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Transport, thermal, and magnetic properties of $RuSr_2(Gd_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$, a magnetic superconductor

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Resistivity, thermoelectric power, heat capacity, and magnetization for samples of $RuSr_2(Gd_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ were investigated in the temperature range 1.8–300 K with a magnetic field up to 8 T. The resistive transitions to the superconducting state are found to be determined by the inhomogeneous (granular) structure, characterized by the intragranular, T_{c0}, and intergranular, T_{cg}, transition temperatures. Heat capacity, $C(T)$, shows a jump at the superconducting transition temperature $T_{c0} \approx 37.5$ K. A Schottky-type anomaly is found in $C(T)$ below 20 K. This low-temperature anomaly can be attributed to splitting of the ground term $^8S_{7/2}$ of paramagnetic Gd^{3+} ions by internal and external magnetic fields. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2163276]

$RuSr_2(Gd_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ belongs to a known family of magnetic superconductors.[1–4] Superconductivity is associated with CuO_2 planes, while magnetic order is thought to be connected with RuO_2 planes. The exact nature of the magnetic order in this compound is still unknown, but it is conjectured that below 80–100 K weak-ferromagnetic order dominates. The paramagnetic magnetic moments of Gd^{3+} ions make a considerable contribution to total magnetization as well as the heat capacity, especially at low temperature. A possible magnetic Ru-Gd interaction cannot be excluded as well. Superconductivity in this family of compounds is apparent below 50 K, where both superconducting and magnetic order coexist.

In this paper, the transport, magnetic, and thermal properties of 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, 62, and 78 atm, are presented. The measurements were made with Quantum Design devices (PPMS and SQUID magnetometer), and a homemade thermopower measuring system.

The samples behave as inhomogeneous (granular) superconductors. This manifests itself to the greatest extent in resistive properties, as can be seen, for example, in Fig. 1 for an annealed (62 atm) sample. The rather broad and shouldered $R(T)$ curves in the region of the superconducting transition are indicative of inhomogeneity effects. The most obvious inhomogeneity source is the granular structure, determined by the polycrystalline structure (with a grain size of a few μm). Nonhomogeneous oxygen distribution can cause oxygen depletion of the grain-boundary regions and, hence, weak electrical connectivity between the grains, as is often the case in cuprates. Above the superconducting transition, the rather high resistivity (about 10^{-2} Ω cm) and the weak increase in resistance with decreasing temperature support this suggestion. The onset temperature of superconductivity, T_c^{onset}, is about 58 K with a zero-resistance temperature about 25 K. Derivatives $dR(T)/dT$ reveal two peaks (Fig. 2) 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}, re-

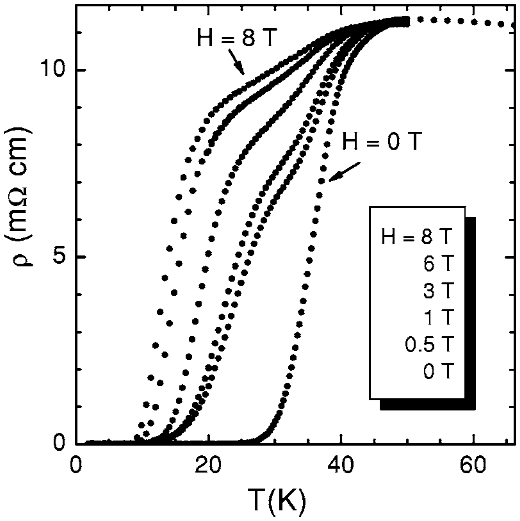

FIG. 1. Temperature dependence of the resistivity $\rho(T)$ at different magnetic fields for sample annealed in pure oxygen at 62 atm.

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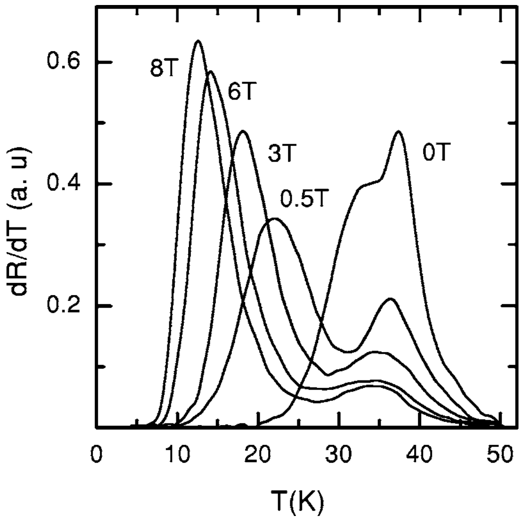

FIG. 2. Derivatives of resistive curves of superconducting transition (for the sample shown in Fig. 1) for different magnetic fields.

spectively. The intergranular superconductivity should be determined by Josephson coupling between the grains. T_{c0} and T_{cg} are equal to 37.5 and 32.8 K, respectively, in zero field. 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 transition temperature T_{c0}. The intergranular T_{cg} is far more sensitive to magnetic field, with the main variations occurring in the low-field region $H<0.5$ T (Fig. 2).

The $R(T)$ behavior of the as-prepared sample (Fig. 3 inset), which is expected to be the most depleted in oxygen, substantiates our assumptions. The $R(T)$ curve of this sample, taken at $H=0$, indicates that T_{c0} and T_{cg} are equal to 35 and 18.5 K, respectively, with T_c^{onset} about 39 K. It is seen that intragranular superconducting properties are much less affected by high-pressure oxygen annealing than the intergranular ones.

The thermoelectric power (S) of the samples studied is found to be sensitive to oxygen annealing as well (Fig. 3). The magnitude of S at $T=290$ K is far larger (1.8 times) in the as-prepared sample than that in the sample annealed at 62 atm of O_2. The temperatures of maximum slope in the $S(T)$ curves at the superconducting transition (which can be taken as T_c values) are 41.5 and 22.8 K in 62-atm annealed and as-prepared samples, respectively. Derivatives dS/dT give estimated values of T_c^{onset} as well, which are found to be roughly 44 and 59 K for as-prepared and 62-atm annealed samples, respectively, which correspond roughly to values obtained from the resistive data (inset).

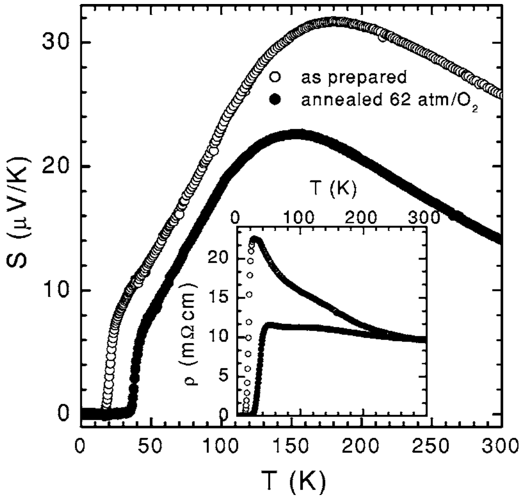

FIG. 3. Temperature dependences of the thermoelectric power for as prepared and 62 atm/O_2 annealed samples. The inset shows $\rho(T)$ at zero field for the same samples.

The measured temperature dependences of the magnetization, $M(T)$, indicate that M becomes appreciable only below 180–200 K with a further sharp jump in M in the range of 100 K at $T=T_{m2}$ due to transition to a weak-ferromagnetic state. The transition temperature T_{m2} is about 99 and 90 K for as-prepared and 100-atm annealed samples, respectively. This shows that oxygen annealing suppresses somewhat the magnetic order in ruthenocuprates in agreement with previous studies.[1,3] $M(T)$ dependences (ZFC) recorded in low field (about 0.5 mT) show a clear diamagnetic transition below 40 K determined by transition to the superconducting state. The values of T_c estimated from the diamagnetic part of $M(T)$ correspond well to T_{c0} obtained from transport properties.

In contrast to transport properties, the heat capacity was found to be rather insensitive to the granular structure and oxygen annealing. The specific heat data are found to be nearly the same for all four samples studied. No features in the temperature dependence of the heat capacity, $C(T)$, associated with magnetic transitions were found. This can be attributed to the absence of long-range magnetic order at the transition point due to magnetic inhomogeneities induced by structural and/or stoichiometric inhomogeneity, or phase separation. The low-temperature behavior of $C(T)$ (below 40 K) indicates the superconducting transition and a magnetic anomaly. To present these features of $C(T)$ more clearly, an estimate of the lattice heat capacity contribution, $C_{ph}(T)$, was subtracted. Measurements of $C(T)$ of a $RuSr_2(Eu_{1.5}Ce_{0.5})Cu_2O_{10-\delta}$ sample of the same composition but with nonmagnetic Eu substituted for magnetic Gd were used for this purpose. The Eu sample displayed a smooth $C(T)$ dependence of the Debye type without any low-temperature magnetic anomaly or jump at the superconducting transition. The function $\Delta C(T) \approx C_{\text{Gd}} - bC_{\text{Eu}}$ (C_{Gd} is as measured data for Gd sample, C_{Eu} is that for Eu sample, and b is a factor close to unity, providing $C_{\text{Gd}}=bC_{\text{Eu}}$ at $T=300$ K) as shown in Fig. 4.

The main features in $\Delta C(T)$ are (i) the jump at the superconducting transition, and (ii) the upturn below 20 K (Schottky-type anomaly). A jump at T_c in the heat capacity of a ruthenocuprate with a similar chemical composition $[RuSr_2(Gd_{1.4}Ce_{0.6})Cu_2O_{10-\delta}]$ was reported earlier.[5]

In heat capacity studies, the temperature of the superconducting transition is usually associated with onset of the $C(T)$ jump (T_c^o) or with the point of maximum slope of $C(T)$ in this region. In zero field $T_c^o \approx 37$ K, which is very close to the intragranular T_{c0} determined from the $R(T)$ curves. An external field up to $H=8$ T hardly produces shifts in T_c^o (Fig. 4). This correlates well with the very weak shift in T_{c0} in a

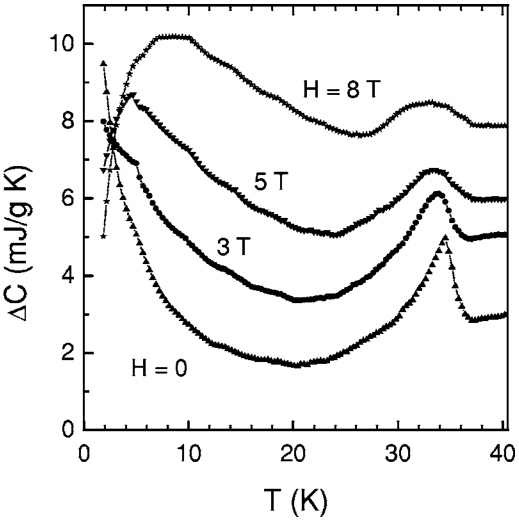

FIG. 4. Temperature curves of the nonphonon part of the heat capacity, measured in different magnetic fields.

magnetic field (Fig. 2) and provides evidence of enormous upper critical fields in the ruthenocuprates.

The low-temperature Schottky-type anomaly can be attributed to splitting of the ground term $^8S_{7/2}$ of paramagnetic Gd^{3+} ions. According to Kramers' theorem, the degenerate ground term should be split into four doublets in tetragonal symmetry. The sources of splitting can be crystal-electric-field effects and the internal and external magnetic fields. The crystal-field effect can be ignored, in the first approximation, since Gd^{3+} has zero orbital angular momentum. Other sources of splitting cannot, however, be excluded. In particular, internal molecular fields can arise in the ruthenocuprate from both the Gd and Ru sublattices[6] and can coexist with superconductivity.[7] Even though a direct Gd-Gd exchange interaction is unlikely, these ions can be magnetically polarized by the $4d$-$4f$ interaction.

Generally, the Schottky term, $C_{\mathrm{Sch}}(T)$, in the heat capacity for compounds with Gd^{3+} ions should be attributed to splitting of all four doublets, although actually only some of them make the dominant contribution to the effect. For any number of influencing levels, however, the function $C_{\mathrm{Sch}}(T)$ should have a maximum at a temperature $T_{\max}$, which is of the order of Δ_s/k_B. Here, the Δ_s is a characteristic energy-level splitting, which is equal to $2\mu_{\mathrm{eff}}(H_{\mathrm{mf}}+H)$, where μ_{eff} is the effective moment of Gd ions, H_{mf} is the effective molecular field at the Gd^{3+} site, and H is the external field. The field H_{mf} can depend on external field as well. It is clear that $T_{\max}$ should increase and the maximum should become more smeared with increasing external field, which is the case (Fig. 4). Thus, the observed low-temperature heat capacity anomaly is in all probability connected with the Schottky effect. An exact numerical analysis of the effect in the sample studied presents a real challenge since most of the important parameters (influence of magnetic field on schemes of energy levels, molecular field, effective moments of Gd^{3+} ions) are not very well known.

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