Magnetotransport Properties of Doped RuSr$_2$GdCu$_2$O$_8$

J.E. McCrone,$^1$ J.L. Tallon,$^2$ J.R. Cooper,$^1$ A.C. MacLaughlin,$^3$ J.P. Attfield,$^3$ and C. Bernhard$^4$

$^1$IRC in Superconductivity, Cambridge University, Cambridge CB3 0HE, U.K.
$^2$Industrial Research Ltd., P.O. Box 31310, Lower Hutt, New Zealand.
$^3$IRC in Superconductivity and Department of Chemistry, Cambridge University, Cambridge CB2 1EW, U.K.
$^4$Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany.

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RuSr$_2$GdCu$_2$O$_8$, in which magnetic order and superconductivity coexist with $T_{\text{Magnetic}} \gg T_c$, is a complex material which poses new and important questions to our understanding of the interplay between magnetic and superconducting (SC) order. Resistivity, Hall effect and thermopower measurements on sintered ceramic RuSr$_2$GdCu$_2$O$_8$ are presented, together with results on a broad range of substituted analogues. The Hall effect and thermopower both show anomalous decreases below $T_{\text{Magnetic}}$ which may be explained within a simple two-band model by a transition from localized to more itinerant behavior in the RuO$_2$ layer at $T_{\text{Magnetic}}$.

Introduction

Soon after the first successful synthesis of RuSr$_2$GdCu$_2$O$_8$ the material was found to display not only superconductivity ($T_c \sim 45$K) but coexisting magnetic order with $T_{\text{Curie}} \sim 135$K. Evidence accumulated from static magnetization, muon spin rotation ($\mu$SR) and from Gd-ESR studies showing that the magnetism is a spatially uniform bulk property. Specific heat measurements and the diamagnetic shielding fraction at low temperatures indicate that the superconductivity is also a bulk property, and that the two phases therefore coexist on a truly microscopic scale. An initial neutron diffraction study eliminated the possibility of ferromagnetic order with the Ru moments lying in the RuO$_2$ plane, but did not rule out ferromagnetic alignment with the moments parallel to the c-axis, canted ferromagnetism or itinerant ferromagnetism. Subsequent polarized neutron diffraction data have thrown the debate on RuSr$_2$GdCu$_2$O$_8$ wide open by appearing to show that the underlying ordering of the Ru moments below the magnetic transition is in fact G-type antiferromagnetic (antiparallel nearest-neighbour ordering in all three crystallographic directions). Finally, the most recent neutron measurements on RuSr$_2$YCu$_2$O$_8$ confirmed that there is indeed a ferromagnetic component of about 0.28 $\mu_B$ which is about 1/5$^{th}$ of the AF component of 1.2 $\mu_B$. The magnetic order shows a rather strong and unusual response to an applied magnetic field, with the FM component growing rapidly in strength and dominating over the AF already at 2T. Whatever the nature of its magnetism, the discovery of this material is an exciting development which poses new and important questions to our understanding of the interplay between magnetic and SC order.

Magnetoresistance (MR), Hall effect and thermopower (TEP) measurements on undoped sintered ceramic RuSr$_2$GdCu$_2$O$_8$ were presented previously. Above $T_{\text{Magnetic}}$ the MR is negative and proportional to the square of the Ru magnetization and was ascribed to spin-scattering of the current carriers. A model for dilute magnetic alloys was used to extract from these data a value ($\approx 25$ meV) for the exchange interaction between the Ru moments and the carriers. Below $T_{\text{Magnetic}}$ the Hall effect and TEP both fall anomalously. It will be shown that these data may be explained within a simple two-band model by a transition from localized to more itinerant behavior in the RuO$_2$ layer at $T_{\text{Magnetic}}$. Evidence for delocalized carriers within the RuO layers has also been obtained from other transport and microwave absorption studies as well as from Ru-NMR measurements where clear anomalies in the Ru-NMR relaxation rate occur near $T_c$. This observation suggests that the Ru nuclear moments experience a sizeable hyperfine coupling to the charge carriers that enter the SC state.

The magneto-thermopower reveals an extremely unusual variation of $T_c$ with applied field: $T_c$ actually increases by $\sim 4$K as the applied field is increased to 2T. The increase saturates along with the Ru magnetization, suggesting that the onset of Ru magnetic order reduces a magnetic pair-breaking effect in the CuO$_2$ layer.

The carrier concentration in RuSr$_2$GdCu$_2$O$_8$ and its magnetic and SC properties, structural deformations, and so forth may be altered by cation substitution. Examining the transport properties of such samples should lead to a better understanding of the parent material. In this paper we present magneto-transport measurements on substituted RuSr$_2$GdCu$_2$O$_8$. It will be shown that the data strongly support a simple two-band model in which the Hall effect and TEP of each sample are determined by the properties of the CuO$_2$ and RuO$_2$ layers, weighted appropriately by their conductivities. The model indicates that the RuO$_2$ layer in the undoped material is very poorly conducting at room temperature, with $\sigma_{\text{Ru}} \sim 0.1 \sigma_{\text{Cu}}$, increasing to $\sim 0.3 \sigma_{\text{Cu}}$ or higher at low temperature. While in most of the samples studied the CuO$_2$ layer remains the better conductor at all temperatures, we find that the RuO$_2$ layer dominates the conductivity below $T_{\text{Magnetic}}$ in a sample with 10% Ce$^{4+}$ substituted for Gd$^{3+}$.


Composition | Substituted site
--- | ---
$\text{Ru}_{0.5}\text{Sn}_{0.5}\text{Sr}_2\text{GdCu}_2\text{O}_8$ | 40% Sn for Ru
$\text{Ru}_{0.8}\text{Sn}_{0.2}\text{Sr}_2\text{GdCu}_2\text{O}_8$ | 20% Sn for Ru
$\text{Ru}_{0.925}\text{Sn}_{0.075}\text{Sr}_2\text{GdCu}_2\text{O}_8$ | 7.5% Sn for Ru
$\text{Ru}_{0.975}\text{Sn}_{0.025}\text{Sr}_2\text{GdCu}_2\text{O}_8$ | 2.5% Sn for Ru
$\text{Ru}_{0.8}\text{Nb}_{0.2}\text{Sr}_2\text{GdCu}_2\text{O}_8$ | 20% Nb for Ru
$\text{Ru}_{0.9}\text{Nb}_{0.1}\text{Sr}_2\text{GdCu}_2\text{O}_8$ | 10% Nb for Ru
$\text{Ru}_2\text{Gd}_2\text{Cu}_0.5\text{O}_2\text{Cu}_2\text{O}_8$ | 20% Ce for Gd
$\text{Ru}_2\text{Gd}_0.9\text{Ce}_0.1\text{Cu}_2\text{O}_8$ | 10% Ce for Gd
$\text{Ru}_2\text{Eucu}_2\text{O}_8$ | 100% Eu for Gd
$\text{Ru}_2\text{Gd}_0.6\text{Dyo}_0.4\text{Cu}_2\text{O}_8$ | 40% Dy for Gd
$\text{Ru}_2\text{Gd}_0.9\text{Y}_0.1\text{Cu}_2\text{O}_8$ | 10% Y for Gd
$\text{Ru}_2\text{GdCu}_1\text{Li}_0.1\text{O}_8$ | 5% Li for Cu

TABLE I: Substituted variants of RuSr$_2$GdCu$_2$O$_8$ studied in this work.

**Experimental Methods**

Phase-pure sintered pellets of RuSr$_2$GdCu$_2$O$_8$ were synthesized as described previously via solid-state reaction of a stoichiometric mixture of high-purity metal oxides and SrCO$_3$. The doped samples, listed in Table I, were produced similarly; the compositions given are nominal. A final extended anneal at 1060°C in flowing high-purity O$_2$ produces a marked improvement in the crystallinity of the undoped material, resulting in a higher resistive $T_c$ (as defined by $\rho(T) = 0$) but no significant change in the thermodynamic $T_c$.

Bars of approximate dimensions $4 \times 1 \times 0.7$ mm$^3$ were cut from the sintered pellets using a diamond wheel, then polished down to a thickness of $\sim 150$ µm in order to increase the measured Hall voltage. They were mounted on quartz substrates in a standard six-contact configuration allowing both resistance and Hall voltage to be measured simultaneously. The contacts were made using $25$ µm gold wire and DuPont 6838 conducting epoxy, cured in air at 450°C for six minutes, giving contact resistances $< 1$ Ω.

Resistivity and Hall effect measurements were made using an ac current source, low-noise transformers and lock-in amplifiers. A frequency of $\sim 77$ Hz was used to avoid mains pick-up, with current densities of around 0.25 A cm$^{-2}$. The Hall coefficient, $R_H$, was usually measured by stabilizing the temperature and field (10T unless stated otherwise), then measuring the Hall voltage with the sample rotated by 0° and 180° with respect to the field. The Hall coefficient is then given by $R_H = \frac{(V_B - V_0)}{IB}$ where $B$ is the magnetic field, $t$ the sample thickness and $I$ the current. This method eliminates the MR of the sample, and the offset voltage from $\rho_{xx}$ due to contact misalignment. Where $R_H$ was measured as a function of field, this was swept to both positive and negative values and $R_H(B)$ determined from $V_B - V_-B$.

TEP measurements were made by the ‘toggled’ heating method. Two 25 µm chromel-alumel thermocouples, attached to the sample with small blobs of silver paint, measure both the thermal emf and temperature gradient, ensuring that these are measured between the same two points. The sample is first stabilized at the measurement temperature, a small thermal gradient is applied, and the resulting thermal emf measured. The thermal gradient is then reversed, allowing slowly changing thermal emfs in the cryostat wires to be nulled out. A ‘rest state’ was added whereby both ends of the sample were heated at half-power, providing two extra measurement points. Adding this state keeps the total power dissipation into the stage constant, avoiding fluctuation of its temperature when the heater currents are changed.

**Results**

**Transport Measurements on Pure RuSr$_2$GdCu$_2$O$_8**

Hall effect, thermopower and resistivity data for undoped RuSr$_2$GdCu$_2$O$_8$ are shown in Fig. 1. The room-temperature value of the TEP implies a hole concentration, $p_{Cu}$, of 0.06-0.07 holes/Cu, while its temperature dependence is typical of other high-$T_c$ materials, with the exception of the unusual linear temperature dependence below $T_{Magnetic}$. The overall magnitude and temperature dependence of the Hall coefficient is consistent with a doping level, $p_{Cu}$, of $\sim 0.07$ holes/Cu, as inferred from the room-temperature TEP. $R_H$ displays a high-$T_c$-like temperature dependence well above $T_{Magnetic}$. However, below about 170 K there is an anomalous downturn in $R_H$ which is not seen in typical high-$T_c$ data. The so-called ‘anomalous’ Hall effect observed in magnetic materials has been measured and discounted as the cause of this downturn.

Alternative possibilities are that it is due to charge delocalization in the RuO$_2$ plane occurring near the magnetic transition, or to charge transfer into the CuO$_2$ layers. It will be shown that a two-band model, with a localized to itinerant transition occurring at $T_{Magnetic}$ in the RuO$_2$ layer, can explain both these and the TEP data.

The conductivity of the RuO$_2$ layer

We now introduce a simple two-band model which successfully describes the features of the above data. The bands in this model are those formed by carriers in the Cu and Ru orbitals; the overall TEP and Hall effect are given by the sum of the CuO$_2$ and RuO$_2$ layer values, weighted by the layer conductivities.

\[
R_H = \frac{R_{Ru}^{H} \left( \sigma_{xx}^{Ru} \right)^2 + R_{Cu}^{H} \left( \sigma_{xx}^{Cu} \right)^2}{\left( \sigma_{xx}^{Ru} + \sigma_{xx}^{Cu} \right)^2} \tag{1}
\]

\[
S = \frac{S_{Ru} \sigma_{xx}^{Ru} + S_{Cu} \sigma_{xx}^{Cu}}{\sigma_{xx}^{Ru} + \sigma_{xx}^{Cu}} \tag{2}
\]
With some reasonable estimates of the RuO$_2$ and CuO$_2$ layer properties, it is possible to use this model and the measured room-temperature Hall effect and TEP to put a limit on the conductivity of the RuO$_2$ layer. To do this, we assume that the Hall coefficient of the RuO$_2$ layer is approximately zero (the maximum value observed in other two-dimensional Ru oxides studied to date is $5 \times 10^{-19}$m$^3$C$^{-1}$)\textsuperscript{20,21,22}. With this assumption in Eqn. 1, the conductivity of the RuO$_2$ layer may be estimated from

$$\frac{\sigma_{R\alpha}}{\sigma_{xx}} = \sqrt{\frac{R_{Cu}^{R\alpha}}{R_H}} - 1$$

$$R_{H}^{Ru} \ll R_{H}^{Cu} ; \sigma_{R\alpha}^{Ru} < \sigma_{xx}^{Cu}$$

The ratio of the Hall coefficient of the CuO$_2$ layers $R_{H}^{Cu}$ to the measured value $R_H$ caused by the presence of the RuO$_2$ layer, is hard to estimate due to the uncertain doping state in RuSr$_2$GdCu$_2$O$_8$ and the spread of values of $R_{H}^{Cu}$ for a given doping level, in the literature\textsuperscript{23,24,25}. Given these uncertainties, a reasonable range of values of $R_{H}^{Cu}/R_H$ is 1-1.4, giving $\sigma_{R\alpha}^{Ru}$ in the range $0 - 0.18\sigma_{xx}^{Cu}$. The summary of $R_{H}^{Cu}$ values in the review by Cooper and Loram\textsuperscript{26} would favor the low end of this range.

For this range of conductivity in the RuO$_2$ layer, Equation 2 predicts that the measured net TEP lies some 0-8µVK$^{-1}$ below the intrinsic CuO$_2$ layer value, i.e. that $75 \leq S_{Cu}^{ab} ≤ 83$. It is very unlikely that $S_{Cu}^{ab}$ lies in the upper half of this range: a value of $S = 83µVK^{-1}$ would imply an extremely small hole concentration for which a $T_c$ as high as 46K would be extraordinary.

Having placed a limit on the conductivity one can use a 2D model to determine $k_F l$, the product of the Fermi wave-vector with the mean free path for the RuO$_2$ layers. This quantity gives an indication as to whether the carriers are localized or itinerant and for a cylindrical Fermi surface may be written as

$$k_F l = 2\pi \hbar c \frac{\sigma}{e^2}$$

where $c$ is the separation of the planes. Data in the literature for the $ab$-plane resistivity of under-doped YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) films and single crystals, with $p \simeq 0.07$, give a consistent value of 1.2m$\Omega$cm at room temperature\textsuperscript{24,27,28,29} giving $k_F l_{Cu} = 1.3$, near the limit of localization. In fact, in only slightly more under-doped samples one sees a semiconducting upturn at low temperatures. Given the range of ratios of $\sigma_{ab}^{Cu}$ to $\sigma_{xx}^{Cu}$ derived from the Hall effect, $k_F l_{Cu} = 0 - 0.45$ at room temperature. The TEP data suggest that the true value is at the low end of this range, indicating that the carriers in the RuO$_2$ layers are at best very poorly metallic.

### Temperature dependence of $\sigma_{R\alpha}$

Having established that the room-temperature conductivity of the RuO$_2$ layer is close to zero, typical $S(T)$ and $R_H(T)$ data for high-$T_c$ superconductors may be scaled so that the room temperature values match those of RuSr$_2$GdCu$_2$O$_8$. The differences below $T_{Magnetic}$ may then be used to follow $\sigma_{R\alpha}$ as a function of temperature.

Typical Hall effect data for the CuO$_2$ layer have been taken from measurements on sintered Ca-doped YBa$_2$Cu$_3$O$_{7-\delta}$, while $R_{H}^{Ru}$ will be set to zero, its value in other RuO$_2$ layer compounds being much lower than $R_{H}^{Cu}$\textsuperscript{20,21,22}. Typical $S^{Cu}$ data are approximated by measurements on sintered YBa$_2$Cu$_3$O$_{7-\delta}$ with $\delta = 0.5$\textsuperscript{26}, multiplied by 1.12 to match the high-temperature RuSr$_2$GdCu$_2$O$_8$ data. Finally, $S^{Ru}$ is approximated by data measured on a sintered sample of SrRuO$_3$, which displays a magnitude and temperature dependence similar to that of Sr$_2$RuO$_4$. All these data are shown in Figure 1, together with the resulting $\beta(T) = \frac{2\pi R_{H}^{Ru}}{\sigma_{Cu}^{xx}}$ calculated from Eqs. 1 and 2.

![Figure 1](image)

FIG. 1: (a) Hall effect and (b) thermopower data for RuSr$_2$GdCu$_2$O$_8$, together with estimated values of the CuO$_2$ and RuO$_2$ layer properties as described in the text. Panel (c) shows the ratio $\beta = \frac{2\pi R_{H}^{Ru}}{\sigma_{Cu}^{xx}}$ calculated in the two-band model, assuming $\sigma_{R\alpha} \simeq 0$ well above $T_{Magnetic}$.

Given the uncertainties in the approximated RuO$_2$ and CuO$_2$ layer properties the two $\beta(T)$ curves calculated independently from the drops in $S(T)$ and $R_H(T)$ agree well qualitatively. If TEP data for a sample of 20% Sn-doped RuSr$_2$GdCu$_2$O$_8$, in which we shall argue that $\sigma_{R\alpha}$ is strongly suppressed below $T_{Magnetic}$, is used to approximate $S^{Cu}$, the agreement is also qualitative. Because the TEP is a less sensitive function of $\beta$ than the Hall effect, the difference between $S^{1212}$ and $S^{Cu}$ is quite small compared with that between $R_{H}^{1212}$ and $R_{H}^{Cu}$. Thus the value of $\beta$ calculated from the TEP data is more sensitive...
to inaccuracy in the assumed $S_{Cu}^C$ data. This explains why using the (only slightly different) 20% Sn-doped data to approximate $S_{Cu}^C(T)$ results in a better match to $\beta(T)$ calculated from the Hall effect. Whichever data are used, the results show a rapid rise in the relative conductivity of the RuO$_2$ layer below 150K, to $\sim 0.3S_{Cu}^C$ or higher.

**Transport Measurements on Substituted RuSr$_2$GdCu$_x$O$_8$**

Sn-Doped RuSr$_2$GdCu$_2$O$_8$

The diamagnetic Sn$^{4+}$ ion substitutes for Ru in solid solution, and is slightly larger in size than Ru$^{4+/5+}$. The effects of doping the Ru site are of extreme interest given the current debate regarding the spin and charge configuration of the Ru ions.

We note that the Sn-doped samples studied here were from two sources prepared with slightly different annealing strategies. Comparison of their sample resistivities is therefore not necessarily meaningful, as annealing strongly affects the grain-boundary conductivity of RuSr$_2$GdCu$_x$O$_8$. In general the resistivity of sintered high-$T_c$ materials is also affected by sample density.

For the 2.5% and 7.5% samples the resistivity (Figure 2) is metallic, and similar in magnitude to the undoped sample. The 20% sample has a higher resistivity and shows a small semiconducting upturn at low temperatures, while both the magnitude and upturn are far larger for the 40% sample. Estimating $T_c$ from the onset of the resistive transition reveals a gradual increase from 40.5K for the 2.5% sample to 43.5K for the 20% sample, while the 40% sample has a reduced $T_c$ of just 30K.

The TEP, $S(T)$, and Hall effect, $R_H(T)$, are much less affected by grain-boundaries than the resistivity. In conventional high-$T_c$ materials they closely reflect bulk CuO$_2$ layer properties in conventional high-$T_c$ material. The Hall effect data show a slow and monotonic increase in $T_c$ with increasing Sn concentration, but it should be remembered that these data were taken in a field of 10T and only partly reflect the zero-field $T_c$. The vertical arrows in Figure 2 (and in subsequent figures) show the location of the magnetic transition. The TEP data show that $T_c$ (defined by the maximum in the derivative) rises by $\sim 4K$ in going from the 2.5% sample to the 20% sample, in good agreement with the resistivity data. The 40% sample shows a much lower transition temperature, both in $R_H$ and $S$. The increase in $T_c$ with Sn concentration is attributed to the transfer of holes into the CuO$_2$ layer, though we observe a smaller increase than the $\sim 12K$ reported previously. In the earlier studies $T_c$ was defined from the resistivity onset, and the $T_c$ values obtained for low doping levels were significantly lower, possibly due to granularity.

On examining the temperature and doping dependence of the normal-state properties, one immediately observes that the room temperature TEP $S_{290}$ is little changed by the addition of Sn. This result is strange given the rise of $\sim 4K$ in $T_c$ as the doping level is increased to 20%. The change in the Hall effect is also counter-intuitive: the 30% increase in going from 0 to 20% Sn would normally indicate a decrease in hole concentration. This apparent paradox is resolved when it is noticed that the anomalous drop in $R_H$ below $T_{Magnetic}$ is diminished in the 2.5% and 7.5% samples, and is absent in the 20% sample: as the Sn concentration is increased the RuO$_2$ layer becomes well localized below $T_{Magnetic}$, reflecting significantly reduced conductivity at all temperatures. The changes in $R_H(290)$ and $S_{290}$ may then be explained quite simply: the introduction of Sn dopes a few extra holes into the CuO$_2$ layer, increasing $p_{Cu}$ and raising $T_c$ by $\sim 4K$, but also drives the RuO$_2$ layer more insulating. Thus while $R_H^{Cu}$ probably decreases slightly, the overall Hall effect increases as the RuO$_2$ layer no longer provides a parallel conduction pathway. The slight increase in $p_{Cu}$ which would normally decrease the measured TEP, is balanced by the decreasing $\sigma_{Ru}$, which removes the suppression of the TEP by the RuO$_2$ layer, leaving it relatively unchanged overall. Certainly, the increase in doping is far smaller than one would expect from substituting Sn$^{4+}$ for Ru$^{5+}$, suggesting that the mean valency of the Ru ion is less than 5+. This conclusion is supported by recent XANES measurements.
The reduction in the room-temperature $R_H$ of pure RuSr$_2$GdCu$_2$O$_8$, due to conductivity in the RuO$_2$ layer, was estimated to be of the order of 30%. This is entirely consistent with the rise in $R_H$ observed as the Sn concentration is increased to 20%, assuming that $\sigma_{Ru} \rightarrow 0$. The 40% Sn-doped sample does not fit well into this picture, having a much larger $R_H$ at all temperatures. Given the much larger resistivity of this sample and its drastically reduced $T_c$, it is possible that some Sn$\leftrightarrow$Cu substitution has occurred, reducing the CuO$_2$ layer doping state, or that there are significant impurities present.

**Nb-Doped RuSr$_2$GdCu$_2$O$_8**

Nb also substitutes for Ru in the RuSr$_2$GdCu$_2$O$_8$ structure, but has a dramatically different effect on the transport properties. In contrast to the Sn ion, which has a charge of 4+, Nb is believed to substitute in its usual 5+ state, and thus for an average Ru valency of less than five will remove holes from the system, further underdoping it. The room-temperature TEP bears this out, showing a large increase proportionate with Nb doping (see Figure 3) and confirming that the CuO$_2$ plane values. In fact, for $T_c=19$K and $T_{max}^{Ru} \approx 100$K, the universal relationship between $\sigma_{Cu}$ and $\sigma_{Ru}$ predicts $\sigma_{Cu} \sim 100\mu$VK$^{-1}$, as observed. Thus, while the increased $\sigma$ and $R_H$ and the reduced $T_c$ are consistent with a reduced hole concentration in the CuO$_2$ layer and a localized RuO$_2$ layer, the relatively good conductivity of the 20% Nb-doped sample is not. One possible explanation is that the behavior of the resistivity is extrinsic to the bulk in the 20% Nb sample, resulting from either increased grain-boundary conductivity, or increased sample density.

**Ce-Doped RuSr$_2$GdCu$_2$O$_8**

Unlike Nb and Sn, which substitute for Ru, Ce substitutes for Gd in the layer separating the two CuO$_2$ planes, and so would be expected to affect these more than the RuO$_2$ layers from which it is relatively remote. The Ce ion is expected to be in the 4+ state in RuSr$_2$GdCu$_2$O$_8$, as it is in the structurally similar compound RuSr$_2$(Gd$_{1+x}$Ce$_{1-x}$)Cu$_2$O$_{10+\delta}$, hence its substitution for Gd$^{3+}$ should further underdope the material.

Two samples (10% and 20% Ce$\leftrightarrow$Gd) were measured, and of all the doped samples studied these exhibit the most remarkable and revealing transport properties: a large drop in $R_H$ below $T_{Magnetic}$ (in fact becoming negative in the 10% sample below $\sim 30$K), and a large TEP at room temperature which, like the Hall effect, drops very rapidly below $T_{Magnetic}$. These data are shown in Figure 4 along with the resistivities of the two samples.

We note first that, as with other electron doping substitutions (Ce for Gd, La for Sr and hydrogen doping), $T_{Magnetic}$ is driven upwards. This appears to reflect an increasing Ru$^{4+}$ fraction. The 10% Ce sample will be dealt with first. As with the undoped sample, the departure from cuprate-like properties below $T_{Magnetic}$ indicates a transition from localized to itinerant behavior in the RuO$_2$ layer. In this case, however, the room temper-
the double maximum in thermopower below 50K. The basis for this assertion is the lower than in the undoped sample, the reason for the dramatic effects seen in $R_H$ and $S$ below $T_{Magnetic}$ becomes clear: the ratio $\sigma_{Ru}/\sigma_{Cu}$ is much larger in the Ce-doped sample at low temperature, allowing the intrinsic RuO$_2$ layer properties to dominate the behavior.

The effect of changes in $\sigma_{Ru}/\sigma_{Cu}$ is greater for $R_H$ than $S$, but for these samples the increased $\sigma_{Ru}$ depresses the $S_{Cu}$ contribution to the total TEP so much that $S_{Ru}$ dominates below 50K. The basis for this assertion is the double maximum in $\frac{dS}{dT}$: initially, at low temperatures, $S(T)$ follows a curve reasonably consistent with the TEP of SrRuO$_3$. This contribution would appear to saturate at a value of $\sim 40\mu V K^{-1}$; however, above 50K increasing $\sigma_{Cu}$ allows $S_{Cu}$ to contribute, and the overall TEP then rises more rapidly.

The same qualitative treatment may be applied successfully to the Hall effect data, though in order to explain the negative values below $\sim 30K$ it is necessary to assume a negative Hall coefficient for the RuO$_2$ layer of around $-1 \times 10^{-9} m^3 C^{-1}$. Examining typical data from the Sr$_{n+1}$Ru$_n$O$_{3n+1}$ series one finds that $R_H$ of Sr$_2$Ru$_2$O$_7$ remains positive at all temperatures, while that of Sr$_2$RuO$_4$ becomes negative below 20K, but reaches just $-1 \times 10^{-10} m^3 C^{-1}$ near 1K. However, SrRuO$_3$, which has the most similar ferromagnetic RuO$_2$ layer to RuSr$_2$GdCu$_2$O$_8$, has a negative $R_H$ below 100K, reaching a field-dependent value of $\sim -1 \times 10^{-9} m^3 C^{-1}$ below 60K. Thus the value of $R_H$ observed in the Ce-doped sample at low temperature is the same order of magnitude as that in SrRuO$_3$, confirming that the RuO$_2$ layer dominates the transport properties. It is interesting to note that, though it may not be a large effect, Ce substitution for Gd should drive the mean Ru valence closer to 4+, as it is in SrRuO$_3$.

Turning now to the resistivity, one encounters a problem: if the RuO$_2$ layer is indeed metallic below $T_{Magnetic}$, why does the resistivity increase so dramatically as $T \rightarrow 0$? There are two possible answers to this question: either both the RuO$_2$ and CuO$_2$ layers are at least semiconducting, but such that $\sigma_{Ru}/\sigma_{Cu} > 1$, or it may be that insulating grain boundaries cause the upturn. The second of these scenarios seems more likely. In this case the TEP and Hall effect, being much less sensitive to intergrain connectivity, are determined by a weakly metallic intrinsic $\sigma_{Ru}$. Support for this conclusion is provided by close examination of the resistivity (Figure 5) which shows an extended metallic region below $T_{Magnetic}$. This type of behavior is not uncommon in RuSr$_2$GdCu$_2$O$_8$ – in fact extrinsic upturns in resistivity are observed in poorly annealed undoped samples. Interestingly though, transport measurements on SrRuO$_3$ also show a minimum in resistivity below $T_{Curie}$ in samples where there is some disorder in the RuO$_2$ layer. The temperature at which the minimum occurs, and the magnitude of the upturn below it both increase with RuO$_2$ layer disorder.

![FIG. 4: (a) Hall effect, $R_H(T)$, thermopower, $S(T)$, and Resistivity, $\rho(T)$, data for Ce-doped RuSr$_2$GdCu$_2$O$_8$. The large error bars shown on the 20% Ce Hall data points result from the exceptionally large resistivity of the sample making balancing difficult at low temperatures. The error bars shown on the 10% Ce data points are more typical.](image)

![FIG. 5: Enlarged view of the resistivity of the 10% Ce-doped RuSr$_2$GdCu$_2$O$_8$ sample showing $T$-linear resistivity below $T_{Magnetic}$.](image)
in good quality films the highest temperature minimum observed is 40K, coincident with the maximum residual resistivity. As the RuO$_2$ layer may be considerably disordered in these doped RuSr$_2$GdCu$_2$O$_8$ samples, it is possible that the behavior shown in Figure 5 is intrinsic to the RuO$_2$ layer, and not a product of grain boundary resistivity. An extended anneal of the Ce-doped sample could be used to test the origin of the effect, as it should improve the quality of the grain boundaries in the material.

The 20% Ce-doped sample appears initially to be inconsistent with the interpretation of the 10% Ce data presented above: $R_H$ is higher at room temperature, as one would expect for even greater under-doping caused by the increase in Ce content, but $S_{290}$ is actually lower than that of the 10% sample, apparently implying an increased hole concentration. The paradox may be resolved straightforwardly if one accepts that $\sigma_{Ru} \approx \sigma_{Ca}$, even at room temperature, in this sample. Then the values of $S_{290}$ and $R_H(290)$ for the material are no longer dominated by the CuO$_2$ layer; $S_{290}^Cu$ and $R_H^{Cu}(290)$ may both in fact be much larger than the overall measured values so long as $S_{290}^Ru$ and $R_H^{Ru}(290)$ are lower, as expected. From the peak in the Hall effect data, $T_{Magnetic}$ of this sample appears to be depressed by about 30K from its value in the undoped sample, while the resistivity at 50K is more than two orders of magnitude greater, and the sample is insulating, probably due to extreme granularity.

**Calculation of $\beta(T)$ in Ce-doped RuSr$_2$GdCu$_2$O$_8$**

The ratio $\beta(T) = \sigma_{Ru}(T)/\sigma_{Ca}(T)$ may be extracted from the data for the 10% Ce doped sample using the two-band model, as described for the undoped material in the previous Chapter. As in the previous calculation, typical $S^Cu(T)$ and $R_H^{Cu}(T)$ data are matched to the high temperature RuSr$_2$GdCu$_2$O$_8$ data, where $\sigma_{Ru}$ is assumed to be small compared with $\sigma_{Ca}$ and the overall properties reflect those of the CuO$_2$ layer most strongly. The deviation from cuprate-like behavior at lower temperatures is then used to extract the ratio $\beta(T)$.

For this sample, $S^Cu(T)$ data were taken as 1.05 times $S(T)$ measured on a sample of under-doped sintered YBa$_2$Cu$_3$O$_{7-\delta}$, with $\delta \approx 0.05$. $R_H^{Cu}(T)$ data were taken as 1.16 times $R_H$ measured on a similar sample with $\delta \approx 0.62$. $R_H$ and $S$ are particularly strong functions of doping in this region of the phase diagram: the good agreement in the values of $\delta$ required for the two sets of data to match those of RuSr$_2$GdCu$_2$O$_8$ suggests that the assumption of negligible $\sigma_{Ru}$ is reasonable. The TEP of the RuO$_2$ layer is approximated by that of sintered SrRuO$_3$, as before. As the Hall effect becomes negative at low temperatures in Ce-doped RuSr$_2$GdCu$_2$O$_8$ taking $R_H^{Ru} \approx 0$, as was done for the undoped material, will not work. Instead a rough approximation to data for SrRuO$_3$ is used, which shows a field-dependent value of $\sim -1 \times 10^{-3}$ at 20K.

The measured and estimated data, together with the results of the calculations are shown in Figure 5. Above 50K there is remarkable agreement between $\beta(T)$ calculated from the TEP data ($\beta_{TEP}$) and that calculated independently from the Hall effect data ($\beta_{Hall}$), lending confidence both to the model and to the estimated $R_H(T)$ and $S(T)$ data for the RuO$_2$ and CuO$_2$ layers. Below 50K the agreement is not so good: $\beta_{Hall}$ carries on increasing, a direct result of the peak in the TEP data, $T_{Magnetic}$ of this sample appears to be depressed by about 30K from its value in the undoped sample, while the resistivity at 50K is more than two orders of magnitude greater, and the sample is insulating, probably due to extreme granularity.

**Other Doped Samples**

The remainder of the doped samples studied contained Y, Dy and Eu on the Gd site, plus a 5% Li-doped sample, in which Cu is substituted. The transport data for all...
these samples are shown in Figure 7. The Hall effect shows the ‘usual’ anomalous downturn below $T_{Magnetic}$ in all these samples. The magnitude of the downturn, due to the transition to a more itinerant Ru layer, is approximately constant, leading to the conclusion that doping the Cu and Gd sites does not greatly affect the localization of carriers in the RuO$_2$ layer.

Substituting a small amount of Li$^+$ for Cu$^{2+}$ causes virtually no change in the TEP, but depresses $T_c$, by approximately 20K. The Hall effect of this sample is slightly larger than that of the undoped sample, possibly due to some cross-substitution of Li with Ru, depressing $\sigma_{Ru}$, or a slight decrease in the CuO$_2$ layer carrier concentration. These results are consistent with Li$^+$ acting as a pair-breaker in the CuO$_2$ layer. However, there is little effect on transport properties. The rate of suppression of $T_c$ with Li substitution in RuSr$_2$GdCu$_2$O$_8$, $\sim 4K$/%, is about one quarter of that observed in under-doped YBa$_2$Cu$_3$O$_{7-\delta}$ ($\delta = 0.4$) when either Li or Zn is substituted for Cu$^{2+}$. However the concentration of Li in the RuSr$_2$GdCu$_2$O$_8$ sample studied is nominal, and the difference in the rate of suppression may simply reflect loss of Li by vaporization during the long synthesis and anneal.

The isovalent substitution of Y or Dy for Gd actually causes a slight decrease in the TEP of RuSr$_2$GdCu$_2$O$_8$, these being the only substitutions studied to do so. The implied increase in the doping level of the CuO$_2$ layers, presumed to arise from an ion-size effect, is confirmed by the increased $T_c$ in these samples - approximately 2K (10% Y) and 6K (40% Dy) higher than in the undoped sample as seen by both resistivity and TEP measurements. However, the magnitude of the Hall effect is larger for these samples than for the undoped ones. Having argued that the CuO$_2$ layer is less under-doped in these two samples, this effect may only arise from a decrease in the conductivity of the RuO$_2$ layer, partially removing the ‘shorting’ of the CuO$_2$ layer Hall effect.

Full substitution of Eu for Gd causes an increase in $S_{290}$ to 90$\mu$VK$^{-1}$, $T_c$ as measured by the TEP or resistivity drops significantly, and $R_H$ is greatly increased. All these results suggest a drop in the CuO$_2$ layer hole concentration, again consistent with the above-mentioned ion-size effect, perhaps coupled with a decrease in $\sigma_{Ru}$. The resistivity of this sample is much less metallic than that of the others (which are all metallic, with magnitudes two to three times the well-annealed undoped sample), consistent with this interpretation.

**Discussion**

The Hall effect and TEP data described in this paper provide strong evidence for a transition from very poorly metallic to more itinerant behavior in the RuO$_2$ layer below $T_{Magnetic}$. Results from substituted RuSr$_2$GdCu$_2$O$_8$ samples confirm this picture. The universal relationship between $S_{290}$ and $p_{Cu}$ appears to hold in RuSr$_2$GdCu$_2$O$_8$ as a result of the low $\sigma_{Ru}$ at room temperature, though below $T_{Magnetic}$ both $S$ and $R_H$ are reduced by ‘shorting’ of $S_{Cu}$ by the RuO$_2$ layer.

The two-band model proposed is successful in explaining most of the existing data qualitatively: the anomalies, which lie mainly in resistivity data, are most likely due to grain boundary and density effects. The quantitative agreement is also reasonably good. The results support a picture in which the RuO$_2$ layer in the pure compound is localized above $T_{Magnetic}$, with $\sigma_{Ru} \sim 0.1 \sigma_{Cu}$, but becomes more conducting below $T_{Magnetic}$, mirroring the behavior of other ruthenates.

The transition from localized to itinerant RuO$_2$ layer behavior at $T_{Magnetic}$ in the undoped compound may be modified by substituting Ru with Sn or Nb. Sn increases the doping level of the CuO$_2$ layers, raising $T_c$ and suppressing $T_{Magnetic}$, and simultaneously drives the RuO$_2$ layer more insulating. Nb under-dopes the CuO$_2$ layers, lowering $T_c$, and also appears to drive the RuO$_2$ layer insulating, though the 20% sample does not show the expected semiconducting resistivity. These results imply an initial Ru valence lying between 4+ and 5+, in agreement with X-ray Absorption Near Edge Spectroscopy (XANES) data which may be modelled as an admixture of Ru$^{4+}$ and Ru$^{5+}$ spectra in a 40:60 ratio.

As might be expected, doping of the Cu site has little effect on $T_{Magnetic}$ or the transport properties of the RuO$_2$ layer. Li$^+$ acts as a pair-breaking impurity in the

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**FIG. 7:** (a) Hall effect, $R_H(T)$, (b) thermopower, $S(T)$, and (c) resistivity, $\rho(T)$, data for RuSr$_2$GdCu$_2$O$_8$ with 10%Y, 40%Dy and 100%Eu substituted for Gd, or 5%Li substituted for Cu.
CuO$_2$ layer and causes a depression of $T_c$ in line with its behavior in other cuprates. Isovalent doping of the Gd site with other lanthanide elements changes the CuO$_2$ layer doping level, with a remarkably strong variation in $T_c$. This appears to be a ion-size doping effect. Atervalent substitution of Ce for Gd rapidly reduces the doping level of the CuO$_2$ layers and drives the material non-superconducting. In all but the Ce-doped samples, the conductivity of the RuO$_2$ layer only ever reaches a modest fraction of that of the CuO$_2$ layer. In the 10% Ce-doped sample the more heavily under-doped CuO$_2$ layer has an insulating upturn at low temperature, whilst the RuO$_2$ layer remains more metallic, and so the ratio of their conductivities reaches at least 1.9.

Conclusions

To a first approximation the electronic properties of the CuO$_2$ layer in RuSr$_2$GdCu$_2$O$_8$ are the same as those of similar CuO$_2$ layers in other high-$T_c$ cuprate superconductors in all respects. This conclusion is supported by the resistivity, TEP and Hall effect data presented here, and by results on the specific heat jump at $T_c$. On a more detailed level, magneto-transport measurements reveal an interaction between the carriers in these layers and the magnetization of the RuO$_2$ layer. This interaction, with an energy which would seem to be of the same order as the SC energy gap, is not sufficient to destroy superconductivity.

The electronic properties of the RuO$_2$ layer appear to bear a remarkable similarity to those observed in the ruthenate SrRuO$_3$. At room temperature the conductivity of the layer is perhaps 10% of that of the CuO$_2$ layer, with $k_F l_{Ru} \approx 0.2$, indicating very badly metallic or localized behavior. Below $T_{Magnetic}$ the conductivity of the layer rises significantly - by at least 0.3$T_c$. This increase raises the weighting of the RuO$_2$ layer properties relative to those of the CuO$_2$ layer in the admixture that determines the overall transport properties of RuSr$_2$GdCu$_2$O$_8$. As the Hall effect and TEP of the RuO$_2$ layer are both considerably smaller than those in the CuO$_2$ layer the result is a drop in both $R_H$ and $S$ below $T_{Magnetic}$. In pure RuSr$_2$GdCu$_2$O$_8$, and also in most of the substituted variants studied, $\sigma_{Ru}$ remains lower than $\sigma_{Cu}$ over the whole temperature range. For the Ce-doped samples studied, however, the CuO$_2$ layer becomes insulating at low temperatures, allowing the poorly metallic RuO$_2$ layer to dominate the conductivity, and its intrinsic transport properties to show strongly in the overall $R_H$ and $S$ of the material.

The two-band model of parallel conduction in the RuO$_2$ and CuO$_2$ layers has been very successful in modelling the transport properties observed in all the RuSr$_2$GdCu$_2$O$_8$ samples studied, and it has been possible to describe well the effects of doping the different atomic sites. The inferred mixed valency of Ru, together with the onset of itinerancy at the magnetic transition suggests a possible role of a double-exchange mechanism in the magnetic interactions but also raises the possibility of charge ordering in these compounds at appropriate doping levels.

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