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High magnetic field study of RuSr$_2$GdCu$_2$O$_8$

T P Papageorgiou$^1$, E Casini$^2$, Y Skourski$^1$, J Freudenberger$^3$, H F Braun$^2$ and J Wosnitza$^3$

$^1$ Hochfeld-Magnetlabor Dresden (HLD), Forschungszentrum Rossendorf, D-01314 Dresden, Germany
$^2$ Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany
$^3$ IFW Dresden, Institute for Metallic Materials, P.O. Box 270116, D-01171 Dresden, Germany

E-mail: T.Papageorgiou@fz-rossendorf.de

Abstract. Magnetization measurements in pulsed magnetic fields up to 47 T have been performed on the magnetic ($T_{M,Ru} \approx 133$ K) RuSr$_2$GdCu$_2$O$_8$ in an attempt to determine the Ru valency in this compound. The Ru ions are most probably in a mixed valence state, but the ratio of Ru$^{5+}$ (S=3/2)/Ru$^{4+}$ (S=1) = 60%/40% suggested by NMR investigations is justified only if one considers the theoretical values of 3 $\mu_B$/Ru$^{5+}$ and 2 $\mu_B$/Ru$^{4+}$. Mixed valency could lead to a competition between ferromagnetic double exchange, evolving Ru$^{4+}$ and Ru$^{5+}$ ions, and antiferromagnetic superexchange, evolving Ru$^{5+}$ ions, leading to magnetic phase separation. We conclude that the magnetic and superconducting properties of the rutheno-cuprates critically depend on the Ru$^{5+}$/Ru$^{4+}$ ratio which can be affected by the preparation conditions.

1. Introduction
RuSr$_2$GdCu$_2$O$_8$ (Ru1212Gd) is a high temperature superconductor ($T_S \approx 50$ K) with a crystal structure similar to the very well known layered structure of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) (see Fig. 1). Apart from superconductivity, Ru1212Gd shows also magnetic order with the Ru and Gd moments ordering magnetically at $T_{M,Ru} \approx 130$ K and $T_{M,Gd} \approx 2.5$ K, respectively. Numerous experimental and theoretical investigations have been carried out for the determination of the magnetic structure and the mechanisms leading to magnetic ordering in an attempt to understand how superconductivity develops in a magnetically ordered state.

In the present study, we investigate the valence state of Ru in Ru1212Gd. NMR investigations [1] suggest that the Ru ions are in a mixed-valence state with a ratio of Ru$^{5+}$ (S=3/2)/Ru$^{4+}$ (S=1) = 60%/40%. This corresponds to an average Ru moment as high as 2.6 $\mu_B$, if one considers the theoretical values of 3 $\mu_B$/Ru$^{5+}$ and 2 $\mu_B$/Ru$^{4+}$. Nevertheless, reduced values of about 2 $\mu_B$/Ru$^{5+}$ and 0.9 $\mu_B$/Ru$^{4+}$ were estimated using NMR [1]. Magnetization measurements so far were limited to static magnetic fields below 10 T. As we will see, in this field range the Ru contribution to the measured magnetic moment does not exceed 1.15 $\mu_B$. This would be consistent with neutron diffraction (ND) studies [2] that indicate a G-type antiferromagnetic structure for the Ru moments with neighboring spins antiparallel in all three crystallographic directions and a magnetic moment per Ru atom of about 1.18 $\mu_B$. The lack of saturation of the measured magnetic moment though, indicates that measurements in even higher magnetic fields are required in order to clarify the validity of the scenarios described above. Here, we present magnetization measurements of Ru1212Gd in pulsed magnetic fields up to about 47 T.
Figure 1. Comparison of the crystal structures of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) (left-hand side), RuSr$_2$GdCu$_2$O$_8$ (Ru1212Gd) (middle) and RuSr$_2$(Ln,Ce)$_2$Cu$_2$O$_{10}$ (Ru1222) (right-hand side).

2. Experimental
The polycrystalline Ru1212Gd sample was prepared using a two-step method. First the compound Sr$_2$GdRuO$_6$ (Sr2116) was prepared by firing a stoichiometric mixture of SrCO$_3$, Gd$_2$O$_3$ and RuO$_2$ at 1250°C in air. Sr2116 was then mixed with CuO and the mixture was calcined for 120 h at 1060°C in flowing oxygen. X-ray powder diffraction investigations indicated that the sample was single phase. Details about the sample preparation and characterization can be found elsewhere [3].

dc-magnetization measurements in static magnetic fields up to 10 T were performed in a Quantum Design physical properties measurement system (PPMS). A SQUID magnetometer of the same manufacturer was utilized for the ac-susceptibility measurements. Magnetization measurements in pulsed fields up to 47 T were performed at IFW Dresden (Institute for Metallic Materials). The facility and the experimental setup have been described in previous works [4, 5].

3. Results and discussion

Figure 2. The real part $\chi'$ of the ac-susceptibility of Ru1212Gd measured with an excitation field $H_{ac} = 3.9$ Oe and frequency $f \approx 22$ Hz. The temperatures of the intra- and intergranular superconducting transitions are marked with $T_{\text{intra}}$ and $T_{\text{inter}}$, respectively.

The magnetic and superconducting properties of the prepared Ru1212Gd sample were investigated using ac-susceptibility measurements which are shown in Fig. 2. The magnetic
transition is clearly seen at about 133 K. At low temperatures a shallow decrease of the susceptibility is observed at $T_{\text{intra}} \approx 46$ K followed by a rapid decrease at $T_{\text{inter}} \approx 32$ K. These features are related to the granular nature of the investigated sample. $T_{\text{intra}} = T_S$ corresponds to the intrinsic critical temperature where the grains become superconducting whereas at $T_{\text{inter}}$ superconducting (Josephson) coupling between the grains is established. It should be noted that the magnetic and superconducting properties of Ru1212Gd depend strongly on the preparation conditions and long annealing in oxygen atmosphere is necessary in order to achieve the properties described previously [8]. We conclude that the sample investigated is representative of high quality rutheno-cuprates similar to those investigated previously [1, 2].

Fig. 3 presents measurements in both static ($B < 10$ T) and pulsed ($B \leq 47$ T) magnetic fields at 4.2 K and 48 K. At the highest temperature, well above $T_{M,Gd}$, the Gd contribution to the measured magnetic moment is calculated using the Brillouin function. The subtraction of this contribution from the measurements performed in static magnetic fields gives an average non-saturated Ru moment of about 1.15 $\mu_B$. Nevertheless, this contribution is increased to about 1.9 $\mu_B$ at 47 T in contrast to the predictions of the ND studies. At 4.2 K the Ru contribution is further increased to 2.16 $\mu_B$ assuming a fully saturated Gd moment of 7 $\mu_B$. Our findings indicate a mixed valence state for the Ru ions. The estimated average Ru moment of 2.16 $\mu_B$ is somewhat lower than that expected for a mixture of Ru$^{5+}$(S=3/2)/Ru$^{4+}$(S=1) = 60%/40% and could be explained by the lack of saturation of the measured magnetic moment even at the highest magnetic field.

It should be noted that the above estimate is based on the theoretical values of 3 $\mu_B$/Ru$^{5+}$ and 2 $\mu_B$/Ru$^{4+}$. This is in contrast to the reduced values of 2 $\mu_B$/Ru$^{5+}$ and 0.9 $\mu_B$/Ru$^{4+}$ suggested from NMR investigations [1]. Nevertheless, the mixed valence might be related to holes that are doped via charge transfer from the RuO$_2$ planes into the CuO$_2$ planes. This doping is necessary to reach the superconducting state at low temperatures. Thus the ratio of Ru$^{5+}$/Ru$^{4+}$ is closely related to the hole concentration $p$ in the CuO$_2$ plane. A ratio Ru$^{5+}$/Ru$^{4+} = 60%/40%$ was suggested assuming $p \approx 0.2$ [1]. Investigations of the thermoelectric properties (Seebeck coefficient) of our Ru1212Gd sample are in progress in an attempt to determine the doping level of the CuO$_2$ planes more directly and to solve the above discrepancy.

It is worthwhile to discuss the possible consequences of the mixed valency of the Ru moments on the magnetic properties of Ru1212Gd. It has been suggested [6] that the RuO$_2$ layers are conducting with the charge carriers remaining in the normal state. The transfer of carriers between Ru ions of different valencies could be responsible for ferromagnetic coupling through the double exchange mechanism. It is possible that the magnetic behavior
of Ru1212Gd is governed by a competition between ferromagnetic double exchange evolving Ru$^{4+}$ and Ru$^{5+}$ ions and antiferromagnetic superexchange evolving Ru$^{5+}$ ions. This could justify effects like the rapid decrease of $T_S$ ($\approx 100$ K/T at low fields) reported previously [7] and attributed to phase separation into superconducting antiferromagnetic and non-superconducting ferromagnetic domains. It can also explain the spin glass behavior observed in another family of rutheno-cuprates of the general chemical formula RuSr$_2$(Ln,Ce)$_2$Cu$_2$O$_{10}$ (Ln = Eu, Gd and Sm for synthesis at ambient pressure) where, because of the larger distance between the RuO$_2$ planes (see Fig. 1), magnetic frustration is expected to have more pronounced consequences.

As discussed previously, the preparation conditions play an important role concerning the magnetic and superconducting properties of Ru1212Gd. Different properties have often been related to the microstructure of the investigated samples [8]. Nevertheless, in view of the volatile character of Ru, differences in the Ru$^{5+}$/Ru$^{4+}$ ratio should also be considered. The above discussions indicate that modifications of this ratio could significantly affect the properties of the rutheno-cuprates.

4. Summary

In summary, magnetization measurements of Ru1212Gd in pulsed magnetic fields up to 47 T indicate that the Ru moments in this compound are in a mixed valence state. It is suggested that both the magnetic and superconducting properties of the rutheno-cuprates critically depend on the Ru$^{5+}$/Ru$^{4+}$ ratio in the sample which can be affected by the preparation conditions.

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