Tuning of the superconducting and ferromagnetic transitions by Cu doping for Ru in GdSrRuCuO$_8$

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Abstract

In order to explore the possibility of tuning superconducting and ferromagnetic transitions by Cu doping (for Ru) in GdSr$_2$RuCu$_2$O$_8$, we have carried out synthesis and characterization of GdSr$_2$Ru$_{1-x}$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 magnetic 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 CuO$_2$ 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 phase, spatially inhomogeneous Fulde-Ferrel-Larkin-Ovchinnikov type superconducting order, etc. can arise if such a coexistence occurs. Thus, the observation of SC (with a high superconducting transition temperature $T_c \sim 46$K) coexisting with FM (with the magnetic transition temperature $T_m \sim 132$K) in the hybrid rutheno-cuprate GdSr$_2$RuCu$_2$O$_8$ has motivated intense activity to characterize the families of compounds LnSr$_2$RuCu$_2$O$_8$ and Ln$_{1+x}$Ce$_{1-x}$Sr$_2$Ru$_2$CuO$_{8}$ (Ln = Sm, Eu, Gd), and to study the nature of superconductivity, magnetism and their inter-relation.

GdSr$_2$RuCu$_2$O$_8$ is isostructural with the well known YBa$_2$Cu$_3$O$_{7-\delta}$ with Y and Ba being completely replaced by Gd and Sr respectively, and the CuO chain replaced by RuO$_2$ planes. While the current broad understanding of the system is that SC originates in the CuO$_2$ planes and FM in the RuO$_2$ planes, details of the nature of both SC and magnetism require further understanding. GdSr$_2$Ru$_{1-x}$Cu$_{2+x}$O$_8$ has a very low $T_{c1} (< \sim 100$ Oe) and the superconducting properties are highly dependent on the details of sample preparation. Rietveld refinement of the x-ray diffraction pattern of GdSr$_2$RuCu$_2$O$_8$ showed 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 annealing. 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 product, thereby rationalizing contradictory reports of existence and non-existence of SC in this compound.

The neutron diffraction studies$^{10,11,12}$ suggest that the magnetic order in GdSr$_2$RuCu$_2$O$_8$ is predominantly G-type antiferromagnetic alignment of the Ru moments with a low temperature moment $\sim 1$ mB along c axis. However, the magnetization studies$^{11,12}$ show a spontaneous magnetization $M_s \sim 0.1$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 studies of the related compound YSr$_2$RuCu$_2$O$_8$ showed a spontaneous magnetic moment $\sim 0.28$ 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 calculation$^{15}$, 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$_2$RuCu$_2$O$_8$. This also entails several possibilities$^{18}$ 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$^{19,21}$. Sn doping$^{20}$ suppresses $T_m$ from 138K for $x = 0$ to 78K for $x = 0.4$ in GdSr$_2$Ru$_{1-x}$Sn$_x$Cu$_2$O$_8$ and $T_c$ increases from 36K at $x = 0$ to 48K at $x = 0.2$ but falls thereafter. On the other


hand even a small fraction of Zn (for Cu) rapidly reduces $T_c$ and superconductivity is completely suppressed for the 3% substituted samples. Motivated by above considerations, we have undertaken a study of tuning of the superconducting and magnetic properties by Cu doping for Ru in GdSr$_2$RuCu$_2$O$_8$. In this regard, and in continuation of our previous work, we have prepared GdSr$_2$Ru$_{1-x}$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 Gd$_2$O$_3$, 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 RuO$_2$ 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. 1: X-ray diffraction patterns of GdSr$_2$Ru$_{1-x}$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 *.
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$_2$RuCu$_2$O$_8$. 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 $a=3.83\,\text{Å}$ and $c=11.58\,\text{Å}$ which are in close agreement with the values reported in the literature. From the analysis of several other samples of GdSr$_2$RuCu$_2$O$_8$ it is estimated that the detectability limit of the impurity phases like SrRuO$_3$ and GdSr$_2$RuO$_6$ type phases and CuO by XRD is < 1%. The crystallite sizes of the sample are small $\sim$500-1000Å as calculated from XRD line widths using the Scherrer formula. Figure 2 shows the resistance (R) vs temperature (T) curve of GdSr$_2$Ru$_{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 GdSr$_2$RuCu$_2$O$_8$. The broadness of the transition may be due to the small crystallite size. Figure 3 shows the ac susceptibility, $\chi$, of GdSr$_2$Ru$_{1-x}$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 GdSr$_2$RuCu$_2$O$_8$. The relatively small value of the signal indicates the weak nature
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 ∼139.2K. The diamagnetic shift corresponding to the superconducting transition at 26.5K is not observed in the susceptibility data for the stoichiometric composition GdSr$_2$RuCu$_2$O$_8$ (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 antiferromagnetically 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 GdSr$_2$RuCu$_2$O$_8$, isothermal magnetization studies have been carried out as a function of field at T=5K. Figure 4a presents the M-H plot for GdSr$_2$RuCu$_2$O$_8$ 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$_2$Ru$_{1-x}$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$_2$Ru$_{1-x}$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$_2$RuCu$_2$O$_8$.

Figure 2 shows the temperature dependence of resistance for GdSr$_2$Ru$_{1-x}$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
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 experi-
ments in a magnetic field would clarify this and are in
progress. However it is interesting to note that the sam-
ple x=0.1, which shows the highest T_c, also has the min-
umum semiconducting upturn. The ac susceptibility vs
temperature plots for GdSr_2Ru_{1-x}Cu_{2.1+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 diamag-
netic 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 transi-
tion 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 GdSr_2RuCu_2O_8. Figure
4b shows the isothermal magnetization hysteresis at 5, 30
and 80K for a typical Cu doped sample with composition
GdSr_2Ru_{0.9}Cu_{2.1}O_8. This confirms the presence of weak
ferromagnetism in the Cu doped samples similar to the
stoichiometric GdSr_2RuCu_2O_8.

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. 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.
FIG. 5: AC susceptibility of GdSr$_2$Ru$_{0.9}$Cu$_{2.1}$O$_8$ for three different measuring fields. The change of slope in $c$ at a temperature $T_m$ 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$_2$Ru$_{0.9}$Cu$_{2.1}$O$_8$. The ac $\chi$ starts to decrease at $T \sim 38$K indicating the onset of superconductivity. A significant change in slope of $\chi$ 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 $\chi$ 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 GdSr$_2$Ru$_{0.9}$Cu$_{2.1}$O$_8$ as a function of temperature under different applied fields are presented in Fig. 6. The magnetization shows a tendency to decrease at $T \sim 38$K. This temperature corresponds to the onset (of superconducting transition) $T_c$ measured by ac $\chi$. However at lower temperature magnetization 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.

IV. CONCLUSIONS

In conclusion, GdSr$_2$Ru$_{1-x}$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
for 0.2 Cu doped composition.

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