

Chemical tuning of ferromagnetism and superconductivity in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ †

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When substituted for Ru in the ferromagnetic superconductor $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, both Sn^{4+} and Nb^{5+} suppress the ferromagnetism in the RuO_2 layers, but they respectively enhance and diminish superconductivity in the CuO_2 planes through hole transfer to and from the CuO_2 layers, showing that these materials are underdoped with an estimated maximum T_c of 65 ± 10 K.

Ferromagnetism and superconductivity are considered to be incompatible in homogenous solids, but a remarkable coexistence of these properties has recently been discovered in the mixed oxide $\text{RuSr}_2\text{GdCu}_2\text{O}_8$.^{1–10} This has a tetragonal ‘1212’ type structure, similar to that of $\text{YBa}_2\text{Cu}_3\text{O}_7$, with layers stacked in the sequence ... RuO_2 · SrO · CuO_2 · Gd · CuO_2 · SrO ...^{6,9,10} Resistivity measurements show that this material displays bulk superconductivity in the CuO_2 planes, with a critical temperature (T_c) of up to 46 K, whilst the ferromagnetic transition at $T_M = 136$ K results from ordering of moments in the RuO_2 planes.^{4,5,7} The presence of ferromagnetism is confirmed by hysteresis loops in magnetisation vs. field measurements, with remnant and saturated moments of 0.1 and $1.0 \mu_B$ per Ru atom. However, recent neutron diffraction measurements detected only an antiferromagnetically ordered component,⁸ so that the overall magnetic arrangement may be canted with both ferro- and antiferro-magnetic components. This canting may result from antisymmetric exchange between Ru moments as a result of local rotations and tilts of the RuO_6 octahedra owing to a size mismatch between the ruthenate and cuprate layers.^{6,9,10} $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ is cation and oxygen stoichiometric, and the hole-doping (oxidation) of the CuO_2 planes needed to induce superconductivity arises from the overlap of the Ru t_{2g} and the Cu $d_{x^2-y^2}$ bands. The formula may thus be written as $\text{Ru}^{5-2p_0}\text{Sr}_2\text{Gd}(\text{Cu}^{2+p_0})_2\text{O}_8$ to show the average Ru and Cu oxidation states. Transport measurements suggest that the intrinsic hole doping is $p_0 \approx 0.07$,⁷ showing that this material is strongly underdoped, as optimum superconductivity in copper oxides is generally found for a hole-doping of $p \approx 0.16$. The average oxidation states are thus $\text{Ru}^{4.86+}$ and $\text{Cu}^{2.07+}$.

To investigate the relationship between the charge distribution, superconductivity and magnetism in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ further, we have attempted to replace Ru by non-magnetic, fixed valent cations. Samples of $\text{Ru}_{1-x}\text{M}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ were previously prepared with nominal compositions $x = 0–0.4$.¹¹ Tin doping was found to suppress T_M and enhance T_c , but firm conclusions about the origin of this effect could not be drawn as the samples were not phase pure. We have subsequently prepared phase pure Sn-doped samples for $x < 0.1$, and a series of >98% pure Nb doped samples, as summarised here.

Ceramic samples of $\text{Ru}_{1-x}\text{M}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ ($M = \text{Sn}$: $x = 0, 0.025, 0.05, 0.075$; $M = \text{Nb}$: $x = 0, 0.05, 0.1, 0.15, 0.2$) were prepared by solid state reaction of stoichiometric powders of RuO_2 , SnO_2 , Nb_2O_5 , SrCO_3 , Gd_2O_3 and CuO . These were

ground, die-pressed into pellets and reacted in flowing nitrogen at 1010°C for 20 h, in flowing oxygen at 1050°C and at 1055°C for 10 h each, then at 1060°C for 4 days, and finally slow cooled to room temperature. X-Ray diffraction patterns demonstrated that the $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ solid solutions were phase pure, however there was a trace of SrRuO_3 in the $\text{Ru}_{1-x}\text{Nb}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ samples. The greatest amount was estimated to be 2.2(1)% SrRuO_3 in the $x = 0.20$ sample by Rietveld analysis. Thermogravimetric analyses gave oxygen contents between 7.95 and 8.05 for all samples, showing them to be stoichiometric within the experimental error of ± 0.05 .

Magnetisations were measured on a Quantum Design SQUID magnetometer in an applied field of 1 kOe after zero-field cooling. A broadening of the magnetic transition and a reduction in the Curie temperature T_M (Table 1) is observed with increasing Nb [Fig. 1(a)] or Sn substitution. Variable field measurements between ± 50 kOe at 10 K revealed hysteresis loops for all samples. The hysteretic parameters all decrease smoothly with Nb or Sn substitution; the coercivity falls from 410 Oe in the undoped material to 320 Oe for 7.5% Sn substitution and 240 Oe for 20% Nb substitution and the remnant Ru moments are 0.13, 0.09 and $0.05 \mu_B$, respectively. The saturated Ru moments, estimated by subtracting the Gd contribution following a procedure described elsewhere,¹¹ are 1.0, 0.8 and $0.6 \mu_B$ in the same three samples. These results are all in keeping with a dilution of the ferromagnetism in the RuO_2 layers by substitution of diamagnetic Sn^{4+} or Nb^{5+} .

The resistivities of sintered polycrystalline bars were measured between 7 and 300 K using the standard four-probe ac technique. Superconducting transitions are observed for the $\text{Ru}_{1-x}\text{Nb}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ samples with $x = 0–0.15$ [Fig. 1(b)] but not for $x = 0.2$ down to 7 K. All the $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ samples are superconducting and the onset T_c increases up to 50 K for $x = 7.5\%$. The thermoelectric powers of the same sintered bars were measured at 290 K. The derived Seebeck coefficient decreases from $80 \mu\text{V K}^{-1}$ in the undoped material to $70 \mu\text{V K}^{-1}$ in $\text{Ru}_{0.925}\text{Sn}_{0.075}\text{Sr}_2\text{GdCu}_2\text{O}_8$ but increases to $120 \mu\text{V K}^{-1}$ in $\text{Ru}_{0.8}\text{Nb}_{0.2}\text{Sr}_2\text{GdCu}_2\text{O}_8$. The proportion (<2%) of SrRuO_3 is too small to affect these bulk transport measurements.

The charge distribution in the doped materials may be written as $(\text{Ru}^{5-2p_0})_{1-x}\text{M}^q_x\text{Sr}_2\text{Gd}(\text{Cu}^{2+p-\Delta p})_2\text{O}_8$ where the extrinsic

Table 1 Variations of the hole doping level p , the onset superconducting critical temperature T_c , and the Curie temperature T_M for $\text{Ru}_{1-x}\text{M}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ solid solutions with values of x for Nb and Sn substitution as shown

p	$x_{\text{Nb}}(\%)$	$x_{\text{Sn}}(\%)$	T_c/K	T_M/K
0.064	20	—	—	103
0.068	15	—	19	110
0.072	10	—	19	118
0.076	5	—	29	127
0.080	0	—	37	136
0.080	—	0	38	136
0.091	—	2.5	45	126
0.101	—	5	46	117
0.112	—	7.5	50	103

† Electronic supplementary information (ESI) available: Rietveld refinement patterns [Fig. 1(a)–(c)] and characterisation data (Table 1). See <http://www.rsc.org/suppdata/cc/b0/b002669g>

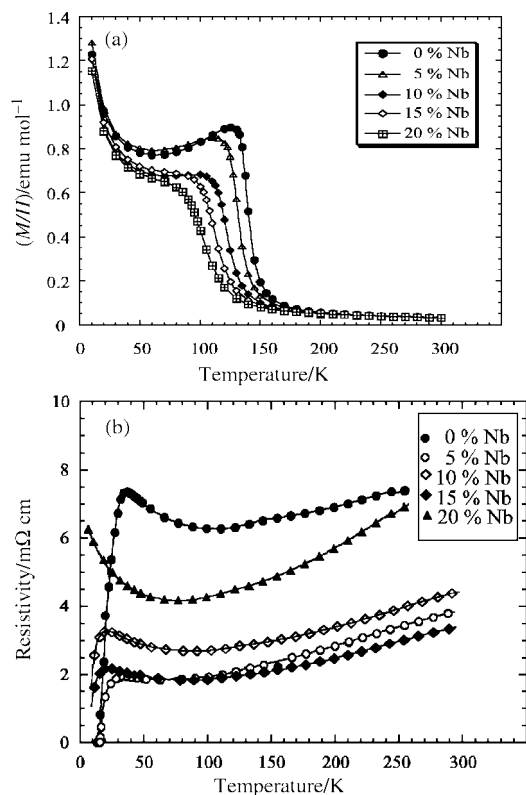


Fig. 1 Temperature variations of (a) magnetisation/field and (b) electronic resistivity for $\text{Ru}_{1-x}\text{Nb}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ solid solutions.

doping introduced by the substituents M of charge q is $\Delta p = (5 - q - 2p_0)x/2$. This assumes that the substituent does not change the intrinsic band structure. This description is verified by the transport data for the $\text{Ru}_{1-x}\text{M}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ solid solutions, which show that the electronic doping can be increased or decreased relative to the intrinsic level. Substitution of $\text{Ru}^{4.86+}$ by Nb^{5+} leads to removal of holes from the CuO_2 planes (chemical reduction), so that the materials become more underdoped and T_c decreases. This is supported by the increase of the 290 K Seebeck coefficient with x in the $\text{Ru}_{1-x}\text{Nb}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ series, as this is known to increase from ≈ 0 in optimally doped materials with $p \approx 0.16$ to $\approx 10^2 \mu\text{V K}^{-1}$ in very underdoped materials.¹² $\text{NbSr}_2\text{GdCu}_2\text{O}_8$ was previously reported to be non-superconducting and could not be doped sufficiently to induce superconductivity,¹³ but we note that this is achieved for $> 85\%$ replacement of Nb by Ru. The trend in superconductivity of the $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ solid solutions is opposite to that of the $\text{Ru}_{1-x}\text{Nb}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ series. The replacement of $\text{Ru}^{4.86+}$ by Sn^{4+} transfers more holes into the CuO_2 planes (chemical oxidation), so T_c increases and the Seebeck coefficient decreases.

The variation of T_c with doping level has been established in many cuprate superconductors and to a good approximation varies quadratically as $T_c = T_c^{\text{max}}[1 - 82.6(p - 0.16)^2]$.¹⁴ This equation has been fitted to the onset T_c values in Table 1 by writing $p = p_0 + \Delta p$, giving values of $p_0 = 0.080(5)$ for the intrinsic doping, in good agreement with the previous value of 0.07,⁷ and $T_c^{\text{max}} = 65(10)$ K as an estimate for the maximum T_c at optimum doping. This is somewhat lower than the highest T_c of ≈ 105 K in comparable 1212 cuprates such as $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca},\text{Y})\text{Cu}_2\text{O}_7$.¹⁵ This suppression could reflect a pairbreaking interaction with the ferromagnetic moments in the RuO_2 plane, but this effect should be greater in the undoped compound than in the less ferromagnetic $\text{Ru}_{1-x}\text{M}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ derivatives, leading to a greater reduction of T_c at $p \approx p_0$ which is not observed in Fig. 2. Lattice strain from the mismatch of the cuprate and ruthenate layers is a more probable explanation for the low T_c 's in this system. This has previously been evidenced by the unusually short apical Cu–O bond of 2.16 Å in

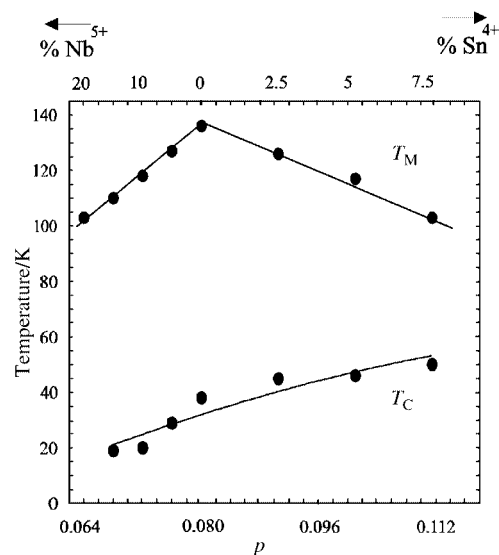


Fig. 2 The variation of the superconducting critical temperature (T_c) and the Curie temperature (T_M) with doping level p (lower scale) and %Nb or Sn substitution (upper scale) in the $\text{Ru}_{1-x}\text{M}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ solid solutions. The T_c values are fitted by the quadratic expression given in the text.

$\text{RuSr}_2\text{GdCu}_2\text{O}_8$,⁶ suggesting that the geometry of the structure is not optimal for superconductivity.

In conclusion, this study shows that up to 20% Nb^{5+} or 7.5% Sn^{4+} can be substituted for Ru in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$. These diamagnetic substituents tune the physical properties by lowering the magnetic ordering temperature and ferromagnetic moment of the ruthenate layers, and respectively removing or adding holes to the copper oxide planes. The $\text{Ru}_{1-x}\text{M}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ materials behave as typical underdoped cuprates and the maximum T_c that could be obtained at optimum doping is estimated to be 65 ± 10 K, which is less than those in comparable materials. This could reflect a magnetic pairbreaking effect but more probably results from lattice strains in the cuprate layers.

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