High critical-temperature superconductivity and large (‘colossal’) magnetoresistances are two important electronic conducting phenomena found in transition metal oxides. High-\(T_c\) materials have applications such as superconducting magnets for MRI and NMR, and magnetoresistive materials may find use in magnetic sensors and spintronic devices. Here we report chemical doping studies of RuSr\(_2\)(\(R_x\)Ce\(_{1-x}\))\(\text{Cu}_2\)O\(_{10.8}\) ruthenocuprates which show that a single oxide system can be tuned between superconductivity at high hole dopings and varied magnetoresistive properties at low doping levels. A robust variation of negative magnetoresistance with hole concentration is shown in the RuSr\(_2\)R\(_{1.8}\)Y\(_{0.2}\)Ce\(_{0.8}\)Cu\(_{0.4}\)O\(_{4.3}\) series, while RuSr\(_2\)R\(_{1.8}\)Ce\(_{0.8}\)Cu\(_{0.4}\)O\(_{10.8}\) materials show an unprecedented crossover from negative to positive magnetoresistance with rare earth (\(R\)) ion radius.

Although the mechanism for superconductivity in layered cuprates remains controversial,\(^1\) the chemical tuning of their properties is well-established. Oxidation of the Cu\(_{2}\)O planes suppresses antiferromagnetic order of Cu\(^{2+}\) \(S = \frac{1}{2}\) spins, and induces superconductivity in the doping range \(p_\text{p} = 0.06-0.25\) (the equivalent Cu oxidation states are \(2+p\)). Ruthenocuprates contain distinct RuO\(_2\) and CuO\(_2\) planes, and display coexisting ferromagnetism and superconductivity in both 1212-type (RuSr\(_2\)RCu\(_2\)O\(_{10.8}\)) \(^2\,^3\) and 1222-type (RuSr\(_2\)R(Ce,\(\text{Cu})_2\)O\(_{10.8}\)) \(^4\,^5\) structures, where \(R\) = Sm, Eu, or Gd. Large negative magnetoresistances (change of electrical resistivity \(\rho\) in an applied magnetic field \(H\), defined as MR= \((\rho(H) - \rho(0))/\rho(0)\)) have recently been observed in non-superconducting \(R = (\text{Nd},\text{Y})\) 1222 materials\(^6\), up to MR = -34% for RuSr\(_2\)Nd\(_{1.1}\)Y\(_{0.9}\)Ce\(_{0.1}\)CuO\(_{0.8}\) at 4 K and 7 T. The results presented here reveal an exquisite chemical tuning of the properties of 1222 ruthenocuprates between superconducting and magnetoresistive properties, including a previously unreported, large positive magnetoresistance state.

1222-type ruthenocuprates contain metal oxide layers in the repeat sequence; \(\text{RuO}_2\),\(\text{SrO}\),\(\text{CuO}_2\),\(\text{(R, Ce)}_2\),\(\text{O}_2\),\(\text{(R, Ce)}_2\),\(\text{CuO}_2\),\(\text{SrO}\). (Table of Contents figure shows the crystal structure). The chemistry of the \(\text{(R, Ce)}_2\)O\(_{2.6}\) slab between the two CuO\(_2\) planes controls the electronic properties. Two series of polycrystalline ceramic 1222 samples, RuSr\(_2\)Nd\(_{1.8}\)Y\(_{0.2}\)Ce\(_{0.8}\)CuO\(_{10.8}\) (0.7 < \(x < 0.95\)) and RuSr\(_2\)R\(_{1.8}\)Ce\(_{0.8}\)CuO\(_{10.8}\) \((R_{1.8} = \text{Nd}_{1.8}\text{Y}_{0.2}\text{Nd}_{0.2}\text{Y}_{0.8};\text{Sm}_{1.8}\text{Y}_{0.2}\text{Eu}_{0.8}\text{Y}_{0.2};\text{Gd}_{0.8}\text{Y}_{0.2};\text{in order of decreasing radius})\), were prepared to determine the respective effects of variable doping and \(R\) cation range. Pelleted stoichiometric mixtures of \(\text{R}_2\)O\(_3\), RuO\(_2\), CuO\(_2\), CeO\(_2\) and SrCO\(_3\) powders were repeatedly sintered at 1025 °C and furnace cooled in air. Tetragonal \(I4/mmm\) 1222 phases (\(\alpha = 3.85\), \(c \approx 28.55\) Å) were formed in all cases.

It is difficult to prepare single phase Nd-based 1222 materials as these only form over a ~10 °C synthesis window around 1025 °C, and a small degree of Y substitution was needed to produce samples having a high degree (>95%) of phase purity. Portions of high (low) \(x\) RuSr\(_2\)Nd\(_{1.8}\)Y\(_{0.2}\)Ce\(_{0.8}\)CuO\(_{10.8}\) samples were annealed under flowing \(N_2\) (O\(_2\)) to increase (decrease) the oxygen deficiency \(\delta\) and thereby extend the available hole-doping range.\(^7\) Precise oxygen stoichiometries were determined by thermogravimetric reduction under 5% \(H_2\) in \(N_2\). Ru is known to be in the +5 state in 1222 materials from previous XANES and doping studies,\(^8\) giving \(p = (1-x-2\delta)/2\). Ten RuSr\(_2\)Nd\(_{1.8}\),Ru\(_{0.2}\)Y\(_{0.8}\)Ce\(_{0.8}\)CuO\(_{10.8}\) samples were synthesised, with 0.70 < \(x < 0.95\) and 0.004 < \(\delta < 0.095\), giving a doping range 0.010 < \(p < 0.059\) that spans the presuperconducting region for cuprates. Further sample details are given in Supporting Information.

All of the RuSr\(_2\)Nd\(_{1.8}\)Y\(_{0.2}\)Ce\(_{0.8}\)CuO\(_{10.8}\) materials are semiconducting with bandgaps of 30-170 meV and the Cu spins order antiferromagnetically at 25-115 K. The magnetoresistance properties are typified by the data for the \(x = 0.9\) sample in Fig. 1(a) and (b). Negative MR is observed below the Ru spin ordering transition ~160 K, diverging to large values below the Cu spin ordering temperature of 60 K, and the 4 K MR varies near-linearly with magnetic field. These properties are characteristic of charge transport by magnetopolarons — small ferromagnetic regions surrounding each Cu-hole within a matrix of antiferromagnetically ordered Cu\(^{2+}\) spins.\(^9\) An applied magnetic field cant the Ru spins into a ferromagnetic arrangement, which induces partial ferromagnetism in the CuO\(_2\) planes thereby increasing the mobility of the magnetopolarons, giving the observed, negative MR’s.\(^6\) Magnetopolaron hopping is a thermally activated process, leading to a characteristic exponential rise in –MR below the Cu spin transition,\(^10\) as seen in Fig. 1(a).

The magnetoresistances in the RuSr\(_2\)Nd\(_{1.8}\)Y\(_{0.2}\)Ce\(_{0.8}\)CuO\(_{10.8}\) series (at 4 K and 7T) shows a striking correlation with the doping level \(p\), as shown in Fig. 2. No such MR trend has been reported previously in any cuprate series. -MR initially rises with \(p\), reflecting the increasing number of hole carriers in the CuO\(_2\) planes, but falls sharply above \(p = 0.04\). The known onset of superconductivity in ruthenocuprates (and cuprates in general) at \(p > 0.06\), suggests that this collapse of –MR corresponds to the onset of hole-pairing, as the singlet Cu hole pairs that carry the supercurrent do not contribute to the magnetotransport. Hence, our magnetoresistance data show that superconducting pair formation starts above a distinct threshold concentration of 4% doping, although the coherent superconducting state is observed only for >6% doping.
strength, or cation radius. A thermal crossover from negative to positive MR has been reported in Zn$_2$-Cu$_{2}$Cr$_{2}$Se$_4$ selenides $^{12}$, but the strong size control of the sign of MR found here is unprecedented.

No magnetic anomaly is observed at the 30 K MR discontinuity in RuSr$_2$Eu$_{0.2}$Y$_{0.8}$Ce$_{0.5}$Cu$_{0.5}$O$_{10.5}$ (Fig. 1(c)), however, a subtle electronic transition is evidenced from a change in the resistivity variation (Fig. 1(d)) from $\rho$ = exp(A.T$^{-1}$) above 30 K to $\rho$ = exp(A.T$^{-2}$) below. These correspond to variable-range hopping of the carriers in two and three dimensions, respectively. Hence, the negative MR above 30 K is associated with two-dimensional transport in the CuO$_2$ planes, whereas below 30 K, additional conduction between planes has a different, positive MR mechanism that dominates the bulk MR of ceramic samples. The correlation between low temperature MR and mean cation radius in Fig. 2 thus results from the decrease in the width of the insulating (R, Ce)$_2$O$_2$- slabs between CuO$_2$ planes as cation size decreases, leading to more three-dimensional conducting behaviour in the small cation materials.

In summary, the combination of electronically active RuO$_2$ and CuO$_2$ planes and a sophisticated chemical tuning from the (R, Ce)$_2$O$_2$- slabs leads to an exquisite variation of low temperature transport properties in RuSr$_2$(R$_{x}$-Ce)$_{2}$CuO$_{10.5}$ materials. Low-doped, large $R^{3+}$ materials such as $R$ = (Nd, Y) show large negative MR’s characteristic of two-dimensional magnetopolaron hopping, suppressed at higher dopings by superconducting pair formation. Analogously, with $R$ = Eu or Gd have positive MR’s associated with three-dimensional hopping, crossing over to negative MR’s at high temperatures or fields. Superconducting materials with $T_c$ up to 50 K can also be prepared using high $R$ = Sm, Eu, or Gd contents $^{4, 5, 13, 14}$. Further studies of these materials may give new insights into superconducting and magnetoresistive transport in oxides, and could lead to improvements in devices such as spin-polarised quasiparticle junctions $^{15}$.

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Supporting information available: Table of RuSr$_2$Nd$_{1.8}$Y$_{0.2}$Ce$_{0.5}$CuO$_{10.5}$ compositions.

References

1 University of Aberdeen.
2 University of Edinburgh
3 (1) Reznik, D.; Pintschovius, L.; Ito, M.; Ikubo, S.; Sato, M.; Goka, H.; Fujita, M.; Yamada, K.; Gu, G. D.; Tranquada, J. M. Nature 440, 1170-1173 (2006).
4 Mclaughlin, A. C.; Janowitz, V.; McAllister, J. A.; Attfield, J. P. Chem. Commun. 2000, 1331-1332.
5 Mclaughlin, A. C.; Janowitz, V.; McAllister, J. A.; Attfield, J. P. J. Mater. Chem. 2001, 11, 173-178.
6 Knee, C. S.; Rainford, B. D.; Weller, M. T. J. Mater. Chem. 2000, 10, 2445-2447.
7 Mclaughlin, A. C.; Attfield, J. P.; Asaf, U.; Felnor, I. Phys. Rev. B 2003, 68, 014503.
8 Mclaughlin, A. C.; Sher, F.; Attfield, J. P. Nature (London) 2005, 436, 829-832, 2005, 437, 1057-1057.
9 Samples were annealed under flowing N$_2$ at 600°C or under flowing O$_2$ at 800°C and then furnace cooled.
10 Williams, G. V. M.; Jiang, L. P.; Liu, R. S. Phys. Rev. B 2002, 65, 064508.
11 Nagaev, E. L. JETP Lett. 1967, 6, 18-20.
12 Majumdar, P.; Littlewood, P. Phys. Rev. Lett. 1998, 81, 1314-1317.
13 Shannon, R. D. Acta Cryst. A. 1976, 32, 751-767.
14 Parker, D. R.; Green, M. A.; Bramwell, S. T.; Wills, A. S.; Gardner, J. S.; Neumann, D. A. J. Am. Chem. Soc. 2004, 126, 2710-2711.
15 Ono, A. Jpn. J. Appl. Phys. 1995, 34, L1121.
16 Felner, I.; Asaf, U.; Levi, Y.; Millo, O. Phys. Rev. B 1997, 55, R3374-R3377.
Dong, Z. W.; Pai, S. P.; Ramesh, R.; Venkatesan, T.; Johnson, M.; Chen, Z. Y.; Cavanaugh, A.; Zhao, Y. G.; Jiang, X. L.; Sharma, R. P.; Ogale, S.; Greene, R. L. J. Appl. Phys. 1998, 83, 6780-6782.
A remarkable variety of conducting states has been found in RuSr$_2$(R$_2$-x, Ce$_x$)Cu$_2$O$_{10-\delta}$ ruthenocuprates by tuning the properties of the magnetic CuO$_2$ and RuO$_2$ layers through small changes in the chemistry of the (R,Ce)$_2$O$_{2-\delta}$ slab. Both the $R^{3+}$ cation size and the charge transfer determined by the R/Ce ratio and the oxygen deficiency $\delta$ are important controlling parameters that tune ground state properties from positive magnetoresistive to negative magnetoresistive to superconducting.