Strong ferromagnetic coupling in the K_2NiF_4-structured oxide $La_{0.8}Sr_{1.2}Mn_{0.6}Rh_{0.4}O_4$

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Substitution of diamagnetic Rh[III] into the antiferromagnet LaSrMnO$_4$ produces the first example of a K_2NiF_4 ($n = 1$ Ruddlesden–Popper) oxide with strong ferromagnetic interactions—in 50 kG at 5 K the magnetisation of $La_{0.8}Sr_{1.2}Mn_{0.6}Rh_{0.4}O_4$ is close to saturation at 2.50 μ_B per Mn cation; the bulk magnetisation stems from the alignment by the magnetic field of ferromagnetic (Mn/Rh)O$_2$ sheets which are not magnetically ordered along [001] in zero applied field.

There has been a resurgence of interest in ferromagnetic oxides owing to the strong coupling between spin ordering and charge transport found in the $La_{1-x}Sr_xMnO_3$ perovskites which display colossal magnetoresistance (MR).[1] This suppression of the zero-field resistance in an applied field can be as large as $100\Delta\rho/\rho(H=0) = 99.9\%$ in fields of over 50 kG, but achieving significant MR in the low fields required for information storage applications has proved a difficult barrier for the current generation of materials. Increasing attention[2] is now being paid to the intrinsically layered $n = 2$ members of the Ruddlesden–Popper (RP) $A_{n+1}B_nO_{3n+1}$ series, for example $La_{1.8}Sr_{1.2}Mn_2O_7$,[3] which display MR in fields as low as 3 kG owing to the small barrier to the field aligning the magnetisation between the perovskite blocks in the layer stacking sequence. Ferromagnetism has not yet been demonstrated in the two-dimensional $Sr_{1+x}La_{1-x}MnO_4$ $n = 1$ member of the RP series, with the Sr_2MnO_4[4] and LaSrMnO$_4$ end-members being antiferromagnets while the Mn[III/IV] solid solutions are spin glasses.[5] Here, we demonstrate that substitution of formally diamagnetic Rh[III] into $Sr_{1.2}La_{0.8}MnO_4$ produces a material with short-range spin ordering in zero field which achieves a moment of 2.50 μ_B per manganese in a 50 kG field.

Preliminary investigation of the Sr–La–Rh–Mn–O phase field at the $n = 1$ RP composition under air and N$_2$ atmospheres indicated that our initial target composition LaSrMn$_{0.6}$Rh$_{0.4}$O$_4$ was strongly polyphasic, with La_2O_3/La(OH)$_3$ impurities showing that a higher Sr/La ratio, and thus metal oxidation state, was required for phase purity. This is consistent with the reported failure to prepare SrLaRhO$_4$[6] in contrast with $Sr_{1.2}La_{0.8}RhO_4$. $Sr_{1.2}La_{0.8}Mn_{0.6}Rh_{0.4}O_4$ was therefore prepared by reaction of Rh$_2$O$_3$, MnO$_2$, SrCO$_3$ and La$_2$O$_3$ at 1000, 1200 and 1250 °C for 24 h each, followed by 4 further days at 1250 °C, all firings being performed in air. This produced a material of 99.5% $n = 1$ RP phase with $a = 3.88761(6)$, $c = 12.5176(2)$ Å. The only impurity visible to X-ray powder diffraction is 0.5% by mass La$_2$O$_3$, a diamagnetic material which will not interfere with magnetic measurements.

Magnetisation *vs.* temperature measurements† made in an applied field of 100 G suggest (Fig. 1) complex magnetism with the possibility of magnetic long range order. Hysteresis is apparent between the ZFC and FC data below an anomaly in M/H at 180 K, and below 35 K both the ZFC and FC magnetisations rise sharply, with the ZFC showing a maximum at 13.5 K. Data collected in a field of 1000 G showed similar features although the ZFC magnetisation continued to rise down to 5 K. The $M(H)$ magnetisation isotherm at 5 K (Fig. 2) indicates strong ferromagnetic coupling, with a moment approaching saturation at 2.50 μ_B per Mn at 5 K; the

magnetisation remains a non-linear function of field to temperatures in excess of 100 K although saturation is clearly not reached in 50 kG. Neutron powder diffraction data† (D2B, ILL) are consistent with the idea of a phase exhibiting strong ferromagnetic coupling but without the long-range magnetic order suggested by the magnetometry experiments. Rietveld-refinement[7] of data collected at both 290 and 1.7 K proceeded smoothly (at 290 K, $R_{wpr} = 5.35\%$, $\chi^2 = 2.4$; at 1.7 K, $R_{wpr} = 5.14\%$, $\chi^2 = 1.6$) within a model which considered only nuclear scattering from the $La_{0.8}Sr_{1.2}Mn_{0.6}Rh_{0.4}O_4$ composition, thus
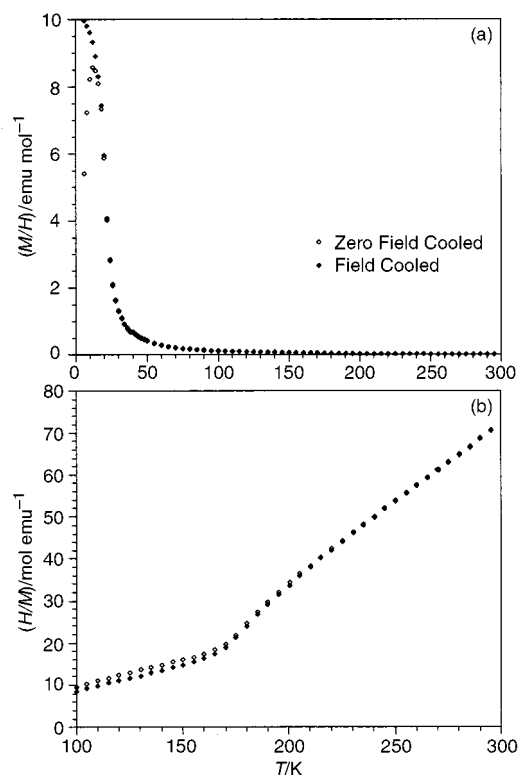

Fig. 1 (a) Molar magnetic susceptibility (M/H) and (b) inverse susceptibility (H/M) of $Sr_{1.2}La_{0.8}Mn_{0.6}Rh_{0.4}O_4$ measured in a field of 100 G: field cooled (FC) and zero-field cooled (ZFC) data are shown as filled and empty symbols, respectively.
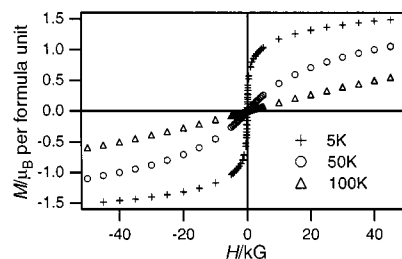

Fig. 2 Magnetisation per formula unit as a function of field and temperature for FC $Sr_{1.2}La_{0.8}Mn_{0.6}Rh_{0.4}O_4$. At 5 K, $H_{M=0} = 72 \pm 5$ G, $M_{H=0} = 0.15 \pm 0.02$ μ_B.
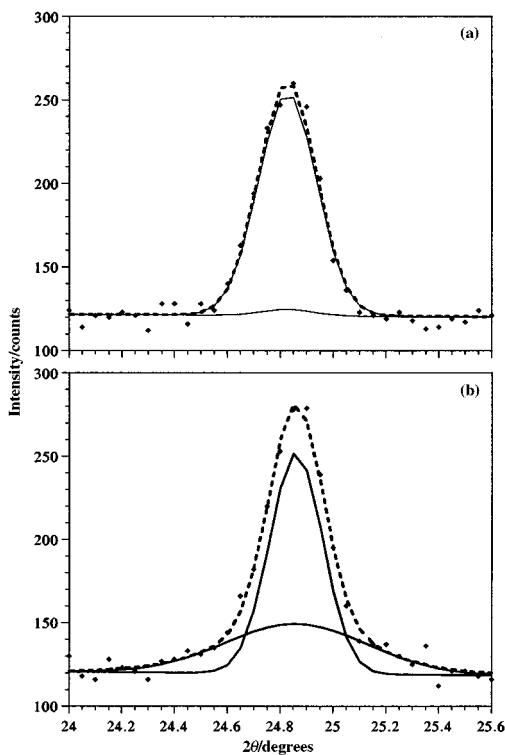
Fig. 3 Neutron powder diffraction measurements on $Sr_{1.2}La_{0.8}Mn_{0.6}Rh_{0.4}O_4$ at (*a*) 290 K and (*b*) 1.7 K, showing the two component fit (solid lines) to the 101 reflection: the extra broad diffuse scattering observed at 1.7 K is suggestive of magnetic short range ordering within the 2D layers.

values are therefore nonsensical. The ferromagnetic Weiss constant of +106 K is however consistent with the lower temperature magnetisation and neutron scattering measurements.

Substitution of diamagnetic low-spin Rh^{III} has a surprising effect on the magnetism of manganates having the K_2NiF_4 structure. Although the presence of both Mn^{III} and Mn^{IV} allows ferromagnetic double and super exchange, and the same oxidation state (3.33) produces ferromagnetism in the $n = \infty$ Mn-only perovskites,[8] in the pure 2D manganate series, oxidation of the antiferromagnet $La_{1-x}Sr_{1+x}MnO_4$ beyond the +3.2 oxidation state results in the suppression of anti-ferromagnetic ordering but not in the onset of ferromagnetism:[9] $La_{0.7}Sr_{1.3}MnO_4$ is a canonical spin-glass showing the classical FC/ZFC magnetisation divergence. The substitution of Rh on the B sites clearly enhances ferromagnetic Mn–Mn coupling in $Sr_{1.2}La_{0.8}Mn_{0.6}Rh_{0.4}O_4$, at least within the $(Mn/Rh)O_2$ layers perpendicular to [001]. One interpretation of the currently available data is that each individual $(Mn/Rh)O_2$ sheet develops a spontaneous magnetisation when 2D magnetic ordering occurs at 180 K, with the resultant magnetic moments being aligned by an applied field; saturation is approached in 50 kG at 5 K, and 100 G has a significant effect below 35 K. However, the magnetic consequences of ferromagnetic $n = \infty$ intergrowths in RP phases are well known[10] and further measurements are necessary before firm conclusions can be drawn. Increasing the Mn concentration further above the 2D square site percolation limit of 0.5 and optimisation of the mean metal oxidation state are important future improvements on this new recipe for generating ferromagnetic interactions in 2D manganates.

Notes and references

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conclusively demonstrating the absence of magnetic long-range order. Close inspection of the low-angle 002 and 101 reflections (which are sensitive to magnetic scattering owing to the angular dependence of the form factor) shows that the latter (Fig. 3), but not the former, develops weak but well defined broad, extra scattering at low temperature. The profile of the 101 reflection at 290 K can be fitted by two pseudo-Voigt functions in the ratio 0.966:0.034; the principal peak has a negligible Lorentzian component. At 1.7 K the ratio is 0.584:0.416; the stronger component is again essentially Gaussian but the weaker, broader component has a significant Lorentzian contribution. The growth in the latter component of the 101, but not the 002, is consistent with ferromagnetic correlations developing within but not between the two-dimensional $(Mn/Rh)O_2$ sheets.

The oxidation state of the Rh substituent at the electronically active B site is not directly defined by our measurements, but consideration of the established oxide chemistries of Mn and Rh leads to the assumption that Rh is present solely as Rh^{III} (low spin $t_{2g}{}^6$), resulting in a mean Mn oxidation state of $+ 3.33$. The measured value of the magnetisation as it approaches saturation is a significant but reduced fraction of that (3.66 μ_B per Mn) to be expected from a fully aligned array of Mn cations in this oxidation state; the cause of the difference has yet to be determined. The presence of a transition at 180 K restricts the temperature range which can be analysed using the Curie–Weiss law and the enforced proximity to a phase transition will limit the validity and accuracy of the value of 5.54 μ_B per Mn derived for the effective magnetic moment in 100 G by fitting in the range $250 \leq T/K \leq 300$; comparisons with calculated