Enhancement of large magnetoresistances in ruthenocuprates by Ta substitution†

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An unexpected enhancement of the large negative magnetoresistance (MR) observed in $RuSr_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$ up to −47% at 4 K and 9 T is evidenced upon dilution of the Ru magnetic order by substitution of Ta for Ru; this enhancement of −MR scales with the cell volume.

The phenomena of high-temperature superconductivity (HTSC) and colossal magnetoresistance (CMR) have been much studied in recent years. Both phenomena are observed in doped transition metal oxides; HTSC is observed in layered cuprates such as $La_{2-x}Sr_xCuO_4$[1] between a Cu oxidation state of 2.06–2.30; and CMR is established in perovskite manganites such as $La_{1-x}Sr_xMnO_3$ for Mn oxidation states of 3.2–3.5.[2]

Ruthenocuprates, containing distinct RuO_2 and CuO_2 layers, are an important class of multifunctional electronic materials that can display both properties. Coexisting weak ferromagnetism and superconductivity has previously been established in several 1212 ($RuSr_2RCu_2O_8$)[3,4] and 1222 ($RuSr_2(R,Ce)_2Cu_2O_{10-\delta}$) type materials,[5–7] where R = Sm, Eu or Gd. We have recently reported that a new 1222 series, $RuSr_2Nd_{1.8-x}Y_{0.2}Ce_xCu_2O_{10-\delta}$, exhibits large negative magnetoresistances (change of electrical resistivity ρ in an applied magnetic field H, defined as MR = $(\rho(H) - \rho(0))/\rho(0)$) for hole dopings $0.01 < p < 0.06$ (the equivalent Cu oxidation states are $2 + p$).[8,9] Weak ferromagnetism arises due to Ru spin ordering below $T_{Ru} \sim 70$–180 K which induces long-range Cu spin ordering at $T_{Cu} \sim 20$–110 K. MR diverges to large negative values below T_{Cu}, for R = Nd, Y as the application of a magnetic field results in a canting of the Ru and Cu spins into a ferromagnetic arrangement in the *ab* plane. In this paper we will demonstrate an unexpected enhancement of the −MR upon dilution of the magnetic order in the RuO_2 layer by substitution of Ta^{5+} for Ru^{5+}.

The 1222 structure consists of metal oxide layers in the repeat sequence RuO_2.SrO.CuO_2.(R,Ce).$O_{2-\delta}$.(R,Ce).CuO_2.SrO. A series of polycrystalline ceramic samples, $Ru_{1-x}Ta_xSr_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$ ($0 < x < 0.4$) were prepared to investigate the effect of diluting the Ru magnetic order on the magnetotransport. Pelleted mixtures of Nd_2O_3, Y_2O_3, RuO_2, Ta_2O_5, CuO, CeO_2 and $SrCO_3$ powders were repeatedly sintered at 1025 °C and furnace cooled in air at a rate of 2 °C min^{-1}. 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 with a high degree (>95%) of phase purity. X-Ray diffraction patterns demonstrated that tetragonal *I*4/*mmm* 1222 phases were formed in all cases (Fig. 1). An increase in both a and c is observed, from 3.8546(2) and 28.5610(9) Å to 3.8644(3) and 28.6405(9) Å, respectively, upon increasing x from 0 to 0.4, in accordance with the substitution of the larger Ta^{5+} ion for Ru^{5+}.

Magnetisations were recorded on a Quantum Design SQUID magnetometer in a 100 Oe magnetic field. As in previous samples,[8,9] a weak ferromagnetic transition of the Ru spins is observed, followed by low temperature antiferromagnetic order of the Cu spins. The Ru spin transition, T_{Ru}, was determined by extrapolating the maximum ($-dM/dT$) slope to zero magnetization. Likewise the Cu antiferromagnetic transition was established from the temperature of the maximum magnetisation recorded in a field of 100 Oe after zero-field cooling.[8,9] A reduction of both T_{Ru} and T_{Cu}, from 144 and 73 K to 102 and 55 K, respectively, is evidenced with increasing x, in keeping with the dilution of magnetic $4d^3$ Ru^{5+} by diamagnetic Ta^{5+}. Similar results are observed upon substitution of Sn^{4+} and Nb^{5+} for Ru in $RuSr_2GdCu_2O_8$[10,11] and $RuSr_2Eu_{1.2}Ce_{0.8}Cu_2O_{10-\delta}$.[12] The Ru spin order induces long-range antiferromagnetism in the CuO_2 plane[9] (this long-range antiferromagnetic order is not normally observed for $p > 0.02$ in HTSC), so the reduction of T_{Ru} by Ta^{5+} substitution results in a decrease in T_{Cu}.

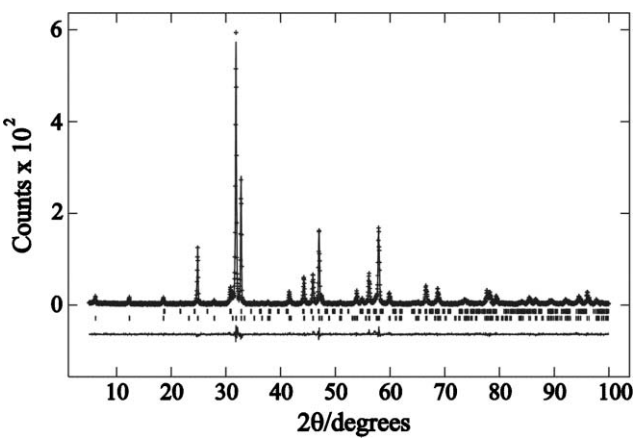

Fig. 1 Rietveld refinement fit to the powder X-ray diffraction pattern of $Ru_{0.6}Ta_{0.4}Sr_2Cu_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$; lower and upper reflection markers correspond to $Ru_{0.6}Ta_{0.4}Sr_2Cu_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$ and a trace of $Sr_2Nd(Ta,Ru)O_6$, respectively.

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† Electronic supplementary information (ESI) available: Table S1: Refined cell parameters and magnetic transition temperatures for the $Ru_{1-x}Ta_xSr_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$ solid solutions. Fig. S1: Temperature variation of zero-field cooled magnetic susceptibility for the $Ru_{1-x}Ta_xSr_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$ solid solutions. See DOI: 10.1039/b617872c

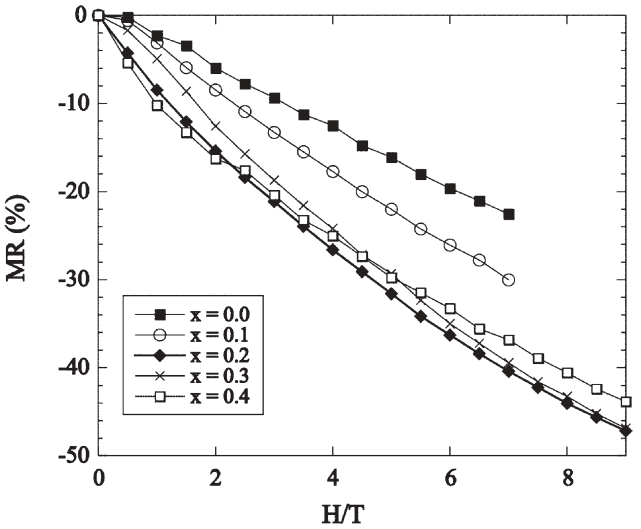

Fig. 2 The field evolution of MR for $Ru_{1-x}Ta_xSr_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$ recorded at 4 K.

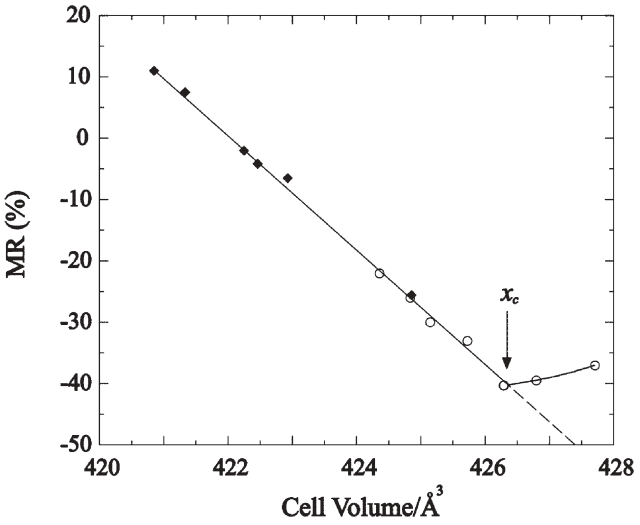

Fig. 3 Variation of MR_{7T}(4 K) with cell volume for $RuSr_2R_{1.1}Ce_{0.9}Cu_2O_{10-\delta}$ (R = Gd, Eu, $Eu_{0.9}Y_{0.2}$, Sm, $Sm_{0.9}Y_{0.2}$, $Nd_{0.9}Y_{0.2}$; diamonds) and $Ru_{1-x}Ta_xSr_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.30, 0.40; circles). A deviation from linearity is observed above x_c = 0.2.

Resistances were measured on sintered polycrystalline bars on a Quantum Design physical property measurement system up to H = 7 or 9 T (Fig. 2). All samples are semiconducting. An unexpected enhancement of −MR is observed as the Ta concentration increases; MR_{7T}(4 K) rises from −23 to −40% as x increases from 0 to 0.2. −MR does not saturate in fields up to 9 T and the value of MR_{9T}(4 K) = −47% for x = 0.2 is the largest reported value for ruthenocuprates so far. A slight reduction in the high field −MR is observed for higher Ta substitutions.

The large magnetoresistances of 1222 ruthenocuprates arise from hole transport in the antiferromagnetically ordered CuO_2 planes. As the Cu spin order is induced by Ru spin order, it is surprising that dilution of the Ru spin order with concomitant reductions of T_{Ru} and T_{Cu} results in a large enhancement of the magnetotransport properties up to 20% Ta substitution.

The likely explanation for the enhanced −MR in $Ru_{1-x}Ta_xSr_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$ lies in the sensitivity of Ru-1222 materials to lattice effects. Previous results[9] have shown an approximately linear change from positive to negative MR as the R^{3+} size increases in the series $RuSr_2R_{1.1}Ce_{0.9}Cu_2O_{10-\delta}$. From analysis of the temperature dependence of MR, the negative regime is assigned to two-dimensional transport within the CuO_2 planes, whereas hole conduction between planes gives rise to positive MR. Fig. 3 shows that the MR's for $Ru_{1-x}Ta_xSr_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$ up to x = 0.2 follow the same linear trend as the former $RuSr_2R_{1.1}Ce_{0.9}Cu_2O_{10-\delta}$ series with unit cell volume (equivalent correlations are observed with the a or c cell parameters, which vary monotonically across the two series). This suggests that the magnetotransport becomes more 'two-dimensional' and negative as the cell expands, due to some combination of the increasing separation of the metal oxide layers, and the flattening of the CuO_2 planes. Thus, the size effect of substituting Ta^{5+} for Ru^{5+} outweighs the electronic effects up to x = 0.2. Above this, −MR decreases and no longer follows the linear trend, showing that the dilution effects on the magnetic order become significant, so that x_c = 0.2 is the critical dilution limit for Ru magnetism. Neutron diffraction will be needed to determine whether long-range order of Ru and/or Cu spins changes at x_c, and study of higher x materials will be interesting to follow the evolution of magnetotransport properties.

In conclusion, we find that the large −MR previously observed in underdoped 1222 type ruthenocuprates can be enhanced by Ta substitution in the new series $Ru_{1-x}Ta_xSr_2Nd_{0.95}Y_{0.15}Ce_{0.9}Cu_2O_{10-\delta}$, as the size effect outweighs the dilution of the magnetic RuO_2 layers up to a critical concentration of x_c = 0.2. Substitution of even larger cations into underdoped 1222 ruthenocuprates could result in further enhancements of the low temperature magnetoresistance of these complex, multifunctional electronic materials.

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