Tuning of the superconducting and ferromagnetic transitions by Cu doping for Ru in GdSr₂RuCu₂O₈

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Abstract

In order to explore the possibility of tuning superconducting and ferromagnetic transitions by Cu doping (for Ru) in $GdSr_2RuCu_2O_8$, we have carried out synthesis and characterization of $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ (x = 0, 0.05, 0.1, 0.2) and studied their physical properties. Coexistence of superconductivity and ferromagnetism is observed in all the Cu doped samples studied here. The zero field susceptibility data suggests formation of a spontaneous vortex phase. Cu doping decreases the ferromagnetic Curie temperature, whereas the superconducting transition temperature increases until an optimal concentration x \sim 0.1. This reflects an increase in hole transfer to the CuO₂ planes and reduction of ferromagnetic order within the ruthenate layers.

Keywords: Ruthenocuprates, Magnetic superconductors, Heterovalent substitution

I. INTRODUCTION

Superconductivity (SC) and ferromagnetism (FM) are generally believed to be two mutually antagonistic orders. However, many interesting consequences like coexistence of triplet SC with FM, formation of a spontaneous vortex phase¹, spatially inhomogeneous Fulde-Ferrel-Larkin-Ovchinnikov type superconducting order², etc. can arise if such a coexistence occurs. Thus, the observation of SC (with a high superconducting transition temperature $T_c \sim 46 \, \mathrm{K}$) coexisting with FM (with the magnetic transition temperature $T_m \sim 132 \, \mathrm{K}$) in the hybrid rutheno-cuprate $\mathrm{GdSr_2RuCu_2O_8}^{3,4,5}$ has motivated intense activity to characterize the families of compounds⁶ $\mathrm{LnSr_2RuCu_2O_8}$ and $\mathrm{Ln_{1+x}Ce_{1-x}Sr_2RuCu_2O_{10}}$ (Ln = Sm, Eu, Gd), and to study the nature of superconductivity, magnetism and their inter-relation.

GdSr₂RuCu₂O₈ is isostructural with the well known $YBa_2Cu_3O_{7-\delta}$ with Y and Ba being completely replaced by Gd and Sr respectively, and the CuO chain replaced by RuO₂ planes. While the current broad understanding of the system is that SC originates in the CuO₂ planes and FM in the RuO₂ planes, details of the nature of both SC and magnetism require further understanding. $GdSr_2RuCu_2O_8$ has a very low H_{c1} (< ~ 100 Oe) and the superconducting properties are highly dependent on the details of sample preparation. Rietveld refinement of the x-ray diffraction pattern of GdSr₂RuCu₂O₈ showed⁷ that oxygen annealing leads to variation of the cation composition without change in the oxygen content. The formal charge of Cu, which is less than the optimal value (for the occurrence of SC) for the as-prepared sample, increases upon prolonged annealing⁷. It thus appears that the purity of the starting materials and the heating schedules play a crucial role in the structure and microstructure of the final product⁸, thereby rationalizing contradictory reports⁹ of existence and non-existence of SC in this compound.

The neutron diffraction studies 10,11,12 suggest that the magnetic order in GdSr₂RuCu₂O₈ is predominantly Gtype antiferromagnitic alignment of the Ru moments with a low temperature moment ~1 mB along c axis. However, the magnetization studies^{11,13} show a spontaneous magnetization Ms ~ 0.1 mB (per Ru). These two results can be reconciled if the Ru moments are canted to give a net magnetic moment in a direction perpendicular to the c axis. Neutron diffraction study¹⁴ of the related compound YSr₂RuCu₂O₈ showed a spontaneous magnetic moment ~ 0.28 mB (which could be enhanced by applying an external magnetic field) perpendicular to the c axis. A recent analysis 15 of the magnetization data suggests I-type ordering consistent with a band structure calculation¹⁶, but inconsistent with the neutron diffraction studies. Further, the magnetism will also be affected by the valence of Ru. The formal valence of Ru has been taken to be 5+ in most of the previous Rietveld analyses. Recent NMR 17 and XANES 18 studies indicate mixed valence for Ru with 40% Ru $^{4+}$ and 60% Ru $^{5+}$ in $GdSr_2RuCu_2O_8$. This also entails several possibilities¹⁸ for the magnetic order in this compound. Thus, the precise nature of magnetic order in this compound still remains controversial and needs to be explored.

The effect of substitution on the physical properties of this system is also very interesting and has been reported in literature^{3,4,19,21}. Sn doping¹⁹ suppresses T_m from 138K for x=0 to 78K for x=0.4 in $GdSr_2Ru_{1-x}Sn_xCu_2O_8$ and T_c increases from 36K at x=0 to 48K at x=0.2 but falls thereafter. On the other

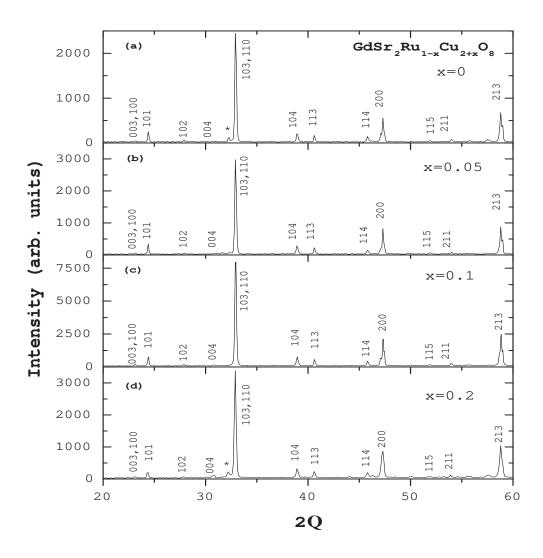


FIG. 1: X-ray diffraction patterns of $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ for (a) x = 0, (b) x=0.05, (c) x=0.1 and (d) x=0.2. The lines corresponding to the impurity phases are shown with *.

hand even a small fraction of Zn (for Cu) rapidly reduces T_c and superconductivity is completely suppressed for the 3% substituted sample^{3,4}. Motivated by above considerations, we have undertaken a study of tuning of the superconducting and magnetic properties by Cu doping for Ru in $GdSr_2RuCu_2O_8$. In this regard, and in continuation of our previous $work^{20}$, we have prepared $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ (x = 0, 0.05, 0.1, 0.2) and investigated their properties, which are presented below.

II. SYNTHESIS AND CHARACTERIZATION

The compounds have been synthesized by the high temperature solid state reaction technique, which is commonly employed for the synthesis of high temperature superconductors. Stoichiometric quantities of Gd₂O₃, $SrCO_3$, CuO and Ru powder, all > 99.99% pure, have been mixed and ground. The mixture (in the form of powder) is heated at 600°C for 48 hours to avoid RuO₂ volatility and then at 950°C, in air, for 24 hours. It is then compressed into pellets and then heated at 1000°C in air for 72 hours. Repeated grinding and heating at 1000°C in air is necessary to obtain phase pure samples. A final step involving annealing at 1060°C in oxygen for 96 hours is necessary to obtain the desired superconducting characteristics. High resolution X-ray powder diffraction analysis is carried out using a STOE Powder diffractometer in the step scanning mode. Electrical resistivity (four probe method, 4.2-300K) and AC Susceptibility (4.2-300K) have been carried out using home-assembled equipments. D.C. Magnetization studies have been per-

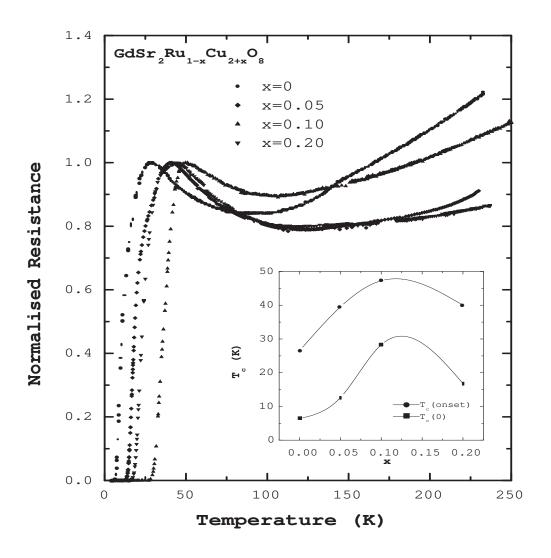


FIG. 2: Normalised Resistance vs temperature curves of $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ for x=0, 0.05, 0.1 and 0.2. T_c corresponding to onset and zero resistance are shown as a function of x in the inset.

formed using a Quantum Design SQUID Magnetometer (5K-300K). All the samples have been prepared in two batches to test for reproducibility.

III. RESULTS AND DISCUSSIONS

Figure 1a shows the XRD of $GdSr_2RuCu_2O_8$. Phase analysis by XRD indicates that the impurity phase content is < 5%. The XRD pattern has been analyzed on the basis of the reported tetragonal structure with space group P4/mmm, and lattice constants have been found to be a=3.83Å and c=11.58Å which are in close agreement with the values reported in the literature^{3,4}. From the analysis of several other samples of $GdSr_2RuCu_2O_8$ it is estimated that the detectability limit of the impu-

rity phases like $SrRuO_3$ and $GdSr_2RuO_6$ type phases and CuO by XRD is < 1%. The crystallite sizes of the sample are small $\sim 500-1000 \text{Å}$ as calculated from XRD line widths using the Scherrer formula. Figure 2 shows the resistance (R) vs temperature (T) curve of $GdSr_2Ru_{1-x}Cu_{2+x}O_8$. This plot clearly indicates the occurrence of superconductivity in these samples, with T_c onset of 26.5K and zero resistance at around 6.4K for the stoichiometric composition GdSr₂RuCu₂O₈. The broadness of the transition may be due to the small crystallite size. Figure 3 shows the ac susceptibility, χ , of $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ as a function of temperature. This figure shows peaks corresponding to the magnetic ordering of the samples with the peak occurring at 139.2K for the stoichiometric composition GdSr₂RuCu₂O₈. The relatively small value of the signal indicates the weak nature

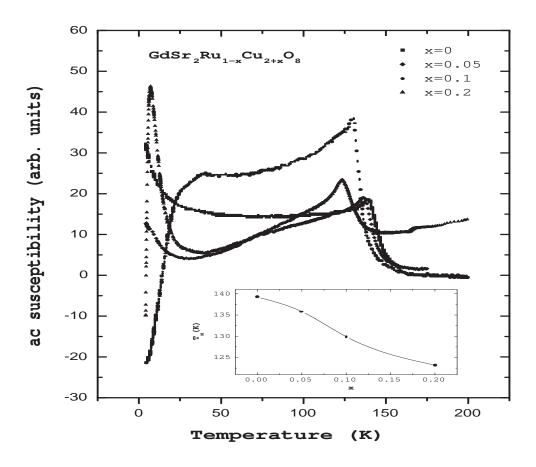


FIG. 3: AC susceptibility vs temperature curve for $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ for x=0, 0.05, 0.1 and 0.2. Magnetic transition temperature T_m is shown as a function of x in the inset.

of ferromagnetism of the material. On closer examination of the R vs T plot, the magnetic ordering transition can be seen as a change in slope at ~ 139.2 K. The diamagnetic shift corresponding to the superconducting transition at 26.5K is not observed in the susceptibility data for the stoichiometric composition GdSr₂RuCu₂O₈ (Figure 3) below 26.5K. On the other hand, the χ increases with decrease in T below 26.5K (Figure 3). The steep increase in χ at low temperature arises due to the paramagnetic contribution of the Gd moments which order antiferromagneticaly at 2.5K. It is believed that the superconductivity is weak and is also perhaps not homogeneous with the result that the magnetic signal due to the paramagnetic contribution of the Gd moments overwhelms the diamagnetic superconducting signal. In order to confirm ferromagnetism in GdSr₂RuCu₂O₈, isothermal magnetization studies have been carried out as a function of field at T=5K. Figure 4a presents the M-H plot for GdSr₂RuCu₂O₈ along with an inset indicating the low field part of the hysteresis loop. The shape of the M-H curve (Fig. 4a) is characteristic of FM and shows weak hysteresis with a low coercive field of ~ 200 Oe (Fig.

4a inset). The magnetization studies at high fields indicate a saturation magnetization of 7 mB corresponding to ordering of Gd moments in high field.

Fig. 1 b, c and d show the XRD patterns of compounds $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ (x = 0.05, 0.1, 0.2). The samples with x = 0.05, x=0.1 and x=0.2 have impurity phase content approximately < 2%, < 1% and < 3%, respectively. All these compositions have the tetragonal structure with space group P4/mmm, isostructural with the stoichiometric composition. The lattice parameters of the compounds $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ (x = 0.05, 0.1, 0.2,) are almost identical, a ~ 3.83 Å and c ~ 11.57 Å and do not differ significantly from the stoichiometric $GdSr_2RuCu_2O_8$.

Figure 2 shows the temperature dependence of resistance for $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ (x = 0.05, 0.1, 0.2) along with that of the x=0 sample. All of them exhibit superconductivity with zero resistance. The onset and zero resistance temperatures are (26.5, 6.4), (39.5, 12.6), (47.2, 28.3) and (40.0, 16.8)K respectively for x = 0, 0.05, 0.1 and 0.2. One of the most important observations is that by Cu doping T_c can be increased and x=0.1 appears to

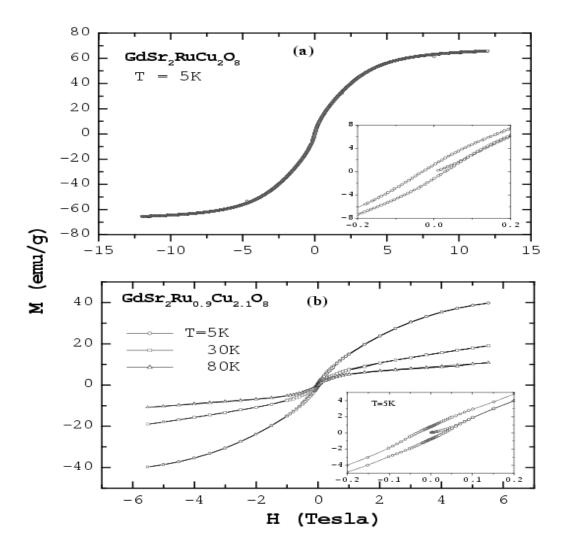


FIG. 4: M vs H curve for (a) $GdSr_2RuCu_2O_8$ at 5K and (b) $GdSr_2Ru_{0.9}Cu_{2.1}O_8$ at T=5K, 30K and 80K. Inset in each figure shows the low field part of the hysteresis loop at 5K.

be the optimum Cu doping concentration. It is also to be noted that these compounds are metallic over most of the temperature range down to 100K. Below 100K there is a semiconducting-like upturn just above the transition to superconducting state. This may be due to the effect of granularity or magnetic scattering. Further experiments in a magnetic field would clarify this and are in progress. However it is interesting to note that the sample x=0.1, which shows the highest T_c , also has the minimum semiconducting upturn. The ac susceptibility vs temperature plots for $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ (x=0, 0.05, 0.1 and 0.2) are shown in Figure 3. It may be noted that the undoped composition did not show a diamagnetic signal corresponding to superconductivity, whereas all the Cu substituted compositions show signature of superconductivity in the ac susceptibility measurements as well. This may be due to an increase in grain size and/or homogeneity. The ferromagnetic transitions are also observed in the Cu doped samples (Figure 3) but at a significantly lower temperature (the magnetic transition temperature T_m being 135.8K, 129.9K and 123.2K respectively for $x=0.05,\ 0.1$ and x=0.2) as compared to 139.2K for the stoichiometric GdSr₂RuCu₂O₈. Figure 4b shows the isothermal magnetization hysteresis at 5, 30 and 80K for a typical Cu doped sample with composition GdSr₂Ru_{0.9}Cu_{2.1}O₈. This confirms the presence of weak ferromagnetism in the Cu doped samples similar to the stoichiometric GdSr₂RuCu₂O₈.

As $GdSr_2Ru_{0.9}Cu_{2.1}O_8$ had the highest T_c and also happens to have the highest purity (< 1% impurity phase content) more detailed measurements have been carried out on it. Zero Field Cooled (ZFC) and Field Cooled

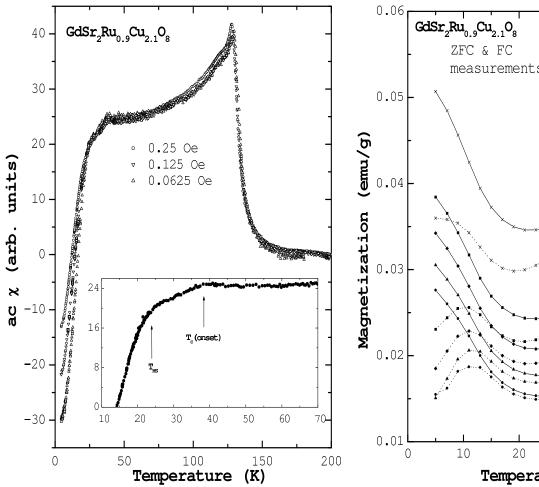


FIG. 5: AC susceptibility of GdSr₂Ru_{0.9}Cu_{2.1}O₈ for three different measuring fields. The change of slope in c at a temperature T_mS less than T_c (onset) is shown in the inset.

(FC) measurements of ac susceptibility yielded identical results. Fig. 5 shows the field cooled ac susceptibility in different measuring fields (amplitude = 0.25, 0.125 and 0.0625 Oe) for $GdSr_2Ru_{0.9}Cu_{2.1}O_8$. The ac χ starts to decrease at T~38K indicating the onset of superconductivity. A significant change in slope of χ vs T is observed at $T_m \sim 23$ K below the superconducting transition. This is perhaps an evidence of the transition from a bulk Meissner state to a spontaneous vortex state similar to that observed by Bernhard et. al.22 in dc χ measurements. A smaller amplitude of the measuring field results in a stronger diamagnetic signal (see Fig. 5). The incomplete shielding effect is due to the low value of the lower critical field H_{c1} that has been reduced by impurity scattering or small grain size.

The dc magnetization studies on GdSr₂Ru_{0.9}Cu_{2.1}O₈ as a function of temperature under different applied fields are presented in Fig. 6. The magnetization shows a tendency to decrease at T~38K. This temperature corresponds to the onset (of superconducting transition) T_c measured by ac χ . However at lower temperature mag-

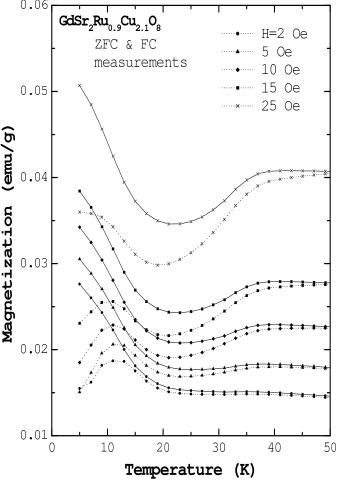


FIG. 6: DC Magnetization vsTemperature $GdSr_{2}Ru_{0.9}Cu_{2.1}O_{8} \quad measured \quad under \quad$ different applied fields. Solid and dotted lines correspond to Field Cooled and Zero Field Cooled measurements, respectively.

netization starts increasing and goes through a maximum in the ZFC measurements and increases monotonically in the FC measurements. The increase may be due to the paramagnetic contribution of Gd moments. The magnetization curves can be reconciled with as an additive effect due to the contributions to the signal of diamagnetism related to superconductivity and the paramagnetic response of the Gd^{3+} ions.

CONCLUSIONS

In conclusion, $GdSr_2Ru_{1-x}Cu_{2+x}O_8(x = 0.05, 0.1,$ 0.2) exhibits superconducting and ferromagnetic transitions, which can be tuned by Cu doping for Ru. T_c is increased by partial substitution of Ru by Cu. A doping level of 0.1 gives a maximum T_c amongst the investigated compositions. Partial substitution of Ru by Cu also has the effect of decreasing the magnetic ordering temperature, from 139.2K for the undoped composition to 123.2K

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