400 Oe) leads to a broadening of the resistive transitions below T_{cJ}, similar to that caused by increasing the current. Both the current and magnetic field depress the Josephson coupling between the grains, producing a dramatically large effect on the resistive transition. The $R(T)$ and $M(T)$ dependences of the annealed sample show a fairly sharp superconducting transition far less affected by granularity. The results obtained imply that oxygen annealing improves the intergranular connection considerably, but it does not exert much influence on the intragrain superconductivity. No indication of intragrain granularity has

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been found in the samples studied. The influence of ageing (due to deoxidation) of samples for different conditions of storage is considered briefly as well.

1. Introduction

Ruthenocuprates of composition $RuSr_2R_{2-x}Ce_xCu_2O_{10-\delta}$ (where R = Gd, Eu) have attracted considerable interest recently due to the coexistence of superconductivity and magnetism [1–3]. Superconductivity is associated with CuO_2 planes, while magnetic order is thought to be connected with the RuO_2 planes. It is conjectured that below 80–100 K weak ferromagnetic order is established. Superconductivity in this family of compounds is apparent for $0.4 \leqslant x \leqslant 0.8$ with T_c up to ≈50 K for $x = 0.5$–0.6, so at low temperature superconducting and magnetic order apparently coexist.

Only polycrystalline samples of these compounds prepared by a solid-state reaction method have been studied [1–3]. The known attempts to grow single crystals of fairly large size have not been successful [4]. In polycrystalline ruthenocuprate samples (with a grain size of a few μm), superconductivity and magnetic ordering are affected by granularity [1–3, 5–10]. The main source of granularity is extrinsic and determined by the preparation conditions, post-preparation oxygen annealing and storage. It is, therefore, important to study this effect and separate it from intrinsic superconducting and magnetic properties of these magnetic superconductors. At the same time, granularity effects are intellectually very interesting in addition to their importance in applications. They have been actively studied in past decades in low- and high-T_c superconductors, and many interesting fundamental phenomena were found.

In this paper, granularity effects in ruthenocuprate $RuSr_2(Gd_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ (Ru1222–Gd) for samples as prepared (by a solid-state reaction method) and annealed (12 h at 845 °C) in pure oxygen at 30 atm are studied. Due to granularity, the resistive transitions to the superconducting state in Ru1222–Gd were found to be fairly broadened or shouldered [1–3, 5–10]. These effects together with reduction of the critical temperature T_c are largely due to the suppression of phase coherence between weakly coupled superconducting regions in inhomogeneous systems [11]. The sources of inhomogeneity in ruthenocuprates should be, primarily, the same as in high-T_c cuprates. In polycrystalline samples of these compounds the regions of grain boundary are disordered and can be not only non-superconductive, but also even dielectric. Therefore, superconducting phase coherence between the grains can be established by Josephson coupling. Beside grain boundaries, another source of granularity can be chemical composition inhomogeneity. The influence of this type of inhomogeneity on superconductivity can be rather strong since the charge carrier density in the high-T_c cuprates and ruthenocuprates depends strongly on the chemical composition. Compositional disorder can contribute to destruction of superconducting phase coherence in the same fashion as granularity induced by polycrystalline structure. In most cases, the inhomogeneous distribution of oxygen leads to this type of disorder. First of all, the grain boundary regions are usually considered to be oxygen deficient, which causes the above-mentioned intergrain granularity. But, furthermore, the inhomogeneous oxygen distribution can provide additional internal barriers even in single-crystal high-T_c superconductors, making the crystal granular [12]. In the case of polycrystalline ruthenocuprates, the oxygen inhomogeneity can provide internal barriers inside the grains inducing intragrain granularity. It should be noted that oxygen inhomogeneity can be caused by extrinsic and intrinsic factors. Extrinsic sources arise from the technological factors of sample preparation. Intrinsic ones might be connected with the phase separation of two phases with different oxygen, and hence charge carrier, concentrations. Besides this, cerium inhomogeneity and the non-homogeneous distribution of the T_c magnitude within grains (or even a possible intragrain phase separation associated with it) should be taken into account also. It is known [1] that T_c in ruthenocuprates depends strongly on the Ce concentration. The rather unreactive nature of CeO_2 [13] makes it, however, difficult to achieve a uniform distribution of Ce within each grain. Intragrain granularity in ruthenocuprates associated with phase separation has been suggested by two groups [2, 5, 8, 9], but corroboration by experiment has remained questionable.

On the whole, granularity effects in ruthenocuprates cannot be considered as properly clear, so additional investigations are necessary. In particular, the influence of magnetic field on resistive transitions to the superconducting state in ruthenocuprates deserves further investigation. The known studies show broadening and shouldering of resistive transitions with application of magnetic field [1–3, 5–10]. In this study, similar effects are found not only with application of a field, but also with increased measuring current as well. In the as-prepared sample, a sufficiently large current causes radical changes in the $R(T)$ transition curves, so that a quasi-re-entrant behaviour (with a minimum in $R(T)$) appears. The results permit discussion of the extrinsic and intrinsic sources of the superconducting and magnetic inhomogeneity in the Ru1222–Gd ruthenocuprates, including the possibility of intragrain granularity suggested in [2, 5, 8, 9]. The part played by oxygen deficiency in developing the granular structure and related effects of the post-preparation oxygen annealing and ageing (due to deoxidation) are considered as well.

2. Samples and experimental details

The samples studied were prepared by a solid-state reaction method [1, 7, 14]. Some of them were set aside (as-prepared samples), while others were annealed (12 h at 845 °C) in pure oxygen at different pressures. The granularity effects were most evident in the as-prepared samples. To provide an illustration of the effect of the post-preparation oxygen annealing, the properties of a sample annealed at 30 atm in pure oxygen are considered briefly here as well. Resistance as a function of temperature and magnetic field (up to 16 kOe) was measured using a standard four-point probe technique in a home-made cryostat. The magnetization measurements were made with a Quantum Design SQUID magnetometer.

3. Results and discussion

3.1. Oxygen deficiency and ageing effects: their part in enhancing granularity of ruthenocuprates

The superconducting and magnetic properties of ruthenocuprates depend essentially on oxygen content [1, 3, 7, 14, 15]. Samples synthesized by solid-state reaction techniques are always oxygen deficient with non-homogeneous distribution of oxygen. The available experimental data suggest that grain boundary regions are the most oxygen deficient. 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 and depresses somewhat the magnetic ordering temperature. To prevent deoxidation of samples, they are often stored in a desiccator filled with oxygen. But this does not completely prevent the oxygen loss, so that superconducting properties deteriorate with time. This process can be called ageing. If samples are stored in open air, the ageing goes faster. One of the as-prepared samples described in this article was stored mainly in a desiccator and will be denoted as sample ASP1. The other as-prepared sample (ASP2) (which is the main object of this study) was stored for a considerable time in ambient air and was measured about one year later than sample ASP1.

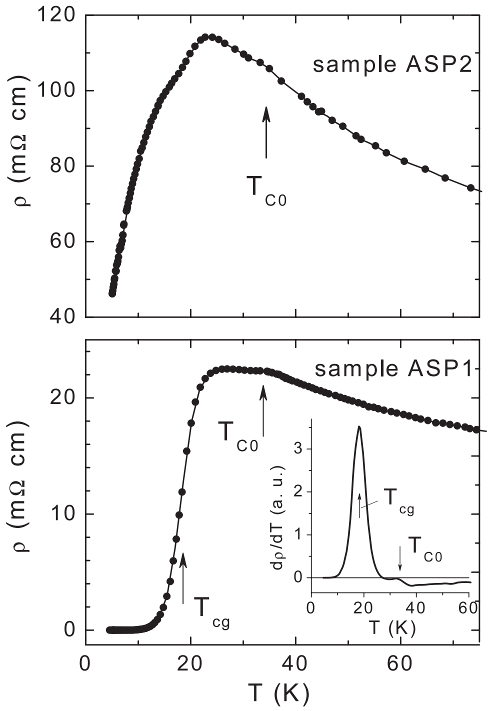

Figure 1. Temperature dependences of the resistivity of the as-prepared $RuSr_2(Gd_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ samples ASP1 and ASP2 measured for currents of 1 and 0.2 mA, respectively. Sample ASP1 was stored mainly in a desiccator filled with pure oxygen. Sample ASP2 was exposed to air for several months. The temperature $T_{c0} \approx 34$ K (shown by arrows) marks a kink in the $R(T)$ dependences and is attributed to the transition of grains to the superconducting state. The position of a peak in the temperature behaviour of the derivative $d\rho/dT$ in the region of superconducting transition for sample ASP1 (inset in the lower panel) was attributed to the intergrain critical temperature of the superconducting transition, $T_{cg} \approx 18.6$ K.

The effect of oxygen deficiency and deoxidation with time (ageing) on the superconducting properties of ruthenocuprates studied can be considered, comparing the low-temperature $R(T)$ dependences of the samples ASP1 and ASP2 shown in figure 1. Sample ASP1 (stored in a desiccator) has a rather broad resistive transition with resistance reaching zero at $T \approx 10$ K while sample ASP2 (stored for some time in ambient air) has a much larger resistivity and a markedly broader resistive transition (of shouldered form). Here zero resistance is not reached even at $T \approx 4$ K. In spite of this essential difference in resistive transitions, $R(T)$ curves for the two samples show the same feature (a kink) at $T \approx 34$ K. This kink (or marked turn in $R(T)$) is determined by the transition of the intragrain material to the superconducting state at $T_{c0} \approx 34$ K. This value of T_{c0} agrees well with results of heat capacity measurements for the same series of the samples [10]. In contrast to transport properties, the heat capacity temperature dependence $C(T)$ was found to be rather insensitive to the granular structure and oxygen annealing. In particular, a jump in $C(T)$ at the superconducting transition takes place at approximately the same temperature for all samples of the series (as prepared, and annealed at 30, 62 and 78 atm of pure oxygen) and reflects mainly the intragrain superconducting transition. The onset of the $C(T)$ jump on going to T_c from above was found at $T \approx 37$ K with the maximum in $C(T)$ at $T \approx 34$ K. Thus, the temperature $T_{c0} \approx 34$ K obtained from resistive curves can be confidently identified as the intragrain critical temperature of the superconducting

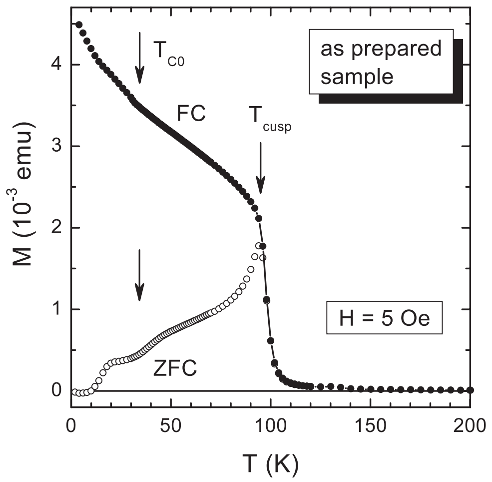

Figure 2. Magnetization as a function of temperature at $H = 5$ Oe for an as-prepared sample with the field-cooled (FC) and zero-field-cooled (ZFC) branches. The temperature $T_{c0} \approx 34$ K (indicated by arrows on FC and ZFC curves) is the intragrain critical temperature of the superconducting transition. The temperature $T_{cusp} \approx 95$ K is a position of a sharp peak in the ZFC curve, determined by magnetic properties of the sample.

transition in the majority of the grains. However, at $T \approx T_{c0}$ and not too far below it, Josephson coupling between grains is so weak that the resistance does not go down with decreasing temperature (or may even increase as in the case of sample ASP2). This occurs because the charge transfer between neighbouring grains in this case is determined by quasiparticle tunnelling solely [11]. With further decrease in temperature, however, percolating chains of Josephson coupling are created, and the resistance starts to decrease, as it should at the resistive superconducting transition.

The granularity and inhomogeneity effects are apparent not only in the resistive transition curves but in the magnetic properties associated with the superconducting state as well. Figure 2 shows the temperature dependence of the magnetization $M(T)$ for a small piece taken from the same batch of as-prepared material as the samples ASP1 and ASP2. We will not discuss here in detail the features of $M(T)$ curves associated with magnetic order of the ruthenocuprates (this is adequately covered in known literature [1–3]). Only features related to the superconducting transition will be addressed here. Both the FC and ZFC $M(T)$ curves show features at a position corresponding to the intragrain critical temperature T_{c0}. In general, judging from figure 2, the transition to the superconducting state does not proceed smoothly. The ZFC curve has shouldered (or two-stage) character: the first stage can be associated with the intragrain superconducting transition, and the second one with establishment of Josephson coupling between grains (intergrain superconducting transition). Due to the high inhomogeneity (granularity) of the as-prepared samples, the diamagnetic response, expected for the superconducting state, is rather weak and appears only below 10 K.

It may be inferred from the results obtained that increasing the oxygen deficiency affects mainly the grain boundary regions. As a result, the intragrain critical temperature $T_{c0} \approx 34$ K does not decrease noticeably with deoxidation, but the intergrain Josephson coupling deteriorates dramatically. For example, the intergrain critical temperature T_{cg} in sample ASP1, derived from the position of a peak in the temperature dependence of the derivative $d\rho(T)/dT$, is about 18.6 K (see figure 1) which is well below T_{c0}. In the far more deoxidated sample ASP2

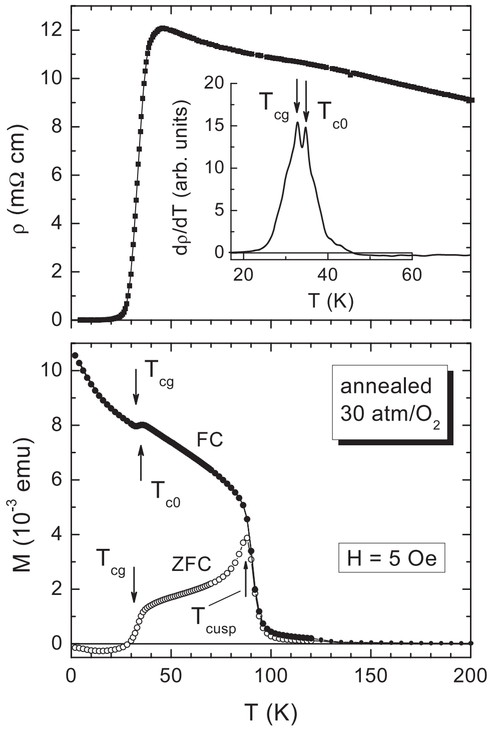

Figure 3. Temperature dependences of the resistivity $\rho(T)$ (upper panel) and the magnetization $M(T)$ (lower panel) of the $RuSr_2(Gd_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ sample annealed after preparation for 12 h at 845 °C at 30 atm in pure oxygen. The FC and ZFC curves of $M(T)$ were taken at $H = 5$ Oe. The inset in the upper panel shows the temperature behaviour of the derivative $d\rho/dT$ in the region of the superconducting transition which reveals indications of inhomogeneity. $T_{cg} \approx 32.7$ K and $T_{c0} \approx 34.7$ K are attributed to the intergrain and intragrain critical temperatures of the superconducting transition. The temperature $T_{cusp} \approx 89$ K is discussed in the main text.

the superconducting transition is broader (figure 1) and the temperature T_{cg} is reduced further to $T_{cg} \approx 10$ K, as will be shown in the next section.

Oxygen annealing can enhance the intergrain Josephson coupling considerably. In figure 3 dependences $R(T)$ and $M(T)$ for the sample annealed at 30 atm/O_2 are shown. It can be seen that its resistivity is much lower than that of the as-prepared samples and that the resistive transition is considerably sharper (with resistance going to zero at $T \approx 20$ K). Derivatives $d\rho(T)/dT$ reveal, however, two rather closely set peaks in the region of the superconducting transition (inset in figure 3). The positions of the peaks can be attributed to intragranular and intergranular superconducting transitions at temperatures T_{c0} and T_{cg}, which are equal to 34.7 and 32.7 K, respectively, in zero field. Since T_{c0} and T_{cg} are rather close to each other, granularity effects in this sample are obviously much weaker than in the as-prepared samples. The improvement of the superconducting properties with annealing is also reflected in the $M(T)$ behaviour of the sample (figure 3). The ZFC curve in the region of the superconducting transition is not shouldered. Very clear features associated with the superconducting transition are seen in both the ZFC and ZC branches of $M(T)$. The diamagnetic transition is more clearly pronounced, occurring at $T \approx 30$ K (figure 3).

Oxygen annealing has a noticeable effect on the magnetic properties of the ruthenocuprates studied as well. The temperature T_{cusp} of the sharp peak in the ZFC curve (which can be

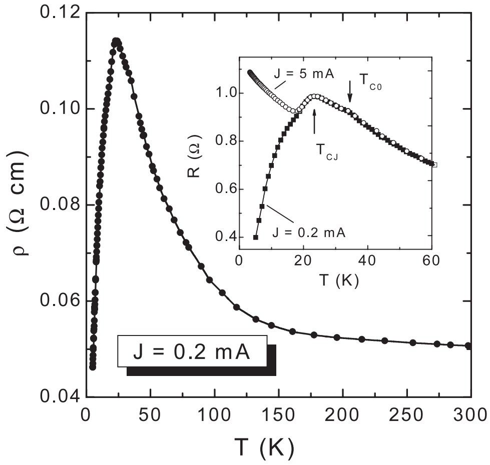

Figure 4. Temperature dependence of the resistivity $\rho(T)$ of the as-prepared sample ASP2 below 300 K at measuring current $J = 0.2$ mA. The inset shows the temperature behaviour of resistance for two currents, 0.2 and 5 mA.

considered also as the point where the FC and ZFC curves branch off strongly) is characteristic of weak ferromagnetic order in ruthenocuprates. It is found that T_{cusp} is about 95 and 89 K for the as-prepared and 30 atm/O_2 annealed samples, respectively (figures 2 and 3). Hence, oxygen annealing simultaneously depresses to some degree the magnetic order and enhances the superconductivity.

It should be mentioned that the properties of the 30 atm/O_2 annealed sample agree closely with those of the 62 atm/O_2 annealed sample described previously [10]. For that sample, temperatures $T_{c0} \approx 37.5$ and $T_{cg} \approx 32.8$ K (derived from derivatives $\mathrm{d}R(T)/\mathrm{d}T$) are also closely situated. T_{c0} has, however, a very weak dependence on the magnetic field (it decreases only by ≈3 K in a field $H = 8$ T), whereas T_{cg} depends on the magnetic field far more strongly, decreasing to 23.5 K in a low field $H = 0.5$ T. The strong decrease in the intergranular critical temperature in low fields is inherent for granular superconductors. This shows that temperatures T_{c0} and T_{cg} obtained from $\mathrm{d}R(T)/\mathrm{d}T$ peaks in annealed ruthenocuprates should be attributed primarily to granularity effects, but not to the influence of other types of inhomogeneity, such as stoichiometric inhomogeneities or a mixed-phase state.

It thus follows that the inhomogeneity and granularity of ruthenocuprates can have a pronounced effect on their superconducting and magnetic properties. The role of these effects is enhanced by oxygen deficiency. The possible cerium intragrain inhomogeneity is determined mainly by conditions of the solid-state synthesis and would not be expected to change in time (ageing) or due to oxygen annealing. Consequently, there is no need to take into account a hypothetical intragrain granularity, as conjectured in some previous studies [2, 5, 8, 9]. The intergrain granularity is quite enough to explain the results obtained. In the next section we consider the influence of the transport current and applied magnetic field on the resistive transition to the superconducting state in the most inhomogeneous sample ASP2.

3.2. Granularity effects in the current and magnetic field behaviour of the resistive transition to the superconducting state

Figure 4 shows $\rho(T)$ in zero magnetic field for sample ASP2 over the full temperature range of measurement (as compared with the reduced range in figure 1) for rather low current (0.2 mA).

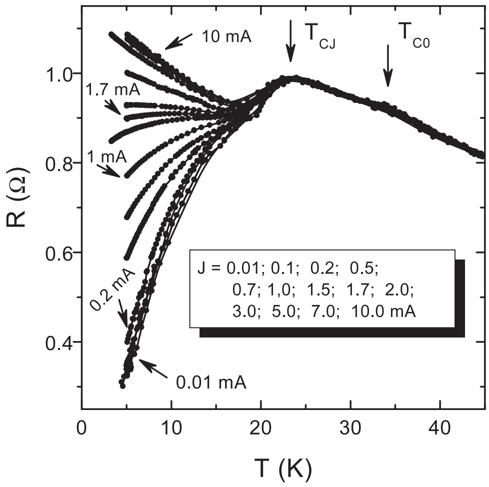

Figure 5. Temperature dependences of the resistance $R(T)$ of the as-prepared sample ASP2 recorded for different measuring currents (from 0.01 to 10 mA).

It demonstrates that $\rho(T)$ has a rather strong non-metallic behaviour above the superconducting transition with the resistive transition being strongly broadened and of shouldered form. The $R(T)$ curves for relatively small (0.2 mA) and rather large (5 mA) currents (the inset in figure 4) demonstrate the striking influence of the current on the resistive transition. The dramatic change in $R(T)$ with increasing current is shown in figure 5 for the full range of applied currents (0.01–10 mA). In both figures, the intragrain critical temperature T_{c0} and the temperature $T_{cJ} \approx 23.2$ K are marked. The latter is defined as the branching point of the family of $R(T)$ curves taken for different currents. Actually, this temperature coincides with the position of the maxima in $R(T)$ curves for all measuring currents (figure 5). The temperature T_{cJ} indicates a temperature point below which percolating chains of intergrain Josephson coupling are created, and the resistance starts to decrease with decreasing temperature. It is also seen in figure 5 that the $R(T)$ curves for low current (0.01 mA $\leqslant J \leqslant$ 1.7 mA) show a decrease in R with decreasing temperature below T_{cJ} as expected for a superconducting transition, whereas the curves recorded for 1.7 mA $\leqslant J \leqslant$ 10 mA have a minimum at $T \approx 17.3$ K, showing non-metallic behaviour ($\mathrm{d}R/\mathrm{d}T < 0$) below this temperature. This kind of $R(T)$ behaviour is usually called quasi-re-entrant and is caused by concurrent tunnelling of unpaired quasi-particle excitations and intergrain Josephson tunnelling of Cooper pairs [11]. The shouldered resistive transitions and quasi-re-entrant behaviour have been observed quite often in the low-T_c granular superconductors [11, 16] and ceramic high-T_c cuprates [17–19].

The results obtained can be explained in a qualitative manner. The system studied represents a 3D Josephson junction array. Two main types of the junctions (tunnel and non-tunnel) are distinguished: SIS (superconductor–insulator–superconductor) and SNS (superconductor–normal–superconductor) [20, 21]. The non-tunnel SNS junctions are often called weak links. Weak links can be realized through both the normal and the superconducting intermediate layers. In the last case, T_c for the intermediate layer should be less than that for the main material. For a junction of two identical superconductors (for example, two neighbouring grains) separated by a thin insulating barrier, the Josephson tunnelling is determined by the characteristic energy E_J of the Josephson coupling [11, 21]

$$E_J = \frac{\pi\hbar}{4e^2 R_N}\Delta(T)\tanh\left[\frac{\Delta(T)}{2k_B T}\right], \tag{1}$$

where $\Delta(T)$ is the superconducting energy gap and R_N is the resistance for single-electron tunnelling, determined by the thickness and effective height of the dielectric barrier. The critical supercurrent in the junction is $J_c = (2e/\hbar)E_J$ [21]. The phase coherence (and the possibility for a supercurrent to flow) in the junction can occur at a low enough temperature ($k_B T \lesssim E_J$) [11].

There is no reason to expect that, in ceramic samples of ruthenocuprates, the thickness of disordered grain boundary regions is the same throughout the system. The oxygen deficiency in grain boundary regions renders these regions as poor superconductors or insulating. Polycrystalline ruthenocuprates have a rather large grain size (of a few μm) with quite pronounced grain boundaries [22]. Since grain boundaries are rather extended, the oxygen concentration (or charge carrier density) in them can be highly inhomogeneous. The percolation description of the superconducting transition [21, 23] should be used in this case. In such systems, reducing the temperature below the intragrain temperature T_{c0} leads, first, to establishing phase coherence only in a limited number of superconducting clusters for which condition $E_J \gtrsim k_B T$ is fulfilled for adjacent grains. As the temperature continues to fall, this condition is satisfied for an increasing number of adjacent grains, the superconducting clusters grow, and an infinite cluster is formed at a certain temperature $T_c < T_{c0}$, at which the resistance becomes zero (note that in the ASP2 sample an infinite cluster is not formed above 4 K). Near the percolation threshold, the conductivity is determined by the presence of 'optimal' chains of grains with maximum probability of tunnelling for adjacent pairs of grains forming the chain. As the measuring current is increased, some of the weakest links of the chains with the least critical current go to the resistive state, increasing the total resistance of the system.

The influence of measuring current on the $R(T)$ curves below T_{cJ} grows stronger with decreasing temperature (figures 4 and 5). This effect together with the quasi-re-entrant phenomenon can be explained by taking into account the existence and concurrence of two kinds of charge carriers in granular superconductors below T_{c0} [11, 16, 21]: Cooper pairs and unpaired electrons, which are usually called quasi-particles. With decreasing temperature the density of quasi-particles decreases simultaneously with the increase in density of Cooper pairs. For superconductors with strongly inhomogeneous grain boundaries, a reduction in the temperature below T_{c0} can produce Josephson coupling only for a certain number of uncoupled superconducting clusters. The formation and growth of these clusters with decreasing temperature leads to a decrease in resistance, but these clusters cannot 'short' the entire system even for $T = 0$ if grain boundary disorder is large enough (an infinite cluster is not formed). The minimum in $R(T)$ is thus due to an increase in resistance of the 'unshorted' parts of the system, for which non-metallic $R(T)$ behaviour is determined by the quasi-particle normal currents. Below T_{c0}, the non-metallic behaviour can be even stronger than that above T_{c0} since the quasi-particle density reduces with decreasing temperature in the range $T < T_{c0}$. Other possible reasons of quasi-re-entrant behaviour are covered in [11, 16, 21] and will not be discussed here.

Important features of granular behaviour are also found in our study of the influence of a magnetic field on the resistive transitions. The measurements were done for the currents 0.1, 0.2, 0.5, 1 and 3 mA. The low-current ($J = 0.2$ mA) results are shown in figures 6–9. It is found (figure 6) that low fields, $0 < H \leqslant H_{cJ} \approx 400$ Oe, exert, in fact, the same effect as an increasing current: broadening of the resistive transitions with the same branching point $T_{cJ} \approx 23.2$ K. This is because in this field range the magnetoresistance (MR) is close to zero or weakly negative for temperatures $T_{cJ} \leqslant T \leqslant T_{c0}$ (see below), whereas MR below T_{cJ} is positive and increases strongly with decreasing temperature (figures 7 and 8).

The magnetic field behaviour of $R(T)$ below T_{c0} in the sample studied is similar to that in ceramic high-T_c cuprates [24, 25] and should be attributed to suppression of intergranular Josephson coupling. This shows itself as (i) a sharp resistance increase in the low-field range

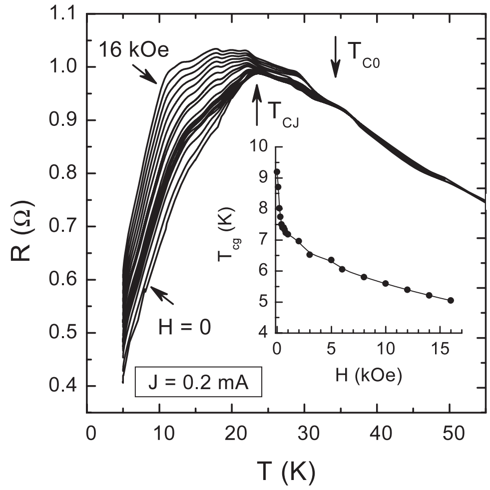

Figure 6. Resistive superconducting transition of the as-prepared sample ASP2 measured at current $J = 0.2$ mA for different magnetic fields (in kOe): 0, 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0; 2.0; 3.0; 4.0; 5.0; 6.0; 8.0; 10; 12; 14; 16. The inset shows the magnetic field variation of the intergrain critical temperature T_{cg}. $T_{c0} \approx 34$ K (indicated by the arrow) is the intragrain critical temperature of the superconducting transition.

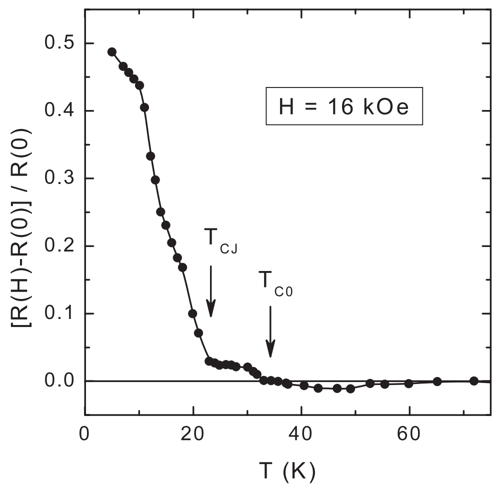

Figure 7. Temperature dependence of the magnetoresistance at $H = 16$ kOe for the as-prepared sample ASP2 measured at current $J = 0.2$ mA.

(figure 8), and (ii) a drastic decrease in the intergrain critical temperature T_{cg} (defined in this case as the temperature at which $R = 0.62\ \Omega$, that corresponds to ≈50% of the estimated normal-state resistance) in the same field range (see the inset in figure 6). The observed behaviour of $T_{cg}(H)$ (including a dramatic decrease in low fields, which are far less than the intragranular critical field H_{c2}) is inherent to granular superconductors and agrees with the model of Gerber *et al* [24].

Above $H_{cJ} \approx 400$ Oe, the resistance rises with H far more slowly than below it. For fields $H \gg H_{cJ}$, an approximately linear rise in the resistance with field is seen (figure 8) which can be related to the suppression of intragrain superconductivity. In this field range

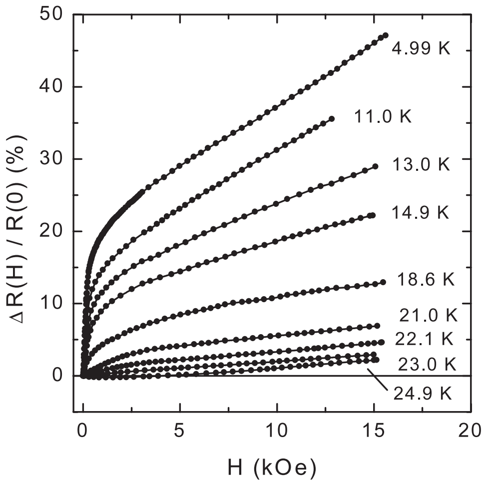

Figure 8. Magnetic field dependences of the magnetoresistance, $[R(H) - R(0)]/R(0) = \Delta R(H)/R(0)$, of sample ASP2 for the temperature range $T \lesssim T_{cJ}$, recorded for increasing fields.

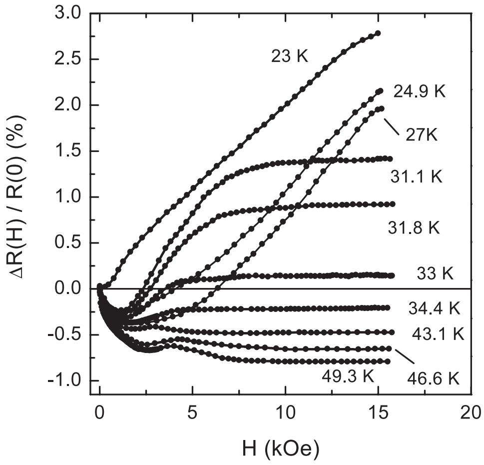

Figure 9. Magnetic field dependences of the magnetoresistance, $[R(H) - R(0)]/R(0) = \Delta R(H)/R(0)$, of sample ASP2 for temperatures in the neighbourhood of the intragrain critical temperature $T_{c0} \approx 34$ K, recorded for increasing fields.

a perceptible positive MR appears in the temperature range $T_{cJ} \leqslant T < T_{c0}$ (figure 7), so that now the intragrain critical temperature $T_{c0} \approx 34$ K becomes a branching point for $R(T)$ curves measured for different fields (figure 6). The temperature dependence of the MR at high ($H \gg H_{cJ}$) field (figure 7) reveals clear features at both T_{cJ} and T_{c0}, characteristic temperatures of the granular sample. T_{c0} reveals itself as a point where MR changes its sign from negative to positive with decreasing temperature (this is seen also in figure 9). The negative MR is inherent in the Ru1222–Gd ruthenocuprates in the temperature range above the superconducting onset temperature [3, 6, 7, 26]. The magnitude of the intragrain critical temperature $T_{c0} \approx 34$ K determined from magnetoresistive measurements coincides, therefore, with that obtained from the analysis of the $R(T)$ dependence at zero field.

Interesting features of the MR, associated with the granular structure, were found in the range $T_{cJ} \leqslant T < T_{c0}$ (figure 9). It is seen that small negative MR appears in this range

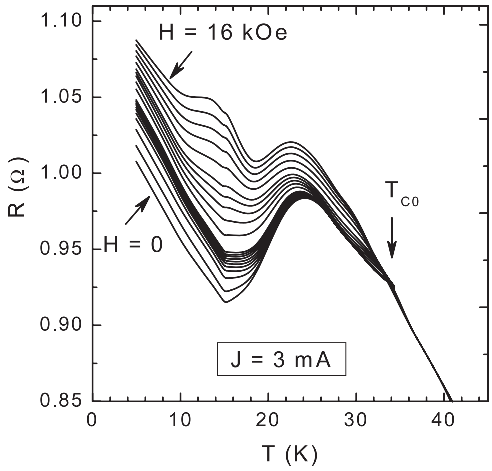

Figure 10. Resistive superconducting transition of the as-prepared sample ASP2 measured at current $J = 3$ mA for different magnetic fields (in kOe): 0, 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0; 2.0; 3.0; 4.0; 5.0; 6.0; 8.0; 10; 12; 14; 16. $T_{c0} \approx 34$ K is the intragrain critical temperature.

for low fields $H \leqslant 3$ kOe. This type of negative MR is well known for weakly coupled systems of superconducting grains [11, 16] including granular high-T_c superconductors [17]. It is associated with the reduction of the intragrain superconducting gap $\Delta(T)$ in an applied magnetic field, that causes an increase in the quasiparticle density and corresponding decrease in resistance [11, 16, 17]. In general, the intragrain upper critical field is expected to be very large in the Ru1222–Gd compound [10]. But close enough to T_{c0}, the field applied in this study (up to 16 kOe) is quite enough to suppress intragrain superconductivity. For example, it is seen in figure 9 that at $T = 31.1$ K the $\Delta R(H)/R(0)$ dependence shows negative MR for low field; then with further increase of the field MR becomes positive and saturates at $H \approx 8$ kOe. Above this field the resistance is constant implying total suppression of the intragrain superconductivity by the magnetic field. Such behaviour of the MR was found in the range 30 K $\leqslant T \leqslant T_{c0} \approx 34$ K.

For higher currents, the resistive curves below T_{c0} show the quasi-re-entrant behaviour (figures 4 and 5). The influence of magnetic field on resistive curves in this case is shown in figure 10 for measuring current $J = 3$ mA. It is seen that the magnetic field which suppresses the intergrain superconductivity simultaneously suppresses the quasi-re-entrant effect: the resistance minimum is shifted to higher temperature with increasing field and should be completely smeared at high enough field. Positive MR can be seen only below T_{c0} (figure 10) (in the same way as for $J = 0.2$ mA; see figure 6).

Thus, the resistive and MR data have permitted disclosure of the main peculiarities of granular superconductivity in the samples studied. Note that no need has arisen to invoke the hypothetical intragrain granularity [2, 5, 8, 9] for the explanation of these data. Even if this is present in the samples, it must make only a very modest contribution to the broadening of the resistive transitions.

4. Conclusions

The current and magnetic field dependences of the resistive transition to the superconducting state in ruthenocuprate $RuSr_2(Gd_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ show clear evidence of granularity effects.

These effects are determined by the polycrystalline structure of samples prepared by the solid-state reaction method. The main source of granularity is the oxygen deficiency. Additional oxygen loss from the samples proceeds during storage and enhances the granularity effects. The influence of granularity can be weakened appreciably by annealing the samples in pure oxygen at high pressure. The results do not reveal effects of intragrain granularity suggested in [2, 5, 8, 9].

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References

[1] Felner I 2003 *Studies of High Temperature Superconductors* vol 46, ed A V Narlikar (New York: Nova Science) pp 41–75
[2] Lorenz B, Xue Y Y and Chu C W 2003 *Studies of High Temperature Superconductors* vol 46, ed A V Narlikar (New York: Nova Science) pp 1–39
[3] Awana V P S 2004 *Preprint* cond-mat/0407799
[4] Mele P, Artini C, Costa G A, Carnasciali M M and Ferretti M 2003 *Int. J. Mod. Phys.* B **17** 716
[5] Xue Y Y, Lorenz B, Baikalov A, Cao D H, Li Z G and Chu C W 2002 *Phys. Rev.* B **66** 014503
[6] Awana V P S, Takayama-Muromachi E, Karppinen M and Yamauchi H 2003 *Physica* C **390** 233
[7] Felner I, Galstyan E, Lorenz B, Cao D, Wang Y S, Xue Y Y and Chu C W 2003 *Phys. Rev.* B **67** 134506
[8] García S, Musa J E, Freitas R S and Ghivelder L 2003 *Phys. Rev.* B **68** 144512
[9] das Virgens M G, García S, Continentino M A and Ghivelder L 2005 *Phys. Rev.* B **71** 064520
[10] Naugle D G, Rathnayaka K D D, Krasovitsky V B, Belevtsev B I, Anatska M P, Agnolet G and Felner I 2006 *J. Appl. Phys.* **99** 08M501
[11] Belevtsev B I 1990 *Sov. Phys.—Usp.* **33** 36
[12] Daeumling M, Seuntjens J M and Larbalester D C 1990 *Nature* **346** 332
[13] López-Morales M E, Savoy R J and Grant P M 1989 *Solid State Commun.* **71** 1079
[14] Felner I, Asaf U, Levi Y and Millo O 2000 *Physica* C **334** 141
[15] Cardoso C A, Lanfredi A J C, Chiquito A J, Araújo-Moreira F M, Awana V P S, Kishan H, de Almeida R L and de Lima O F 2005 *Phys. Rev.* B **71** 134509
[16] Belevtsev B I, Komnik Yu F and Fomin A V 1987 *J. Low Temp. Phys.* **69** 401
[17] Gerber A, Grenet T, Cyrot M and Beille J 1990 *Phys. Rev. Lett.* **65** 3201
Gerber A, Grenet T, Cyrot M and Beille J 1991 *Phys. Rev.* B **43** 12935
[18] Early E A, Almasan C C, Jardim R F and Maple M B 1993 *Phys. Rev.* B **47** 433
[19] dos Santos C A M, Oliveira C J V, da Luz M S, Bortolozo A D, Sandim M J R and Machado A J S 2006 *Preprint* cond-mat/0601064
[20] Barone A and Paterno G 1982 *Physics and Application of the Josephson Effect* (New York: Wiley)
[21] Likharev K K 1985 *Introduction to Dynamics of Josephson Junctions* (Moscow: Nauka)
[22] Živković I, Hirai Y, Fraser B H, Prester M, Drobac D, Ariosa D, Berger H, Pavuna D, Margaritondo G, Felner I and Onellion M 2002 *Phys. Rev.* B **65** 144420
[23] Deutscher G, Entin-Wohlman O, Fishman S and Shapira Y 1980 *Phys. Rev.* B **21** 5041
[24] Gerber A, Grenet Th, Cyrot M and Beille J 1992 *Phys. Rev.* B **45** 5099
[25] dos Santos C A M, da Luz M S, Ferreira B and Machado A J S 2003 *Physica* C **391** 345
[26] Chen X H, Sun Z, Wang K Q, Li S Y, Xiong Y M, Yu M and Cao L Z 2001 *Phys. Rev.* B **63** 064506