

Magnetic Order from Cation Disorder in $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ Perovskite Oxides

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Disorder of magnetic cations usually suppresses long-range spin order: the Curie or Néel temperature drops rapidly, and a spin glass state often results at high disorder levels. It was therefore very surprising to discover, in a preliminary survey of the $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ system,¹ that the solid solution $\text{SrCr}_{0.4}\text{Ru}_{0.6}\text{O}_3$ was magnetically ordered at room temperature. Here we present further studies of materials in the $0.4 < x < 0.6$ region, which demonstrate that long-range magnetic order occurs up to 480 K, and a model that accounts for the robust magnetism. Four distinct exchange networks all cooperate to produce long-range magnetic order in these highly disordered materials.

SrRuO_3 and SrCrO_3 are both conducting perovskite oxides. SrRuO_3 orders ferromagnetically at $T_C = 160$ K,^{2,3} whereas SrCrO_3 shows electronic phase separation resulting from coupled orbital and antiferromagnetic order below 70 K. SrCrO_3 is synthesized under high pressure (> 4 GPa) conditions,^{4–6} and by using appropriate high pressures and temperatures, the entire series of $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ solid solutions was prepared.¹ No Cr/Ru cation order was observed at any x value. A small enhancement of the Curie temperature of the metallic Ru-rich materials, up to 188 K at $x = 0.15$, was observed, as reported in other studies.⁷ Materials in the $0.4 < x < 0.6$ region were found to be semiconducting, and long-range magnetic order up to at least 300 K was observed in the $x = 0.4$ sample.

Polycrystalline samples were prepared at pressures of 3.5 GPa in a piston cylinder apparatus or at 10 GPa in a Walker-

type multianvil press, as described previously.¹ High temperature SQUID magnetization measurements were made in a 1 T field. Neutron diffraction data were collected on the constant wavelength diffractometer D20 at ILL, Grenoble, France, and on the GEM time-of-flight spectrometer at the ISIS spallation source, U.K. (Figure 1). Data from the GEM detector banks at $2\theta = 90^\circ$, 64° , and 35° were Rietveld analyzed simultaneously using the GSAS suite.⁸ Refinement of the oxygen fractional occupancy showed the materials to be stoichiometric to an experimental uncertainty of less than 1%. Magnetic Bragg intensities were fitted by a G-type antiferromagnetic model, with moments at the Cr/Ru sites parallel to the hexagonal c -axis (equivalent to the [111] direction in rhombohedral or cubic settings).

A sharp (1/2 1/2 1/2) magnetic superstructure peak, which provides unambiguous evidence for bulk, long-range spin ordering, has been observed in the powder neutron diffraction patterns of $x = 0.4$, 0.5, and 0.6 samples (Figure 1). This is fitted by an antiferromagnetic (G-type) model in which each Cr/Ru spin is antiparallel to its six neighbors. Variable temperature studies of the (1/2 1/2 1/2) peak in the $x = 0.4$ and 0.6 materials show that their magnetic ordering temperatures are respectively 410 and 480 K. The saturated moments are respectively 1.7 and 1.8 μ_B and show a typical reduction from the ideal range of 2–3 μ_B depending on the degree of charge transfer as discussed later. The absence of any residual diffraction intensity at the (1/2 1/2 1/2) position above the magnetic transition confirms that no Cr/Ru cation order is present, as an alternating “double perovskite” arrangement of these cations would result in strong scattering at this point.

$\text{SrCr}_{0.4}\text{Ru}_{0.6}\text{O}_3$ was previously found to have a rhombohedral superstructure (space group $R\bar{3}c$) of the cubic perovskite arrangement. Peak broadenings in the neutron diffraction data for the $x = 0.5$ and 0.6 materials show that they are also rhombohedral at room temperature, and the same model was fitted to extract the lattice parameters. Such lattice distortions are sometimes caused by magnetic ordering and so the temperature variations of the distortion, quantified by the rhombohedral strain $\epsilon_H = [3(a - c/\sqrt{6})]/[2a + c/\sqrt{6}]$ for the hexagonal setting of the unit cell, and the ordered magnetic moment are compared for $\text{SrCr}_{0.6}\text{Ru}_{0.4}\text{O}_3$ in Figure 2. The strain goes to zero at the rhombohedral to cubic structural transition which is found to occur at 340 K, whereas the moment vanishes at the 480 K magnetic transition. Hence the two transitions are not coupled, and so the rhombohedral distortion is purely a structural transition at which the Cr/RuO₆ octahedra tilt cooperatively.

The changes of slope in the inverse magnetic susceptibilities in Figure 3 also confirm the magnetic ordering transitions in the $x = 0.4$ and 0.6 $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ samples, although the transition temperatures are not precisely located. The downturn in inverse susceptibility (increase in magnetization)

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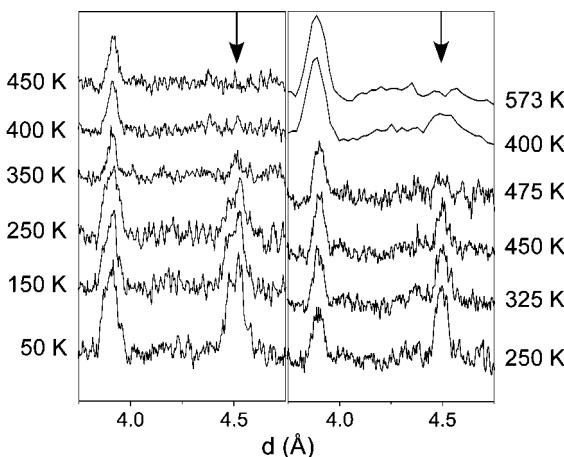


Figure 1. Powder neutron diffraction data for $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ solid solutions, showing the persistence of the $(1/2\ 1/2\ 1/2)$ magnetic superstructure peak (arrowed) to high temperatures. Spectra in the left column are for $x = 0.4$ (GEM diffractometer), the top two in the right column are for $x = 0.5$ (D20), and the remainder are for $x = 0.6$ (GEM). The lack of intensity at the $(1/2\ 1/2\ 1/2)$ position in the top two high temperature spectra confirms the absence of Cr/Ru cation order.

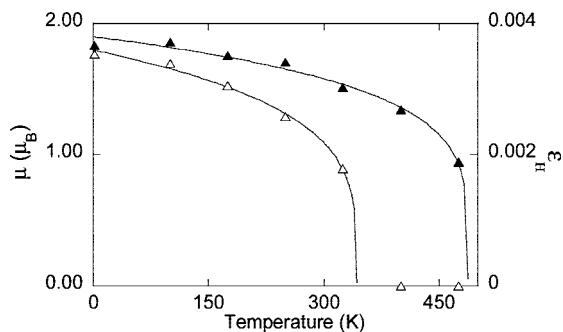


Figure 2. Thermal variation of the magnetic moment (μ , left scale) and rhombohedral strain (ϵ_H , right scale) for $\text{SrCr}_{0.6}\text{Ru}_{0.4}\text{O}_3$.

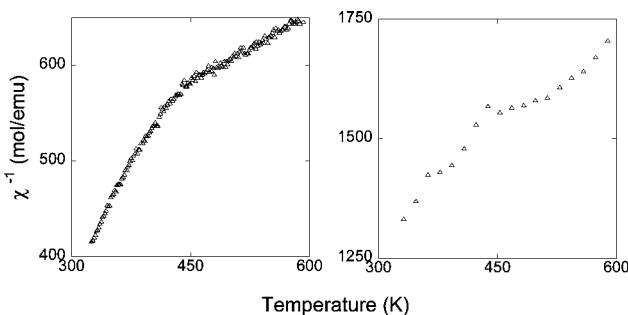
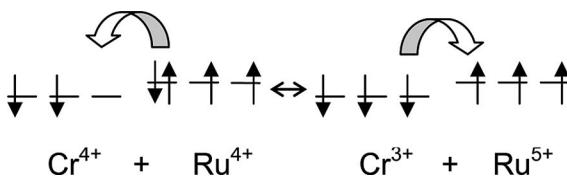


Figure 3. High temperature inverse magnetic susceptibilities for $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ ($x = 0.4$, left, and $x = 0.6$, right). Their respective paramagnetic moments in the $450\text{--}550\text{ K}$ region are 4.0 and $3.7\ \mu_B$, consistent with a substantial charge transfer toward $S = 3/2\ \text{Cr}^{3+}/\text{Ru}^{5+}$.

below the transition shows that the order is not strictly antiferromagnetic, as a small magnetization ($<0.001\ \mu_B$) develops. This is consistent with the magnetic model described below.

The above results demonstrate that antiferromagnetic Cr/Ru spin order occurs at high temperatures (410–480 K) throughout the insulating $x = 0.4\text{--}0.6$ region of the $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ system. The magnetic ordering temperatures are remarkable when compared against those for simple, well-ordered Cr or Ru oxides. The commercial ferromagnet

Scheme 1. Facile Transfer of Down-Spin t_{2g} Electrons between Up-Spin Ru and Down-Spin Cr Ions



CrO_2 has $T_C = 400\text{ K}$ ⁹ while insulating Cr^{3+} oxides order at lower temperatures, for example, $T_N = 310\text{ K}$ for Cr_2O_3 , and the perovskite LaCrO_3 has $T_N = 280\text{ K}$.¹⁰ Spin order in simple Ru oxides occurs far below room temperature; conducting SrRuO_3 has $T_C = 160\text{ K}$ while insulating antiferromagnetic Ru oxides again have lower transition temperatures. Even well-ordered double perovskites of first row transition metals and Ru, in which the two magnetic ions have an alternating arrangement, have low transition temperatures, for example, $\text{La}_2\text{CoRuO}_6$ ¹¹ and $(\text{LaSr})\text{CoRuO}_6$ ¹² have $T_N = 25$ and 85 K , respectively. These comparisons demonstrate that the high ordering temperatures in $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ cannot be ascribed to the sum of cooperative Cr–Cr, Cr–Ru, and Ru–Ru superexchange interactions but instead that a distinctive electronic interaction between Cr and Ru operates.

High Curie temperatures are found in ferrimagnetic Cr double perovskites Sr_2CrBO_6 ($T_C \approx 450, 500, 635$, and 700 K for $\text{B} = \text{Mo, W, Re, and Os}$, respectively),^{13–16} so it is likely that the hypothetical $\text{B} = \text{Ru}$ analogue would have a similarly high Curie temperature. These materials are similar to the magnetoresistive material $\text{Sr}_2\text{FeMoO}_6$ ($T_C = 440\text{ K}$)¹⁷ and are half-metallic, spin polarized conductors (the conduction electrons all have the same spin direction). However, the long-range ordering of the Cr and B cations is essential to stabilize this electronic structure. Intersite disorder of the magnetic cations rapidly suppresses the conductivity and T_C , so it is very surprising that high ordering temperatures are found in the fully cation-disordered $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ materials near $x = 0.5$.

SrCrO_3 and SrRuO_3 both contain tetravalent transition metal cations, but when these are mixed in the solid solutions, their different redox properties lead to electron transfer from ruthenium to chromium. The electronic states are thus intermediate between the $\text{Cr}^{4+}/\text{Ru}^{4+}$ and $\text{Cr}^{3+}/\text{Ru}^{5+}$ combinations. Electron transfer is facilitated when the Cr and Ru majority spins are coupled antiferromagnetically, as shown in Scheme 1. The total number of up and down spins

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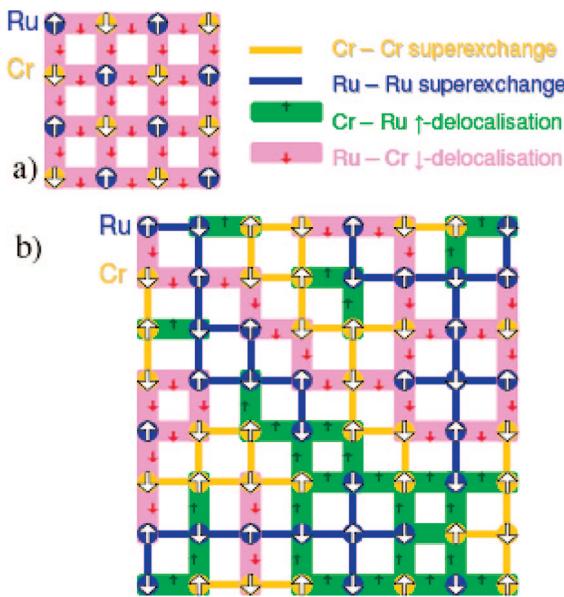


Figure 4. Two-dimensional representations of the M–O–M magnetic interactions in Cr,Ru perovskites. Part a represents a hypothetical, cation-ordered $\text{Sr}_2\text{CrRuO}_6$ double perovskite with all interactions mediated by the transfer of down-spin electrons as in Scheme 1 - this material would be half-metallic. Part b shows the interactions in cation-disordered $\text{SrCr}_{0.5}\text{Ru}_{0.5}\text{O}_3$, where four distinct networks operate, as described in the text.

is equal whatever the degree of $\text{Cr}^{4+}/\text{Ru}^{4+} \leftrightarrow \text{Cr}^{3+}/\text{Ru}^{5+}$ charge transfer. Hence, if a perfectly ordered alternating array of Cr and Ru were present, as in the hypothetical double perovskite $\text{Sr}_2\text{CrRuO}_6$, then this would give rise to the “half-metallic antiferromagnet” (HMAF) scenario¹⁸ (more correctly a “half-metallic compensated ferrimagnet”) which remarkably exhibits spin-polarized conduction (by down spins as shown in Scheme 1) while having no net magnetization. In this arrangement all Cr and Ru spins would contribute to a single, down-spin delocalized exchange network, as shown in Figure 4a.

Although no long-range Cr/Ru cation order is evident in $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ and the 0.4–0.6 materials are nonmetallic, the high magnetic ordering temperatures reveal that the spin-polarized mechanism of Scheme 1 is at least operating locally. A model that accounts for the magnetic properties is shown in Figure 4b. A cubic array of sites randomly occupied by Cr and Ru ions gives rise to Cr–O–Cr, Ru–O–Ru, and Cr–O–Ru linkages. Electron transfer gives near- t_{2g}^3 configurations on both ions, and orbital overlap with O:2p_π orbitals results in antiferromagnetic Cr–O–Cr and Ru–O–Ru superexchange interactions, without electron delocalization, as found in simple Cr³⁺ and Ru⁵⁺ oxides.

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Cr–O–Ru interactions are also antiferromagnetic, but much more strongly so, as they are mediated by the spin-polarized delocalization mechanism shown in Scheme 1.

Compared to the hypothetical double perovskite $\text{Sr}_2\text{CrRuO}_6$, half of the Cr/Ru cations in the fully disordered $\text{SrCr}_{0.5}\text{Ru}_{0.5}\text{O}_3$, are in the “correct” positions, while the other half are in the antisite (“inverse”) positions. t_{2g} electrons of one spin polarity will be delocalized through Cr–O–Ru interactions between the “correct” ions, while the opposite spin electrons are delocalized between the “inverse” sites. Hence, the disordered cation array in $\text{SrCr}_{0.5}\text{Ru}_{0.5}\text{O}_3$ results in equal numbers of four distinct interactions as shown in Figure 4b; Cr–O–Cr and Ru–O–Ru superexchange and Cr–O–Ru with either spin-up or spin-down polarization. In a fully disordered $x = 0.5$ composition, each of the four interactions accounts for 25% of the exchange couplings, so all are below the percolation limit of 31% for a simple cubic lattice. Hence, the two delocalized, spin-polarized networks are not sufficiently connected to result in bulk electronic conductivity. However, all four magnetic networks are cooperative, and with 50% of the interactions being strongly antiferromagnetic, robust long-range spin order is supported. This model is antiferromagnetic in zero field, but an applied field may reorient some of the smaller, more weakly coupled regions within the disordered matrix, leading to the small ferromagnetic response observed in the susceptibility measurements (Figure 3).

The $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ solid solutions represent a new paradigm of robust magnetic order arising within a highly disordered yet magnetically cooperative network comprising several (four) physically distinct interactions. They show that having strong local interactions and avoiding competition and frustration may be more important than promoting structural order. The presence of strong Cr–O–Ru magnetic exchange, which reveals the presence of spin-polarized electron delocalization, is particularly surprising. Until now such interactions have only been considered to arise from the electronic structures of well-ordered double perovskites, but it is now evident that these interactions can operate locally even in the absence of long-range cation order. This interaction requires good energy matching between the d-states of the two transition metals (band overlap), and this should be considered an important factor even in the design of magnetic insulators. Further work will aim to induce partial Cr/Ru ordering in $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ in order to create an imbalance of the up- and down-spin conducting networks, enabling significant spin polarization to be observed.

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