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The Superconducting and Magnetic States in $RuSr_2GdCu_2O_8$, Based on the Magnetic, Transport and Magneto-Caloric Characteristics

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The article discusses selected properties of the non- and superconducting polycrystalline samples of $RuSr_2GdCu_2O_8$ and comments on the consequences of introducing insignificant sub-stoichiometry of Ru into the nominal formula. The magneto-resistive and the magnetic characteristics are interpreted in favour of the formation of intrinsically inhomogeneous superconducting phase, which seems stabilized along with the structural modifications enhanced with the modification of starting stoichiometry. The specific heat data reveals the small shift of the temperature of magnetic ordering T_m, which may suggest dilution of the magnetic sublattice of the Ru moments. The measurements of the magnetic field dependences of the isothermal magnetocaloric coefficient M_T reveal no gain in the system magnetic entropy in a broad range of accessed fields and temperature. Whereas the multi-component character of the compound's magnetsm precludes from concluding on the magnetic ground state, the maximum in $M_T(H)$, which occurs at comparably weak magnetic field for temperatures in a vicinity of T_m may reflect dominance of the ferromagnetic type interactions with a constrained correlation range. The literature explored models for the Ru magnetic ordering and also possible phase separation are brought into the discussion.

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1. Introduction

Ruthenate-cuprates form a separate class in the family of complex copper oxides, which is distinguished by the magnetically active sublattice of Ru built of the Ru–O structural layers. There have been few types of the ruthenate-cuprate crystal structures identified, which contain structural blocks characteristic for the HTSC cuprates and differ by the length of their unit cells. Manifold properties of these compounds were covered in numerous reports, also in several review texts, which are complementary for emphasising different aspects of the field ([1–6] and the references therein). The so called 1212-type structure of $RuSr_2GdCu_2O_8$ resembles that of $REBa_2Cu_3O_7$ (RE = rare earth) superconductor, in which the so-called chain positions of Cu ions are replaced with Ru in then full octahedral coordination with oxygens. The Sr alkaline earth metal assumes analogous structural positions to Ba in the $REBa_2Cu_3O_7$. The 1212-type M-cuprates were reported with several transition metal ions M = Ru, Cr, Ir, and several RE elements [7]. The magnetic ordering in the Ru sublattice in $RuSr_2GdCu_2O_8$ extends up to $T_m \approx 135$ K whereas the paramagnetic sublattice of Gd^{3+} ions orders antiferromagnetically (AFM) below 2.5 K [8]. Since $RuSr_2GdCu_2O_8$ was reported superconducting with T_c as high as approximately 50 K, it became interesting to investigate for the simultaneous accommodation and/or mutual influence of the superconducting order parameter and the Ru magnetism. In the temperature range below T_m, the field dependences of the dc magnetisation become hysteretic resembling the behaviour of magnetisation characteristic for a weak ferromagnet. The temperature dependence of the internal field associated with the Ru ordered state below T_m was established in zero field muon spin rotation (μSR) measurements, with no change in the internal field values detected upon entering temperature range of the superconducting phase at low temperatures [9].

The magnetic ground state of the Ru sublattice in $RuSr_2GdCu_2O_8$ was approached with several different models, which are based in several different experiments. Due to lack of suitable single crystals, most of these were based in investigation of the properties of sintered polycrystalline samples, which for some experiments contributes complexity to their interpretation. Early neutron powder diffraction (NPD) [8, 10, 11] conclude the G-type antiferromagnetic order of Ru with easy axis along the c direction and associated ferromagnetic build-up of the diffractive maxima to possible effect of the field dependent canting of the Ru^{5+} magnetic moments [11].

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The field dependent magnetic diffraction analyzed in the following Gd^{160} NPD experiment for assuming the above, pointed to necessity of rather fast increase of the canting angle, with more than 75° at the magnetic field values above 1.5 T [12]. Measurements of the zero-field and field dependent Ru-NMR spectra provided arguments for the type-I AFM ground state in the Ru sublattice. The observed field dependences of the resonance frequencies led to propose the model structure built of the ferromagnetic *a*–*b* planes, with expectance of the field induced spin flop transition to ferromagnetism involving the in-plane components of the magnetisation, likely to occur also in view of expected substantial magnetic anisotropy of the Ru magnetic lattice [13]. Several experiments evidenced presence of the Ru^{5+} and Ru^{4+} valence states in $RuSr_2GdCu_2O_8$, [13–16]. Recently communicated investigation of the magnetic ground state by means of the resonant X-ray diffraction with data collected for the small single crystal of superconducting $RuSr_2GdCu_2O_8$, has reconciled some of the previous hypotheses with an observation of the *G*-type structure with the Ru magnetic moments pointing along the low symmetry direction, and with the ferromagnetic in-plane components proposed to align antiparallely in the adjacent Ru-O layers [17]. Last not the least, we note the analyses of the temperature and the field dependencies of several macroscopic characteristics of the superconducting and magnetic phases in the ceramic samples of $RuSr_2RECu_2O_8$ (RE = Gd, Eu) which led to postulate the material inherent spatial phase separation in form of an ensemble of antiferromagnetic/superconducting and ferromagnetic/non-superconducting domains to be present within single crystallites [1].

2. Results and discussion

The superconducting samples of $RuSr_2GdCu_2O_8$ were reported with wide spread of T_c and with the maximum onset temperature for the transition at 52–55 K [18, 19], the latter found also characteristic for the first reported single crystals. Nominally same stoichiometric $RuSr_2GdCu_2O_8$ was, however, also found non-superconducting [19–21]. Figure 1, after [21], shows the temperature dependences of the ac susceptibility collected for three ceramic samples of the $RuSr_2GdCu_2O_8$, two of which (*B* and *C*) were obtained through additional annealing (1060 ℃ in oxygen) of the initially non-superconducting compound (*A*). The difference between samples *B* and *C* is in slow vs. fast cooling, i.e. the annealing converted the material superconducting (sample *B*) and its diamagnetic shielding was secured only for the slow cooled (sample *C*). The non-superconducting sample *A* was synthesised in the solid state reaction performed at 935 ℃ in flow of $1\%O_2/Ar$ (Ar balance gas), i.e. at substantially lower temperature than 1050–1060 ℃ required for synthesis of that phase in flowing oxygen. Modified conditions were based in finding of the approximately 20 K wide plateau in the mass–temperature thermogravimetric (TGA) data collected at $1\%O_2/Ar$, which indicated the range of thermodynamical stability for the 1212-type phase. Neither the phase purity of these samples (single phase powder X-ray diffraction (XRD) patterns) nor their overall oxygen content, were found distinguishable. The temperature dependences of the crystal lattice parameters for the non-superconducting sample *A* and the superconducting sample *B* were accessed in the synchrotron X-ray diffraction experiment [11], which revealed insignificant decrease of the Cu–O2 distance and larger increase of the Cu–O3 distance in the superconducting material, with latter difference being more evident below the temperature of magnetic ordering of the Ru sublattice ($T_m \approx$ 133–136 K). The O3 refers here to the bridging position of the oxygen atom in between the Ru and Cu (i.e. the apical for the RuO_6 and for the CuO_5 pyramid) and the O2 refers to the oxygen atoms in the CuO_2 plane (the Cu–O2–Cu angle was established in that experiment at approximately 168.6°–169.1° for both the NSC and SC samples). The differences translated to a slightly larger c/a ratio for the superconducting sample (3.0145 vs. 3.0163 at 10 K) which, what is interesting, was found to increase at temperature close to T_m for both samples. The Williamson–Hall plots constructed for the $(hk0)$ and $(00l)$ synchrotron XRD reflections showed a difference in the slope, indicating a higher degree of the lattice strain in the non-superconducting compound [11].

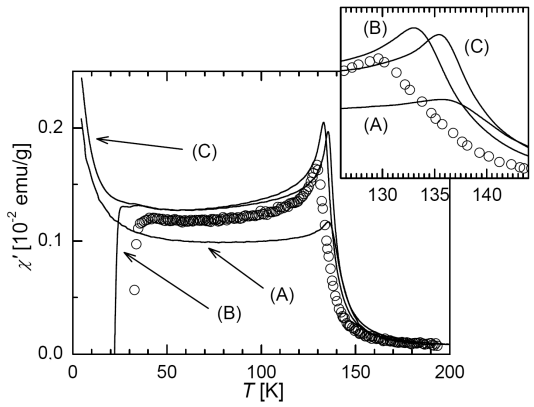

Fig. 1. Temperature dependences of the real component of the ac susceptibility (H_{ac} = 1 Oe, f = 200 Hz) for three samples obtained from the initially non-superconducting (NSC) $RuSr_2GdCu_2O_8$: $(A) \rightarrow (B) \rightarrow (C)$ represents the sequence of annealing: (*A*) as grown in $1\%O_2/Ar$ at 935 ℃, (*B*) after subsequent annealing at 1060 ℃ in O_2 for 140 h with slow cooling, (*C*) same to *B* but quenched from O_2/1060 ℃. Open circles: sample obtained afer annealing of the NSC $RuSr_2GdCu_2O_8$ in 600 bar of oxygen at 1100 ℃, slow cooled (after [21]). Inset shows the susceptibility maxima associated with the magnetic transition at T_m in expanded scale.

In Ref. [22] we comment more extensively on the synthesis of the two samples with slightly altered nominal

stoichiometry, $RuSr_2GdCu_2O_8$ and $Ru_{0.98}Sr_2GdCu_2O_8$, whose selected properties also are discussed here. The approach was to modify the nominal formula of one of the to be compared samples by introducing slight deficiency of Ru, and for assuring the same reaction conditions during their simultaneous synthesis, to end up with the materials which properties may be compared in investigation for results of probable modification of the phase. This acquires additional context in the reported studies of local crystal structure of the superconducting sample of $RuSr_2GdCu_2O_8$ by means of the high resolution electron microscopy [23]. The found alternations of the local structure led there to suggestion that the superconducting phase may originate within the nanometre range domains distinguished by doubled c axis parameter for replacing every second Ru-O layer with the Cu-O layer, which would resemble the so called Cu-O chain layers in related structure of $YBa_2Cu_3O_7$.

The solid state synthesis of two here considered samples was done in flowing oxygen at 1060 ℃, which corresponds to the conditions often reported for synthesis of $RuSr_2GdCu_2O_8$, albeit which are close to the melting point for the phase. Even the final reaction was performed out of the mixture of preformed precursors (in the intermediate step previously calcined substrates were reacted to the mixture of Sr_2RuGdO_6 and the rest oxides, predominantly Cu_2O), the final reaction may be affected by a rather high sublimation rate of Ru characteristic for the Ru rich oxides at high temperature oxidative conditions, which treatment in turn appears required for final result of the XRD single-phase and superconducting sample. The samples then may be set vulnerable to local modifications of their stoichiometry with candidate Ru/Cu sites in the 1212-type phase. The structural modifications may occur preferentially in the micro-regions of slightly altered stoichiometry, also for the nominally stoichiometric material, even associating with trace melting for larger local off-stoichiometries [20, 22]. The compared samples were simultaneously slowly cooled at the rate 1 ℃/min, which is comparable to the cooling rate of separately prepared sample B (Fig. 1). The influence of rate of cooling, which appears to determine the diamagnetic shielding is still difficult to interpret. It would be intuitive to associate it with the uptake of oxygen along the superconducting paths in the material, there is however a possibility of structural ordering processes which were not verified experimentally. Interestingly, the Tm seems also be affected in the process (see inset to Fig.1). We note that recent investigation of the synthesis associated sublimation processes suggests developing even macroscopic inhomogeneity of the Ru content in the bulk vs. surface of the ceramic sample of $RuSr_2GdCu_2O_8$ [24] (extensive commentary on the synthesis issues for ruthenocuprates was presented by this group in [2, 25]). In our comparative study, by including the sample with subtle modified nominal stoichiometry, we set an alternative approach, aiming at induced differences in the material properties when promoting different extent of the processes associated with expected Ru/Cu off-stoichiometry.

Figure 2 presents the magnetic field dependences of the temperatures, which were chosen characteristic for the superconducting transitions in the $RuSr_2GdCu_2O_8$ and $Ru_{0.98}Sr_2GdCu_2O_8$ samples, and compares them to analogous temperatures read of the resistivity-temperature dependence of the $Ru_{0.5}Sr_2GdCu_{2.5}O_{8-d}$. The latter, which is structurally related superconductor has higher maximal T_c and shows no signatures of the Ru magnetism in its then paramagnetic normal state [26, 21]. These characteristics were more extensively discussed in [27] also for the observed anomalous field induced increase of conductivity in the temperature range directly preceding the superconducting transition - which we linked to complex response of the constrained dimensionality superconducting phase in presence of the field dependent compound's magnetism (see also Ref. [28]). Figure 3 presents the corresponding temperature dependences of the ac susceptibility measured at two small amplitudes of the ac field — 1 Oe and 0.1 Oe. The increase of T_c observed in the $Ru_{0.98}Sr_2GdCu_2O_8$ comparing to in the $RuSr_2GdCu_2O_8$ (Figs. 2 and 3) may suggest modification of effective charge doping in the superconducting phase, which is common for shifting T_c in superconducting cuprates. It is, however, of other noted differences, as is the different slope of the magnetic field dependence of T_c^{on} (Fig. 2) and shift of the magnetically measured onset of the transition in response to changing amplitude of the ac field for its limiting small values (Fig. 3), that the superconducting phase appears rather as spatially confined with the characteristic length scale of order of the magnetic penetration depth λ. It would then seem intuitive that the phase may develop along with these structural modifications, which associate or reflect from the nominally decreased Ru/Cu ratio. Such scenario would accommodate also differently prepared not superconducting samples of $RuSr_2GdCu_2O_8$, and may link to the superconductivity of related $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-d}$ ($T_{c,max} = 72$ K for the $x = 0.5$, oxygen annealed phase), which for larger x were stabilised in course of the high pressure annealing [26]. The moderate increase of the superconducting T_c was also observed in the nominal $Ru_{0.9}Sr_2GdCu_{2.1}O_8$ vs. $RuSr_2GdCu_2O_8$ samples [29], together with the effect of an increase of T_c for the prolonged time of annealing in oxygen.

Beyond in the ceramic $RuSr_2GdCu_2O_8$, an issue of the intrinsic spatial homogeneity of its superconducting phase was accessed in the experiments performed on single crystal [30], which evidenced presence of the Josephson type coupling along the c axis, so and the effectively layered structure built of interlaced SC–I–SC slabs. No peculiar features in the I–V characteristics measured in that experiment were found to be associated with presence of the Ru magnetism. The qualitatively similar Josephson characteristics were observed also for several other charge underdoped HTSC cuprates of sufficiently large structural anisotropy (Bi-2212, Tl-2223 [31], and

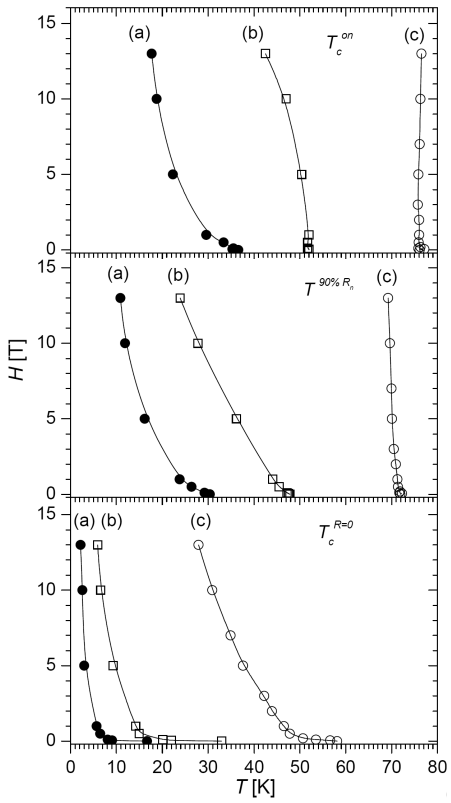

Fig. 2. The magnetic field dependences of the temperatures characteristic for the resistive superconducting transitions in the samples: (*a*) $RuSr_2GdCu_2O_8$, (*b*) $Ru_{0.98}Sr_2GdCu_2O_8$ and (*c*) $Ru_{0.5}Sr_2GdCu_{2.5}O_{8-d}$ (oxygen annealed for small d). Upper part: T_c^{on} — temperature of the onset of transition, middle part: $T_c^{R=0}$ — uppermost temperature of the zero resistivity state, lower part: $T^{90\%Rn}$ — temperature corresponding to the 10% decrease of resistivity relative to its value at T_c^{on}.

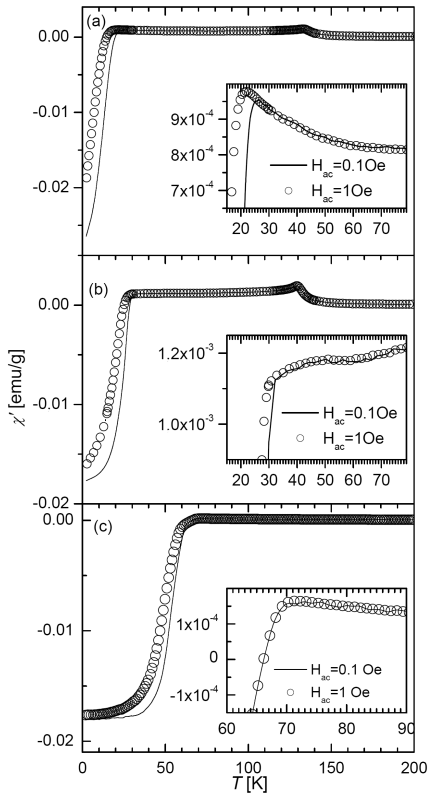

Fig. 3. Temperature dependences of the real component of the ac susceptibility for (a) $RuSr_2GdCu_2O_8$, (b) $Ru_{0.98}Sr_2GdCu_2O_8$, (c) $Ru_{0.5}Sr_2GdCu_{2.5}O_{8-d}$ samples. $f = 1$ kHz.

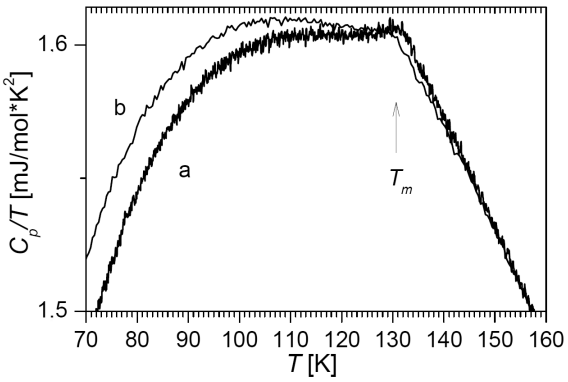

Fig. 4. Plot of C_p/T vs. T for (*a*) the $RuSr_2GdCu_2O_8$ and (*b*) $Ru_{0.98}Sr_2GdCu_2O_8$ sample. Let us note slight shift of the characteristic temperature associated with T_m.

therein) so that the feature remains nonspecific to the ruthenocuprate in the HTSC family [30]. It should be noted that for the single crystals similar to those communicated in [30] and [32], the resonant X-ray diffraction yet concluded [17] presence of the ferromagnetic component along the RuO_2 layers, which is essentially in agreement with the model proposed in result of earlier NMR studies [13]. What may turn relevant from perspective of eventual presence of the local alternations in the 1212-type structure, all of the so far investigated crystals show comparatively high values of the superconducting $T_c \approx 45$–60 K and substantially lowered temperature of the Ru magnetic transition $T_m = 102$ K was inferred from the temperature dependence of the intensities of two resonant XRD magnetic reflections as well as from the dc magnetisation data [17]. The upturn of the magnetic susceptibility found for this crystal at approximately 40 K above such established Tm was then proposed to originate in presence of non-compensated ferromagnetic moments, which may appear at local structural modifications in consequence of substantial magnetic anisotropy of the magnetic lattice of Ru moments. One may comment that such an increase could also result from presence of lower dimensional magnetic correlations in a whole structure, preceding the bulk transition. Possibly modified distribution of the Cu, Ru or O ions in the crystal in respect to the polycrystalline materials was brought in [17] for a likely reason of the

observed difference in T_m. It may be commented after [2] that for such crystal grown at equilibrium of the liquid and solid phases the homogeneity range may become restricted in result of the temperature dependence of the process, so and the crystal may turn be not homogeneous, perhaps leaving superiority to polycrystalline materials. Figure 4 presents the temperature dependences of the specific heat measured for the considered samples $Ru_{0.98}Sr_2GdCu_2O_8$ and $RuSr_2GdCu_2O_8$, after [6]. Notice the small shift of T_m toward lower temperatures for the $Ru_{0.98}Sr_2GdCu_2O_8$. The same was observed in the ac susceptibility data (Fig. 1), the specific heat, however, proves bulk character of the feature.

Figure 5 presents the magnetic field dependence of T_m as derived from the specific heat-temperature dependences collected for the $RuSr_2GdCu_2O_8$ sample, compared with the field dependencies of the onset temperatures of magnetically ordered state which are inferred from the magneto-resistivity data for the $Ru_{0.98}Sr_2GdCu_2O_8$ and $RuSr_2GdCu_2O_8$ samples. These temperatures correspond to initial extra increase of the conductivity, which always signals the Ru magnetic ordering, by itself interesting for associating the magnetic order with a conduction channel in the Ru sublattice. Despite rather large temperature error (dotted lines) coming with such determination of T_m from transport data, note that sufficient agreement holds between such determined and the $C_p(T)$ determined characteristic temperatures, which suggests bulk character of the feature accessed in the transport measurement.

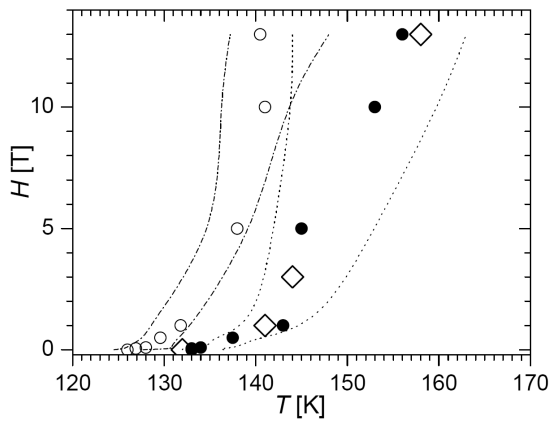

Fig. 5. The magnetic field dependences of the temperatures characteristic for increase of conductivity in a vicinity of T_m measured for simultaneously prepared $RuSr_2GdCu_2O_8$ (closed circles) and $Ru_{0.98}Sr_2GdCu_2O_8$ (open circles). Dotted and dash-dotted lines show estimated uncertainty of determination of these temperatures from the $\rho(T)$ data. Open diamonds show the T_m associated temperatures in $RuSr_2GdCu_2O_8$ as they were determined from the temperature dependences of the specific heat.

It may be noted that since the effect of magnetic field is to increase the T_m, it would be less usual to assume the antiferromagnetic type of interactions as leading to 3D long range order at T_m. Note that a considerable shift of T_m occurs at comparatively small field values — which may suggest substantial magnetic anisotropy of the probed system, in agreement with same assumed for modelling the ground state with AFM-I magnetic structure [13] or in the hyphotesis of progressing the 3D ordering with long range, weak dipolar interactions (formulated in [33] for the related 1222-type structure ruthenate-cuprate). The different slope of the $T_m(H)$ dependencies estimated in Fig. 5 for the $Ru_{0.98}Sr_2GdCu_2O_8$ and $RuSr_2GdCu_2O_8$ samples may result from the nonlinear correspondence between an extent of dilution occurring in the magnetic sublattice of Ru and its effect on the T_m. Last not the least, since in $RuSr_2GdCu_2O_8$ one may deal with itinerant $4d$ electrons on the Ru lattice there is no priori reason for excluding the band polarisation effects (also note similarity in the conductivity response at the magnetic ordering temperatures for the $RuSr_2GdCu_2O_8$ and the $SrRuO_3$ itinerant ferromagnet).

In the following part we will comment the results of the measurements of isothermal magnetocaloric coefficient, M_T, which has an advantage of probing the magnetic state by directly accessing changes of magnetic entropy and which as a thermodynamic measure addresses bulk magnetic features of the samples. Measurements of the M_T were performed in a heat flow calorimetric setup described in [34]. At the conditions of constant temperature and at the constant rate of sweeping magnetic field M_T equals:

$$M_T = \frac{\mathrm{d}q}{\mathrm{d}B} = \frac{-q}{B} = \frac{-U}{AB}\,,$$

where q — heat flux, B — magnetic induction, U — voltage generated by the heat flow meter, A — sensitivity parameter.

The M_T relates to magnetization with the formula

$$M_T = -T\left(\frac{\mathrm{d}M}{\mathrm{d}T}\right)_B .$$

and the measurement accesses changes of magnetic entropy according to the relation:

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

Figure 6 presents the set of the magnetic field dependences of M_T measured for the sample of $RuSr_2GdCu_2O_8$, which properties were commented for the measurements of the ac susceptibility and resistivity. For a simple antiferromagnet, in expectance of the field driven increase of magnetic entropy, one would expect the negative values of the M_T. The $RuSr_2GdCu_2O_8$ compound contains, however, few magnetic sublattices with the sublattice of comparatively large Gd^{3+} magnetic moments ($\mu_{\mathrm{eff}}(Gd^{3+}) = 7 \simeq \mu_B$ [8]), which remains paramagnetic in the entire range of accessed temperatures. Predominant contribution of the Gd^{3+} paramagnetism to M_T is seen (Fig. 6) at temperatures sufficiently above T_m. The maximum of the $M_T(H)$ at approximately 0.5

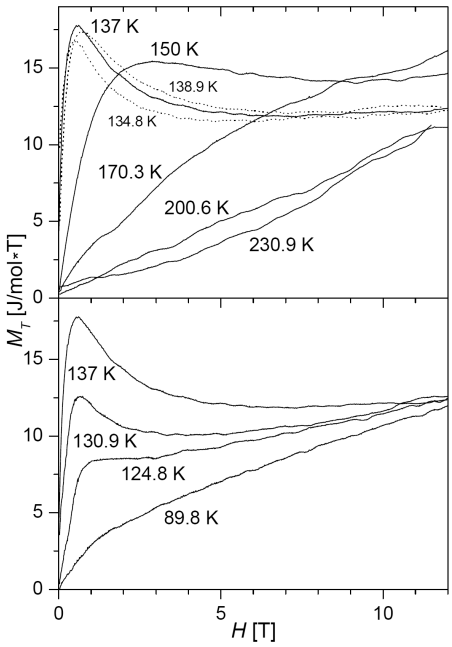

Fig. 6. Magnetic field dependences of the isothermal magneto-caloric coefficient measured for the $RuSr_2GdCu_2O_8$ sample at several temperatures above (upper part) and below (lower part) T_m. The maximal height of the maximum at the field of approximately 0.5 T (note the surrounding dependences collected at 138.9 K and 134.8 K) was found for 137 K, which temperature matches the T_m ($H = 0.5$ T) determined from the specific heat data for this sample (see Fig. 5) [28].

T, which is observed for temperatures in a vicinity of T_m, may suggest presence of ferromagnetic interactions associated with the magnetic ordering set at T_m. The field dependence of the magnetocaloric coefficient at the transition temperature should in principle strongly diverge at zero field [35], so and the maximum observed for the finite field values may suggest no spontaneous long range order in favor of the field induced ferromagnetism. Then, only finite increase of the M_T would signal constrained correlation length of the responsible magnetic interactions. Such conclusions fit into the literature proposed presence of inherent inhomogeneities in the Ru magnetic system [1] as well as for a role of the magnetic field in inducing the long range ferromagnetic state. For further interpretation of the $M_T(H)$ data one should take into account possible polarization effects between the compound's separate magnetic sublattices [36]. It would then seem desirable to extend such measurements also for other rare earth based ruthenate-cuprates, including stabilized at the high pressure conditions $RuSr_2YCu_2O_8$.

3. Summary

The text comments on several characteristics of the superconducting and magnetic transitions in the samples of $RuSr_2GdCu_2O_8$, possibly coupled with postulated for this compound local scale alternations of crystal structure. It would be interesting to elucidate if apparently constrained dimensionality of the superconducting phase in $RuSr_2GdCu_2O_8$ in future studies may meet with sufficient material perfecy to become more relevant for investigation of quasi 2D regime of superconductivity in the underdoped cuprates.

Acknowledgments

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