The magnetic state of 1212-type ruthenocuprate in magnetocaloric and magnetoresistivity measurements of polycrystalline samples of RuSr$_2$Gd$_{1-x}$Ce$_x$Cu$_2$O$_8$ and Ru$_{1-x}$Sr$_2$GdCu$_2$O$_8$

Piotr W Klamut$^1$ and Tomasz Plackowski

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P Nr 1410, PL-50950 Wrocław 2, Poland

E-mail: P.Klamut@int.pan.wroc.pl

Received 20 October 2008, in final form 20 November 2008
Published 26 January 2009
Online at stacks.iop.org/SUST/22/025021

Abstract

The magnetic properties of superconducting Ru$_{1-x}$Sr$_2$GdCu$_2$O$_8$ ($x = 0, 0.02$) and non-superconducting RuSr$_2$Gd$_{1-x}$Ce$_x$Cu$_2$O$_8$ ($x = 0.07, 0.1$) were investigated by means of magnetocaloric experiments with complementary magnetoresistivity and ac susceptibility measurements. The isothermal magnetocaloric coefficient $M_T(B)$ assumes positive values in a broad range of temperatures ($20 \leq T \leq 231$ K) and magnetic fields ($0 \leq B \leq 13$ T), i.e. also in the magnetically ordered state ($T_m = 132$ K for RuSr$_2$GdCu$_2$O$_8$ and $T_m = 150$ K for RuSr$_2$Gd$_{0.93}$Ce$_{0.07}$Cu$_2$O$_8$) which indicates no gain in the system’s magnetic entropy with increasing magnetic field. The maximum in the $M_T(B)$ dependence was observed for RuSr$_2$GdCu$_2$O$_8$ in the temperature vicinity of $T_m$, which indicates a ferromagnetic character of the accessed magnetic correlations. No spontaneous ferromagnetic order was revealed as the $M_T$ assumes limiting zero values at zero magnetic field for the whole range of investigated temperatures. Temperature dependences of the specific heat reveal the magnetic-field-induced positive temperature shift of the anomaly associated with the magnetic transition in the Ru spin system. The $M_T(B)$ dependences and the magnetoresistivity data suggest that the magnetic system may be inhomogeneous.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Ruthenocuprates are a family of complex copper oxides crystallizing in a few derivative layered crystal structures, which contain both the CuO$_2$ and RuO$_2$ layers. Several of these compounds were reported as superconducting with $T_c$ up to approximately 50 K bearing close resemblance to other structurally related copper oxide high temperature superconductors (HTSC) [1, 2]. The sublattice of Ru ions in ruthenocuprates becomes magnetically ordered at temperatures higher than the superconducting $T_c$, in the range of approximately 70–200 K, depending on the particular structural type [3, 4]. This feature makes these compounds distinct from other HTSC and consequently stimulates considerable interest in their properties. Magnetism due to ordering in the Ru sublattice was usually explained by invoking the presence of a ferromagnetic component in the antiferromagnetically aligned
as relevant synthesis issues were reviewed in [11]. Ferromagnetic properties could certainly add to the fundamental interest, if the emerging phase diagram would involve a coexisting superconducting domain at lower temperatures. Such coexistence indeed seems present for non-zero magnetic fields, if one assumes that the crystal lattice has sufficient phase homogeneity for simultaneously supporting both states. This, however, remains as a dispute [8, 9]. Elucidation of the magnetic ground state of the Ru sublattice and its magnetic field dependence proved to be quite complex. Therefore, considerable effort has been addressed in the literature on finding a consistent interpretation of the experimental results provided by several different experimental techniques.

Due to some complexity of the synthesis, comparatively only a few experiments addressed relevant properties in the single-crystal and epitaxial thin film form of the ruthénocuprates. With this, we note that the usually reported polycrystalline samples possess a comparatively fine granular structure with the characteristic grain size of approximately 1 μm and are characterized with a comparatively long superconducting magnetic field penetration depth $\lambda(0) \approx 3 \mu m$ [10]. The intrinsic structural inhomogeneity, recently reported for superconducting RuSr$_2$GdCu$_2$O$_8$ [8] with high resolution electron microscopy, may be viewed in the context of earlier reports of the phase separation [10]. This further complicates the interpretation of the combined superconducting and magnetic characteristics that have been measured. Manifold properties of the ruthénocuprates were more recently approached in several review texts [10–15]. The systematic approach to the phase diagram for the class, as well as relevant synthesis issues were reviewed in [11].

The RuSr$_2$GdCu$_2$O$_8$ is usually indexed in tetragonal symmetry with P4/mmm or P4/mmbm space groups [16, 17], although a slight orthorhombicity was also reported [18]. In resemblance to the 123-type GdBa$_2$Cu$_3$O$_7$ superconductor, the 1212-type structure may be visualized with Ba atoms replaced by Sr, and the Cu chain atoms replaced by Ru coordinated by the octahedra of oxygens, which increases to eight the total number of oxygen atoms per formula. Temperature of the superconducting transition in RuSr$_2$GdCu$_2$O$_8$ was found to be synthesis-dependent, with the maximum $T_c$ usually reported at 46 K for the polycrystalline samples and the magnetically established onset $T_{cs} = 51 K$ reported in single crystals [19]. By altering the conditions of synthesis non-superconducting samples of RuSr$_2$GdCu$_2$O$_8$ were also found [20, 21]. The Ru sublattice in RuSr$_2$GdCu$_2$O$_8$ orders magnetically below $T_m \approx 131–136 K$. The few Kelvin difference in $T_m$ was found for the samples obtained with slightly altered processing conditions, for which the lower $T_m$ usually corresponds to higher superconducting $T_c$ (see [15] and references therein). The assumption of the perfect stoichiometry of the compound and of the Ru ions present in the pentavalent oxidation state leads to divalent Cu ions, placing the compound below the threshold for superconductivity on the generic phase diagram for HTSC. Partially tetravalent character of the Ru ions was, however, reported in the results of NMR i.a. in [22], and XANES [23]. Then, the average valence of Cu would be expected to increase and may reach into ranges characteristic of the HTSC superconductor.

![Figure 1. Powder x-ray diffraction spectra of RuSr$_2$GdCu$_2$O$_8$ (black line, circles in the inset) and Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ (sample A, red line, squares in the inset). Inset shows the scans at expanded scale in the range where the main diffraction maxima of the SrRuO$_3$ phase are expected. The vertical lines mark positions of the 004, 013 and 110 maxima for the RuSr$_2$GdCu$_2$O$_8$ derived in the tetragonal P4/mmm space group. The dashed vertical lines from left to right mark positions of the 200, 112 and 020 maxima for SrRuO$_3$ in the orthorhombic Pbnm space group. Co Kα radiation, $T = 293 K$.](image)

2. Experimental details

In this paper we report on the magnetic properties of polycrystalline samples of RuSr$_2$GdCu$_2$O$_8$, Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$, Ru$_{0.93}$Ce$_{0.07}$Cu$_2$O$_8$ and Ru$_{0.9}$Ce$_{0.1}$Cu$_2$O$_8$ by means of magnetocalorimetric measurements. We will also discuss the complementary results of the magnetoresistivity and susceptibility measurements.

The samples were prepared in a two-step solid state reaction. First, the powders of RuO$_2$ (99.9% purity, preheated at 600 °C), Gd$_2$O$_3$ (99.9% purity), SrCO$_3$ (99.9% purity) and CuO (99.9% purity) were reacted by powder calcination in air at 920 °C for 53 h with intermediate grinding and then sintering in the controlled flow of Ar gas at 1015 °C for 20 h. At this stage, reducing conditions benefited formation of the double perovskite precursor instead of ruthenate strontium perovskite phases, which, when formed, would subsequently react only with slow kinetics to the final Ru1212-type phase [11]. The x-ray powder diffraction scans confirmed the mixture of Cu$_2$O and Ru$_2$Sr$_2$GdO$_8$ phases. Then the samples were sintered at 1060 °C in flowing O$_2$ gas with intermediate grinding and pelletizing, finally cooled at a rate of 1 °C min$^{-1}$ in the controlled flow of O$_2$ gas and removed from the furnace at 600 °C. The samples (except for sample B of Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$, which was prepared separately) were synthesized simultaneously, with care being taken to provide the same heat treatment conditions for the series. In figure 1 we compared the powder x-ray diffraction spectra for RuSr$_2$GdCu$_2$O$_8$ and Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ (sample A) in the 2θ range where the diffractive signature of the bulk SrRuO$_3$ impurity might be expected.

Compositions of the investigated samples were chosen for accessing the effect of charge doping in the 1212-type structure.
following conventional routes of crystal chemistry, which are being used in the investigation of many complex copper oxides. Partial substitution of Ce$^{4+}$ ions into the Gd$^{3+}$ site should provide the means for electron doping. Such substituted compounds were indeed found non-superconducting, as would be expected in the case of the lowered Cu valence [24, 25]. The Ru deficiency was considered to allow for an effective hole doping in the electronic structure, although we note that such an intuition may well turn misleading for the intrinsically inhomogeneous material. Nevertheless, the superconducting $T_c$ was found higher for nominally deficient Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ than in the simultaneously synthesized RuSr$_2$GdCu$_2$O$_8$ (see also [15] and references therein). This is in qualitative agreement with the increased $T_c$ reported earlier for Ru$_{0.9}$Sr$_2$GdCu$_2$O$_8$ in [26]. The ac susceptibility measurements, which show the superconducting transitions in the Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ and RuSr$_2$GdCu$_2$O$_8$ samples, are presented in figure 2. For both samples, however, the specific heat measurements did not reveal any $T_c$-associated anomaly. The total specific heat of Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ in the corresponding temperature range is presented in the inset to figure 2. This agrees with the specific heat data discussed recently in [27] for the superconducting sample of RuSr$_2$GdCu$_2$O$_8$ and the discussion of specific heat results provided in [28]. Comparative analysis in [27] estimated the anomaly expected in the electronic part of the specific heat at $T_c$ within one percent range of the measured signal, i.e. below the accuracy of that measurement. Considering the fact that the superconducting phase may form in only constrained volume, it further shifts the limit beyond experimental accuracy.

Temperature dependences of the dc resistivity were measured by the four-contact method with 1 mA dc current passed through the bar-shaped (approx. 5 mm $\times$ 2 mm$^2$) sample. Temperature was changed continuously at 1 °C min$^{-1}$ with the error of a single measurement being less than 0.1 K with data collected on heating and cooling. Magnetoresistivity was measured for the magnetic field values in between 0 and 13 T. The same experimental set-up was used for the calorimetric measurements, then with the heat flow calorimeter probe, built for measurements of the specific heat $C_p$ and the isothermal magnetocaloric coefficient $M_T$ [29]. The samples were cut and polished to cuboid size with a footprint of 9 mm$^2$ and mounted on the sensitive heat flow meter, which contacted the sample with the heat sink. The meter was made of the commercially available, miniature Peltier cells of high thermal conductance. When changing the temperature, the voltage generated on terminals of the Peltier cells is directly proportional to the $C_p$, which was measured on cooling and warming. At a constant temperature and for a steady change of the magnetic field, the generated voltage is proportional to the isothermal magnetocaloric coefficient $M_T$. The $M_T$ was measured at increasing and decreasing magnetic field, with the measurement preceded with precise stabilization of the sample temperature. Temperature dependences of the specific heat were also measured with the relaxation method using the commercial micro-calorimeter probe in the PPMS measurement platform by Quantum Design Inc. Temperature dependences of the ac susceptibility were measured with the ac susceptibility probe also in the PPMS platform.

![Figure 2](image-url)  
**Figure 2.** Temperature dependences of the real and imaginary components of ac susceptibility in the vicinity of the superconducting transitions in Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ (sample A, squares, red in colour) and RuSr$_2$GdCu$_2$O$_8$ (circles, black in colour). Open symbols correspond to the ac field $H_{ac} = 1$ Oe, closed symbols to $H_{ac} = 0.1$ Oe, $f = 1$ kHz. Inset presents $C_p/T$ versus $T$ for Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ (sample A) in the corresponding range of temperatures.

### 3. Remarks on synthesis

Prior to the discussion of the results, which are the merits of the report, we present a few remarks on the investigated samples. The formulae used throughout present their nominal stoichiometries, i.e. reflect the mass proportions of precisely weighted powder substrates. We note that the element selectivity of the sublimation processes, which occur during the synthesis at high temperatures, may effectively alter the final stoichiometry of the sample. For most samples used in this study (except sample B of Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$) the reaction proceeded in the closed glass system in which we noticed a minor film residue aggravating in the cooler part of the apparatus, which was brought there along with the gas which was leaving the heating zone. The EDAX analysis of this residue revealed more Ru than would be expected based on the sample stoichiometry. We note that, within the accuracy of our laboratory powder x-ray diffraction measurements, we could not distinguish between the lattice constants for the RuSr$_2$GdCu$_2$O$_8$ and the Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ samples. Neither could we quantify the expected element ratio difference with...
EDAX analysis. Then, the nominal Ru deficiency in one of the samples reflects the direction in which we believe the stoichiometric material could evolve, i.e. for here only a comparatively controlled decrease of the Ru/Cu ratio. Such Ru deficiency, as expressed in the nominal formula, could be accommodated for the finite domain of existence of the 1212-type phase or, alternatively, it should result in the formation of the 1212-type stoichiometric phase accompanied with the other minor phases related by the summation over all of the reaction-available elements. For intrinsically inhomogeneous materials, slight altering of the average stoichiometry should result in a larger amount of these structural inclusions, the formation of which is promoted by the nominal stoichiometry. We note that the recent electron microscopy studies revealed that superconducting RuSr$_2$GdCu$_2$O$_{8}$ is intrinsically inhomogeneous at the nanoscale and its overall structure accommodates the phase inclusions with the diminished Ru/Cu ratio [8]. No data such as that are available for the nominally Ru-deficient compounds, which could allow us to investigate the extent of the nanoscale inhomogeneities. The uniformity of the Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ sample composition was investigated only at the microscopic scale with conventional scanning electron microscopy. The lower right picture in figure 3 presents the backscattered electrons’ scan of the fracture surface area, the same as pictured in the topological scan in the lower left picture. Uniformity of the composition is indicated by the uniform grey colour of the uppermost surfaces seen in the backscatter scan. The synthesis approach applied in this work may be considered complementary to the recent experiments communicated in [30] in which the mass flow control method was used to synthesize samples with slightly different Ru content evident in the Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ structural framework.

The solid state synthesis of samples discussed here proceeded at the temperature of 1060°C, communicated in many reports as the standard conditions of synthesis for most of the ruthenocuprate phases. It means that the reaction occurs only several kelvins below the melting temperature for the phase. We note that the single-phase RuSr$_2$GdCu$_2$O$_8$ was also synthesized by the sol–gel method, for which molecular level mixing allowed for a significantly lower temperature of the final reaction [21]. These samples, however, were not superconducting and their considerably smaller grains were invoked for the explanation of the absence of superconductivity. Other possible causes assisting the superconductivity seem to be the alterations of ruthenocuprate stoichiometry [8, 15], which may be promoted during the synthesis in temperature proximity to the phase melting temperature. A potentially related effect was recently communicated for subtle alterations of stoichiometry found induced in a trace melting in the polycrystalline samples of double perovskite Ru$_{1-x}$Cu$_x$Sr$_2$YO$_6$ with local intergrowths of double perovskite Ru$_{1-x}$Cu$_x$Sr$_2$YO$_6$ with local intergrowths found to be the superconducting 123-type phase [31]. If such a phase accommodates partial substitution of the Ru ions into the chain Cu sites, it would correspond to the Cu-substituted 1212-type. The upper SEM picture in figure 3 presents the selected area in Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ (sample B), which was found characteristic by several similar images which were identified for this sample. The pillar-like region in the central part of the picture has a different morphology than the surrounding fine granular structure, and thus may be suspected of a modified phase character. We note that, in our specific heat data between 175 and 276 K (not shown), we found the ‘add-on’ feature that could be linked to the presence of the CO$_2$ trapped in the sample, possibly during the locally occurring re-solidification process. Analysis of the residual gases present in the commercial O$_2$ gas used in synthesis showed traces of CO$_2$ at 0.08%. We are not aware of the other sources of CO$_2$ that the sample could be exposed to. We note, however, that enthalpy estimation for the area associated with the observed feature corresponds to approximately 0.1 mg of CO$_2$.

4. Results and discussion

In the following part we shall discuss the results of our measurements of the specific heat, isothermal magnetocaloric coefficient, magnetic susceptibility and magnetoresistance. The specific heat data of the RuSr$_2$GdCu$_2$O$_8$ and Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ samples revealed a subtle modification (132 K versus 129 K) of the magnetic transition temperature $T_m$ (see inset to figure 4, also discussed in [15]), which are also observed in a corresponding shift of the ac susceptibility maxima at $T_m$ (not shown). This slightly lower $T_m$ in the sample with nominally deficient Ru sublattice confirms that its composition was modified compared to the nominally stoichiometric material. For the RuSr$_2$Gd$_{0.93}$Ce$_{0.07}$Cu$_2$O$_8$
sample the $C_p/T$ bends off at a higher temperature of approximately 150 K (inset to figure 4) and instead of forming a sharp cusp the change is more gradual. We note that there are no characteristic features observed in the specific heat for the Ce-doped sample at temperatures corresponding to $T_m$ of the parent compound. Figure 4 presents the dependences of $C_p/T$ versus $T$ measured for the RuSr$_2$GdCu$_2$O$_8$ at several different magnetic fields in the range between 0 and 13 T. These measurements reveal that the characteristic feature associated with the magnetic transition in the Ru sublattice shifts towards higher temperatures with an increasing magnetic field, as would be considered usual for the ferromagnetic character of dominant magnetic interactions in the corresponding range of magnetic fields.

Since the Cu and Ru ions may formally accept different valence states in the 1212-type structure, the Ce-induced electron doping may affect the charge balance between the CuO$_2$ and RuO$_2$ layers. Our specific heat data for the $x = 0.07$ sample show a similar increase of the $T_m$ to that previously communicated in [24, 25], and to the effect of the partial substitution of La$^{3+}$ ions into the Sr$^{2+}$ site in RuSr$_{2-δ}$La$_δ$GdCu$_2$O$_8$ [32, 33], all of which seem to be caused by the electron doping. The comparable rise of $T_m$ was, however, communicated also for RuSr$_2$Gd$_{1-x}$La$_x$Cu$_2$O$_8$ [34], i.e. for the isovalent substitution into the Gd site. We should then allow that the modification of the $T_m$ may also be driven structurally and, if allowing for band effects, would not only be by differing characteristic distance between the Ru ions. Such an example is provided in the properties of the itinerant Sr$_{1-x}$Ca$_x$RuO$_3$ (0 $\leq x \leq 1$) where the isovalent substitution induces distortion of the Ru–O–Ru bonds, causing the electronic structure driven modification of magnetic properties. Detailed structural data for the RuSr$_2$Gd$_{1-x}$Ce$_x$Cu$_2$O$_8$ series would allow for further insight. For expected electron doping then, lowered Cu valence would result in less conducting Cu–O structural slabs and the sample resistivity should reflect more of the RuO$_2$ layers’ contribution to scattering. In figure 5 we present the negative magnetoresistance observed for RuSr$_2$Gd$_{0.93}$Ce$_{0.07}$Cu$_2$O$_8$ and RuSr$_2$Gd$_{0.9}$Ce$_{0.1}$Cu$_2$O$_8$. Increase in the conductivity in a magnetic field is more pronounced for the Ce-doped sample, in qualitative agreement with the data reported earlier for RuSr$_2$Gd$_{0.9}$Ce$_{0.1}$Cu$_2$O$_8$ in [25]. The magnetoresistive effect associates with the magnetic transition at $T_m$ at which it is at its largest (arrows in figure 5 show the $T_m$ values as established from the specific heat data). For small magnetic fields the magnetoresistivity becomes positive below $T_m$ (see figure 6), which may be explained by the positive contribution to scattering in the presence of the antiferromagnetic order. Temperature dependences of the ac susceptibility measured for RuSr$_2$Gd$_{0.93}$Ce$_{0.07}$Cu$_2$O$_8$, see figure 7, reveal more complex magnetic properties than only the increased $T_m$ comparing to the parent compound. Both components of the ac susceptibility ($\chi'$, $\chi''$) form maxima at approximately 210 K, which shift to lower temperatures with the dc field. We note that only a small dc field (see the dependence at $H_d = 500$ Oe in figure 7) is required to shift the onset temperature of susceptibility maxima to approximately 170 K and the tendency saturates for higher fields. The ac susceptibility measurement could, in principle, reflect the magnetism of some phase impurity: even the amount of such

![Figure 4](image_url)

**Figure 4.** $C_p/T$ versus $T$ in a vicinity of $T_m$ for RuSr$_2$GdCu$_2$O$_8$ (sample A) measured at different magnetic fields. At 130 K the $C_p$ decreases with increasing magnetic field and the field values for different curves are: 0 T (black in colour), 1 T (green in colour), 3 T (dark green in colour) and 13 T (orange in colour). Arrows show the magnetic transition temperatures, which increase with the field. Inset shows the $C_p/T$ versus $T$ for: (a) RuSr$_2$GdCu$_2$O$_8$ (black in colour), (b) Ru$_{0.96}$Sr$_{2}$Gd$_{0.04}$Cu$_2$O$_8$ (red in colour) and (c) Ru$_{0.97}$Sr$_{2}$Gd$_{0.03}$Cu$_2$O$_8$ (blue in colour), also in [15].

![Figure 5](image_url)

**Figure 5.** Negative magnetoresistance for samples: (a) RuSr$_2$Gd$_{0.93}$Ce$_{0.07}$Cu$_2$O$_8$ and (b) RuSr$_2$Gd$_{0.9}$Ce$_{0.1}$Cu$_2$O$_8$. Dependencies shown are measured at: 0 T (black in colour, higher resistance values) and 13 T (orange in colour, lower resistance values). Arrows show the temperatures of magnetic transitions as established in the specific heat measurements.
phases would remain below the detection limit for standard powder x-ray diffraction. However, among other ruthenate phases which may be considered, the highest temperature of magnetic transition belongs to the ferromagnetic SrRuO$_3$ at $T_C = 163$ K, i.e. at a significantly lower temperature than that of the maxima observed in ac susceptibility. The Ru$_2$SrGdCu$_2$O$_8$ may be considered charge underdoped in the sense of the HTSC phase diagram and the extra electrons provided with Ce substitution should further that state. Then, in analogy to other complex cuprates, antiferromagnetism of the Cu sublattice could be set at temperatures comparable to $200$ K. The negative field-induced shift of the maxima suggests an antiferromagnetic character of the underlying interactions. This tentative interpretation, with a cautionary remark for investigating a possibly inhomogeneous magnetic system, may suggest further element-specific measurements like Cu-NQR and Ru-NMR for the Ru$_2$Sr$_{2}$Gd$_{1-x}$Ce$_x$Cu$_2$O$_8$ series.

In the following part we will analyse the magnetic field dependences of the isothermal magnetocaloric coefficient $M_T$. These measurements have an advantage of accessing information directly related to the magnetic state of the sample as well as reflecting its bulk features. The experiments were performed in a heat flow calorimetric set-up, which is described in detail in [29]. At a constant temperature and steady change of magnetic field conditions, the isothermal magnetocaloric coefficient may be described by the formula

$$M_T = \frac{dq}{dB} = -\frac{q}{B} = -\frac{U}{AB},$$

where $q$ represents the heat flux from the heat sink to the sample, $B$ is the magnetic induction, $A$ is the sensitivity parameter and $U$ is the voltage generated by the heat flow meter. The negative sign at $q$ preserves consistency with the expression

$$C_p = \frac{dq}{dT} = \frac{q}{T} = \frac{U}{AT},$$

which we used for deriving the $C_p$ from data collected at constant magnetic field and changing temperature. Figure 8 presents the magnetic field dependences of the $M_T$ measured for the Ru$_2$SrGdCu$_2$O$_8$ and Ru$_2$Sr$_2$Gd$_{0.9}$Ce$_{0.1}$Cu$_2$O$_8$ samples at temperatures above the magnetic transition temperature $T_m$. Figure 9 shows the $M_T(B)$ dependences for the same samples at a temperature of $137$ K and below the $T_m$. Since two samples were measured simultaneously, the temperature sequences are the same. Change in the magnetic entropy can be accessed by integrating one of the Maxwell equations:

$$\Delta S_{mag}(T, B) = \int_0^B \left( \frac{dT}{AT} \right) dM,$$

and relating the $M_T$ with the magnetization: $M_T = -T \left( \frac{dM}{dT} \right)_B$, which leads to

$$\Delta S_{mag}(T, B) = -\int_0^B \left( \frac{M_T}{T} \right) dB.$$

The positive sign of the isothermal magnetocaloric coefficient, observed for both samples in the whole range of the accessed magnetic fields and temperatures (figures 8 and 9), reveals that the system entropy universally decreases with magnetic field. We note that for a simple antiferromagnet there is rather an increase in the magnetic entropy, i.e. negative $M_T(B)$ would be expected. Simultaneously, the dependences differ from the behaviour expected for a simple ferromagnetic...
system. We note that the presence of spontaneous magnetization would lead to \((\frac{\partial M}{\partial T})_{B \to 0} < 0\), i.e. positive values of the \(M_T\) in the limit of zero field. Instead, the limiting zero-field value of the \(M_T\) remains zero for all temperatures below \(T_m\), i.e. well into the ordered state (the small shift of approximately 1 J mol\(^{-1}\) T\(^{-1}\) we attribute to the absolute measurement error). In the magnetically ordered state of the RuSr\(_2\)GdCu\(_2\)O\(_8\) sample, at temperatures sufficiently close to \(T_m\), the \(M_T\) increases significantly at low fields and forms the maximum centred at approximately 8 kOe (note the isotherms at \(T = 137\) K and at the neighbouring 130.9 and 134.8 K). In the paramagnetic state, the \(M_T\) equals zero at the zero field and approximately obeys the expected linear field dependence. For the characteristic behaviour of the \(M_T(B)\) observed in RuSr\(_2\)GdCu\(_2\)O\(_8\) close to \(T_m\), we note that at the phase transition the \(M_T\) should follow thermodynamic scaling: \(M_T \approx A_m b^{-\omega}\), where \(b = \frac{B}{R_C}\) is the reduced magnetic field and \(A_m\) is the critical amplitude. It was shown in [35] that the critical exponent \(\omega\) should assume comparatively high values, with \(\omega = 0.4 \pm 0.1\) found for several universality classes, in particular \(\omega = 0.39\) for the 3D XY system. Thus, the \(M_T\) would diverge rather fast at zero magnetic field. The maximum in \(M_T(B)\) observed close to \(T_m\) (see figure 8) indicates that the ordering acquires ferromagnetic character at comparatively low magnetic fields. However, within the accuracy of our measurements, no spontaneous ferromagnetic order is revealed at zero field. The isothermal magnetocaloric coefficient measured in analogous experiments for the ferromagnetic UCuP\(_2\) [35] and antiferromagnetic UNi\(_{0.5}\)Sb\(_2\) [36] may be referenced for possible comparison. We also conclude that in the investigated range of magnetic fields and temperatures we did not identify the regime in which the system becomes less ordered as a result of an application of the magnetic field. The presence of the magnetic domains and randomly aligned crystallites in the polycrystalline specimens of an anisotropic magnetic compound may also contribute to the rounded character of the observed maximum. The \(M_T(B)\) dependences for the RuSr\(_2\)Gd\(_{0.9}\)Ce\(_{0.1}\)Cu\(_2\)O\(_8\) sample (figures 8 and 9) are different in the sense that there is no maximum formed at low magnetic fields at temperatures which are close to the expected magnetic transition temperature. Note that the specific heat for this sample, instead of forming a sharp feature at \(T_m\), shows only a gradually changing slope with onset at 150 K (see inset to figure 4). Both indicate a pronounced disorder in the magnetic spin system of RuSr\(_2\)Gd\(_{0.9}\)Ce\(_{0.1}\)Cu\(_2\)O\(_8\). What seems common for all the \(M_T(B)\) dependences, also measured below \(T_m\), i.e. in the magnetically ordered state, is the lack of saturation of \(M_T(B)\) in the magnetic field. We may conclude that it reflects the significant paramagnetic contribution to

**Figure 8.** Magnetic field dependences of isothermal magnetocaloric coefficient for: (a) RuSr\(_2\)GdCu\(_2\)O\(_8\) and (b) RuSr\(_2\)Gd\(_{0.9}\)Ce\(_{0.1}\)Cu\(_2\)O\(_8\) measured at different temperatures above \(T_m\): 1) \(T = 230.9\) K (magenta in colour), 2) 200.6 K (red in colour), 3) 170.3 K (green in colour), 4) 150.0 K (blue in colour) and 5) 137.0 K (black in colour). Dashed line dependences for RuSr\(_2\)GdCu\(_2\)O\(_8\) correspond to 138.9 K (upper) and 134.8 K (lower), which neighbour the dependence at 137 K, for which highest maximum at low fields was found.

**Figure 9.** Magnetic field dependences of isothermal magnetocaloric coefficient for: (a) RuSr\(_2\)GdCu\(_2\)O\(_8\) and (b) RuSr\(_2\)Gd\(_{0.9}\)Ce\(_{0.1}\)Cu\(_2\)O\(_8\) measured at different temperatures at 137 K and below \(T_m\): 1) \(T = 137.0\) K (magenta in colour), 2) 130.9 K (red in colour), 3) 124.8 K (green in colour) and 4) 89.8 K (blue in colour).
the system magnetic entropy, most probably originating in the subsystem of the Gd magnetic moments, which alone remains paramagnetic down to 2.5 K [5]. Due to the degraded sensitivity of our $M_T (B)$ measurements at lower temperatures, we only present the results above 90 K. We do, however, note that for the RuSr$_2$GdCu$_2$O$_8$ the $M_T$ at the lowest accessed temperature of 20 K did not change to a negative at the low field as would be expected for a reflecting bulk superconducting phase [37]. Instead, the $M_T (B)$ dependences at 20 K were found similar for both the $\alpha = 0$ and 0.7 samples.

Figure 10 presents the magnetic field dependences of the magnetoresistivity measured for Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ at several temperatures below and above $T_m$. The dependences become linear in the magnetic field at $T_m$, which becomes the magnetic field induced at higher temperatures. Positive magnetoresistivity emerges at temperatures considerably lower than $T_m$ and only at low magnetic fields, for the higher fields assuming the same linear field dependence. Such behaviour may be explained with the use of two components which are simultaneously contributing to the scattering: firstly, the ferromagnetic component which is field-induced in a broad range of temperatures, also well above $T_m$, and the positive antiferromagnetic contribution which becomes dominant only at temperatures considerably lower than $T_m$ and at low magnetic fields. The additional effect of anomalously lowered resistivity observed in the temperature vicinity of the onset of the superconducting transition for intermediate fields of approximately 1 T (see the isotherm at 50 K in figure 10) is commented on$^2$.

Most of the models of the magnetic ordering in the Ru sublattice were formulated for the experimental data collected for the polycrystalline samples, for which it is difficult to account for the expected anisotropy of the magnetic system. It is then worth mentioning the recent analysis of the magnetization data for epitaxial thin films of RuSr$_2$GdCu$_2$O$_8$, in which the ferromagnetic component of ordering was considered to form cluster type domains out of planar components of the Ru moments, proposed there to couple within $a$–$b$ planes with weak and long range dipolar interactions [38]. The model was essentially meant for reflecting on the experimentally suggested frustrated magnetic ground state and for the presence of the magnetic-field-induced ferromagnetism in the $a$–$b$ plane of the investigated films. Since our measurements of the isothermal magnetocaloric coefficient indicate the absence of spontaneous ferromagnetism, this would match the conclusion$^2$.

We associate this anomaly with the negative contribution to magnetoresistivity induced by the superconducting phase. The effect may be approached with the use of two components which are simultaneously contributing to the scattering: firstly, the ferromagnetic component which is field-induced in a broad range of temperatures, also well above $T_m$, and the positive antiferromagnetic contribution which becomes dominant only at temperatures considerably lower than $T_m$ and at low magnetic fields. The additional effect of anomalously lowered resistivity observed in the temperature vicinity of the onset of the superconducting transition for intermediate fields of approximately 1 T (see the isotherm at 50 K in figure 10) is commented on$^2$.

Figure 10. Magnetic field dependences of magnetoresistivity for Ru$_{0.98}$Sr$_2$GdCu$_2$O$_8$ (sample B) at different temperatures above (a) and below (b) $T_m$. Temperatures for (a): 1) 140 K (blue in colour), 2) 130 K (purple in colour), 3) 120 K (dark blue in colour), 4) 100 K (green in colour), 5) 60 K (red in colour) and 6) 50 K (black in colour). Temperatures for (b): 1) 300 K (red in colour), 2) 250 K (black in colour), 3) 200 K (green in colour), 4) 170 K (dark blue in colour), 5) 150 K (purple in colour) and 6) 140 K (blue in colour).
probing thermodynamics of the multi-component magnetic system there is a possibility of accessing induced magnetic polarization effects, for RuSr$_2$GdCu$_2$O$_8$ in the sublattice of large Gd magnetic moments. Our $M_T$ measurements, while indicating the dominance of ferromagnetic type correlations, and not the spontaneous long range ferromagnetism, may then not rule out the antiferromagnetic background in the Ru sublattice. To further comment on the possible multi-component nature of the magnetic system in RuSr$_2$GdCu$_2$O$_8$ one should note a different character for the two shown Ru ions. It seems then the contribution of polarized band effects may also be considered when approaching the magnetic-field-dependent magnetism of the samples. 

In conclusion, the measurements of the isothermal magnetocaloric effect have been communicated for a broad range of magnetic fields and applied magnetic fields up to 13 T in the magnetically ordered and paramagnetic states of RuSr$_2$GdCu$_2$O$_8$ and RuSr$_2$Gd$_{0.9}$Ce$_{0.1}$Cu$_2$O$_8$. The results show no gain in the system’s magnetic entropy in the investigated range of magnetic fields and temperatures, indicating a dominant ferromagnetic character of the accessed magnetic interactions. Simultaneously, no spontaneous ferromagnetic order was shown in the $M_T$ data in favour of the magnetic-field-induced net ferromagnetism. The specific heat data reveal that the anomaly associated with the magnetic transition in the Ru spin system shifts to higher temperatures with an increasing field. The $M_T(B)$ and magnetoresistivity in the broad range of temperatures seems to also be consistent with the response of the inhomogeneous magnetic system with more disorder present for the Ce-doped ruthenocuprate. The superconducting transition temperature for Ru$_{99.8}$Sr$_2$GdCu$_2$O$_8$ is found to be higher compared to that of the nominally stoichiometric sample. However, no bulk superconductivity could be proved in the specific heat data.

Acknowledgments

PKW expresses gratitude to Dr Russ Cook of the Materials Science Division of Argonne National Laboratory for the electron microscopy analysis of several samples investigated within NSF grant DMR-0105398, the SEM pictures of one of which are included in figure 3. The ac susceptibility measurements were performed at the University of Zürich and the author thanks Professor Hugo Keller at that university for his hospitality. The research was financed by the Polish Ministry of Science and Higher Education research project funding for the years 2007–2010.

References

[1] Bauernfeind L, Widder W and Braun H F 1995 Physica C 254 15
[2] Felner I, Asaf U, Levi Y and Millo O 1997 Phys. Rev. B 55 R3374
[3] Bernhard C, Tallon J L, Niedermayer Ch, Blasius Th, Golnik A, Bruecher E, Kremer R K, Noakes D R, Stronach C E and Ansaldo E J 1999 Phys. Rev. B 59 14099
[4] Shengelaya A, Khasanov R, Eshchenko D G, Felner I, Asaf U, Savić I M, Keller H and Müller K A 2004 Phys. Rev. B 69 024517
[5] Lynn J W, Keimer B, Ulrich C, Bernhard Ch and Tallon J L 2000 Phys. Rev. B 61 R14964
[6] Jorgensen J D, Chihasseim O, Shaked H, Short S, Kammlut P W, Dabrowski B and Tallon J L 2001 Phys. Rev. B 63 54440
[7] Nakamura K and Freeman A J 2002 Phys. Rev. B 66 140405
[8] Lebedev O I, Van Tendeloo G, Attfield J P and Mclaughlin A C 2006 Phys. Rev. B 73 224524
[9] Yokosawa T, Awana V P S, Kimoto K, Takayama-Muromachi E, Karppinen M, Yamauchi H and Matsui Y 2004 Ultramicroscopy 98 283
[10] Lorenz B, Xue Y Y and Chu C W 2004 Studies of High-Temperature Superconductors vol 46, ed A V Narlikar (New York: Nova Science)
[11] Braun H, Bauernfeind L, Kort O and Papageorgiou T P 2002 Ruthenate and Rutheno-Cuprate Materials Unconventional Superconductivity, Magnetism and Quantum Phase Transitions (Springer Lecture Notes in Physics vol 603) ed C Noce, A Vecchione, M Cuoco and A Romano (Berlin: Springer)
[12] Awana V P S, Karppinen M and Yamauchi H 2004 Studies of High-Temperature Superconductors vol 46, ed A V Narlikar (New York: Nova Science)
[13] Felner I 2004 Studies of High-Temperature Superconductors vol 46, ed A V Narlikar (New York: Nova Science)
[14] Nachtrab T, Bernhard Ch, Lin C T, Koelle D and Kleiner R 2006 C. R. Physique 7 6
[15] Klamut P W 2008 Supercond. Sci. Technol. 21 093001
[16] McLaughlin A C, Zhou W, Attfield J P, Fitch A N and Tallon J L 1999 Phys. Rev. B 60 7512
[17] Chihasseim O, Jorgensen J D, Shaked H, Dollar P and Tallon J L 2000 Phys. Rev. B 61 6401
[18] Martinelli A, Artini C, Cimberle M R, Costa G A, Ferretti M, Masini R and Mele P 2004 Phys. Rev. B 69 052052
[19] Lin C T, Liang B, Ulrich C and Bernhard C 2001 Physica C 364 373
[20] Felner I, Asaf U, Reich S and Tsabba Y 1999 Physica C 313 163
[21] Zhigadlo N D, Odier P, Marty J Ch, Bordet P and Sulpic A 2003 Physica C 387 347
[22] Tokunaga Y, Kogetawa H, Ishida K, Katoaka Y, Takagiwa H and Akimitsu J 2001 Phys. Rev. Lett. 86 5767
[23] Liu R S, Jang L-Y, Hung H-H and Tallon J L 2001 Phys. Rev. B 63 212507
[24] Klamut P W, Dabrowski B, Maïs J and Maxwell M 2001 Physica C 350 24
[25] McCrone J E, Tallon J L, Cooper J R, McLaughlin A C, Attfield J P and Bernhard C 2003 Phys. Rev. B 68 064514
[26] Sader E, Matveev A T and Habermeier H-U 2006 Supercond. Sci. Technol. 19 L29
[27] Chang B C, Yang C Y, Ku H C, Tsai C B, Chen Y Y and Ling D C 2007 arXiv:cond-mat/0702040
[28] Papageorgiou T P, Casini E, Braun H F, Herrmannsdörfer T, Bianchi A D and Wosnitza J 2006 Eur. Phys. J. B 52 383
[29] Plackowski T, Wang Y and Junod A 2002 Rev. Sci. Instrum. 73 2755
[30] Casini E, Papageorgiou T P, Herrmannsdörfer T, Wosnitza J and Braun H F 2007 Physica C 460–462 401
[31] Galstyan E, Xue Y, Illiev M, Sun Y and Chu C-W 2007 Phys. Rev. B 76 014501
[32] Williams G V M, Lee H K and Krümer S 2003 Phys. Rev. B 67 104514
[33] Hassen A and Mandal P 2006 Supercond. Sciotechnol 19 902
[34] Liu C-J, Sheu C-S, Wu T-W, Huang L-C, Hsu F H, Yang H D, Williams G V M and Liu Chia-Jung C 2005 Phys. Rev. B 71 014502
[35] Plackowski T and Kaczorowski D 2005 Phys. Rev. B 72 224407
[36] Plackowski T, Kaczorowski D and Bukowski Z 2005 Phys. Rev. B 72 184418
[37] Plackowski T, Wang Y, Lortz R, Junod A and Wolf Th 2005 J. Phys.: Condens. Matter 17 6871
[38] Lu W Q, Yamamoto Y, Itaka K, Petrykin V V, Kakihana M, Matsumoto Y, Hasegava T and Koinuma H 2006 Phys. Rev. B 74 092402
[39] Han Z H, Budnick J I, Hines W A, Klamut P W, Maxwell M and Dabrowski B 2006 J. Magn. Magn. Mater. 299 338
[40] Nachtrab T, Koelle D and Kleiner R 2004 Phys. Rev. Lett. 92 117001
[41] Klamut P W and Plackowski T, in preparation