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Ferromagnetic ordering in the perovskite $La_{1.5}Sr_{0.5}RhMnO_6$

B. Bakowski,[a] P. D. Battle,*[a] E. J. Cussen,[a] L. D. Noailles,[a] M. J. Rosseinsky,*[a] A. I. Coldea[b] and J. Singleton[b]

[a] *Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: peter.battle@chem.ox.ac.uk; matthew.rosseinsky@chem.ox.ac.uk*
[b] *Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford, UK OX1 3PU*

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The non-metallic, magnetically-dilute, cation-disordered perovskite $La_{1.5}Sr_{0.5}RhMnO_6$ is shown to be a soft ferromagnet with T_C = 105 K with an ordered magnetic moment of 3.56(8) μ_B per Mn.

There has been a resurgence of interest in ferromagnetic oxides due 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] The Mn(III) perovskite $LaMnO_3$ is an antiferromagnetic insulator below 143 K, but the partial oxidation to Mn(IV) which occurs when Sr^{2+} is substituted for La^{3+} changes the electronic properties markedly. At low temperatures, $La_{1-x}Sr_xMnO_3$ is a ferromagnetic insulator for $0.1 \leqslant x \leqslant 0.15$ and a ferromagnetic metal for $0.15 \leqslant x \leqslant 0.6$.[2] The temperature of the transition to the magnetically ordered phase is a function of x, but for $x \geqslant 0.15$ it is coincident with the metal–insulator transition, and the highest MR effects are seen around this point. The 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. The present lack of understanding of the MR effect in perovskites has hindered attempts to overcome this barrier; although it is agreed that double exchange is an important factor, it is also recognised that it is not the only factor.[3] A number of strategies have been adopted in order to enhance our understanding of the electronic properties relevant to MR in oxides, with particular emphasis on the magnetic behaviour of mixed-valence manganates. We demonstrate here that ferromagnetism is retained in $La_{1.5}Sr_{0.5}RhMnO_6$, a non-metallic perovskite with a 50% diluted Mn sublattice where the mean oxidation state is $Mn^{3.5+}$.

Preliminary investigation of the $La_{2-x}Sr_xRhMnO_6$ system in air showed that a sample with the nominal composition La_2MnRhO_6 was polyphasic, with La_2O_3/$La(OH)_3$ impurities being apparent in diffraction patterns. However, we were able to prepare monophasic perovskite samples in the system $La_{2-x}Sr_xRhMnO_6$ for x = 0.2, 0.5 and 0.6, that is by increasing the mean oxidation state of the transition metal; the composition $La_{1.5}Sr_{0.5}RhMnO_6$ will be the focus of this communication. Samples were prepared by the reaction of pre-dried La_2O_3, $SrCO_3$, MnO_2 and Rh_2O_3 for 24 h at 800 °C, followed by 48 h at 1000 and 1200 °C and ending with 96 h at 1400 °C. The products were quenched in liquid nitrogen after the final heating to ensure the formation of a highly crystalline, homogeneous product. The X-ray diffraction patterns of samples prepared in this way showed only the peaks expected from a $GdFeO_3$ - like pseudo-cubic perovskite.[4]

Magnetisation *versus* temperature measurements† made in an applied field of 100 G suggested that all three compositions order ferromagnetically, with T_C = 95, 105 and 105 K for x = 0.2, 0.5 and 0.6 respectively. The data collected on the composition x = 0.5 are shown in Fig. 1; Curie–Weiss behaviour is not observed within the measured temperature range, and hysteresis is apparent between the ZFC and FC data below T_C. The $M(H)$ magnetisation isotherm at 5 K is characteristic of a soft ferromagnet, with a saturation magnetisation of 3.9(1) μ_B per Mn being achieved in 10 kG at 5 K. Neutron powder diffraction data† (D2B, ILL) collected on the $x = 0.5$ composition prove that this sample exhibits long range ferromagnetic ordering at low temperature. Rietveld[5] refinement of data collected at 290 K proceeded smoothly (R_{wpr} = 4.97%, χ^2 = 1.96) within a model which considered only nuclear scattering; there was no evidence of Mn/Rh cation ordering over the six-coordinate sites. Successful analysis (R_{wpr} = 5.30 %, χ^2 = 2.0) of the data collected at 1.7 K required the inclusion of an ordered magnetic moment of 3.56(8) μ_B on the Mn cations; the atomic moments align along the [010] axis. Four-probe dc conductivity measurements showed (Fig. 2) that the compound is non-metallic, albeit with a varying activation energy, both above and below the Curie temperature.

The oxidation states of the different cations which occupy the electronically active B site are 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

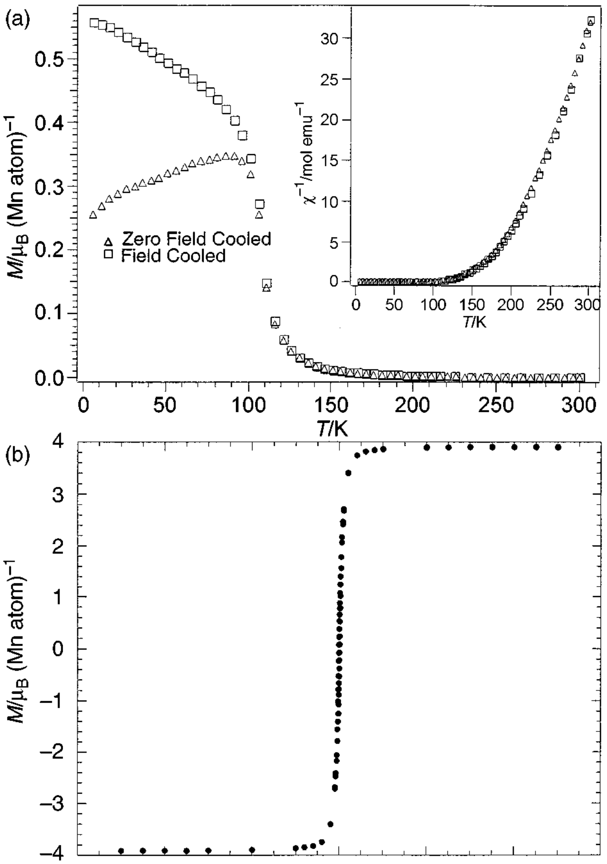

Fig. 1 (a) Temperature dependence of magnetisation and (inset) inverse molar susceptibility of $La_{1.5}Sr_{0.5}RhMnO_6$, measured in a field of 100 G. (b) Magnetisation as a function of field at 5 K for $La_{1.5}Sr_{0.5}RhMnO_6$.

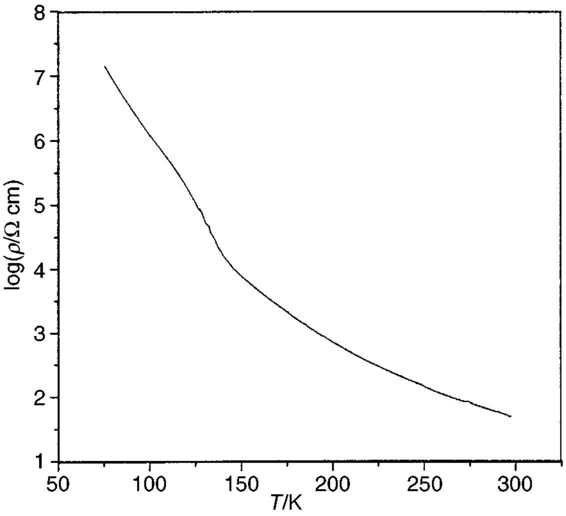

Fig. 2 Temperature dependence of the electrical resistivity of $La_{1.5}Sr_{0.5}RhMnO_6$.

oxidation state of +3.5 in $La_{1.5}Sr_{0.5}RhMnO_6$. This is the same oxidation state that occurs in $La_{0.5}Sr_{0.5}MnO_3$, a ferromagnetic, metallic composition with $T_C \approx 350$ K. Although the ferromagnetism of the Rh-free sample has been ascribed to double exchange, the non-metallic nature of the $x = 0.5$ composition rules out the conventional form of that mechanism in $La_{1.5}Sr_{0.5}RhMnO_6$. Our results suggest that ferromagnetic superexchange interactions dominate the magnetic coupling in the 1:1 random array of localised-electron Mn^{3+} and Mn^{4+} cations, and that they are strong enough to produce long-range magnetic order at 105 K, even with 50% dilution by a diamagnetic cation. The magnitude of the ordered magnetic moment determined by neutron diffraction is as large as can be expected for a mean oxidation state of $Mn^{3.5+}$. The Goodenough–Kanomori rules[6] would then suggest that ferromagnetic σ superexchange between Mn^{3+} and Mn^{4+} cations is a very strong effect in this compound, and that it outweighs the antiferromagnetic interactions between pairs of like ions. However, this argument ignores the effect that local atomic displacements will have on the sign of the magnetic exchange constants. Although our neutron diffraction data indicate that the six-coordinate environment of the disordered transition metal species is an essentially regular octahedron, this is a description of the average site, and the temperature-dependence of the anisotropic thermal parameters indicates that static disorder is present, most noticably on the O(1) sublattice. We must therefore guard against over-simplification of the problem. The behaviour of $La_{1.5}Sr_{0.5}RhMnO_6$ contrasts sharply with that of another magnetically-dilute, mixed-valence perovskite, $Sr_2FeTiO_{5.81}$, which shows spin-glass behaviour at low temperatures.[7] In this and other related materials, the absence of ordering in the cation distribution has been held responsible for the lack of long-range magnetic order. It is therefore reasonable to postulate that in the present case, Mn^{3+}/Mn^{4+} ordering does occur, but over a distance scale too short to be detected in a neutron diffraction experiment. This should be investigated using the appropriate experimental techniques. An alternative explanation to that based on superexchange could lie in the relatively extensive nature of the Rh 4d orbitals, which might allow significant Mn–Rh–Mn coupling, leading to the partial delocalisation of an e_g electron and hence ferromagnetic coupling. This model effectively removes the distinction between Mn^{3+} and Mn^{4+} oxidation states and invokes double exchange over a limited volume. Although we are not yet able to elucidate in detail the cause of ferromagnetism in $La_{1.5}Sr_{0.5}RhMnO_6$, it is a significant observation to be considered when discussing the relative importance of double exchange and superexchange in oxides which show colossal MR.

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Notes and references

† X-Ray powder diffraction data were recorded using a Siemens D5000 diffractometer with Cu-Kα_1 radiation. Magnetisation measurements were made with a Quantum Design MPMS5 SQUID magnetometer on samples contained within gelatin capsules. Electrical resistivity measurements were made on a sintered pellet using graphite-paste contacts and a current of $\leqslant 10$ μA. Neutron powder diffraction data were recorded at $\lambda = 1.59$ Å on the powder diffractometer D2B with the sample contained within a vanadium can in an ILL 'Orange' cryostat at both 1.7 and 290 K. Space group *Pbnm*, Sr/La on $x,y,1/4$, Mn/Rh on 1/2,0,0, O1 on $x,y,1/4$, O2 on x,y,z. At 290 K, $a = 5.5544(1)$, $b = 5.5216(1)$, $c = 7.8258(2)$ Å, $x_{Sr/La} = -0.0051(4)$, $y_{Sr/La} = 0.0286(3)$, $x_{O(1)} = 0.0703(5)$, $y_{O(1)} = 0.4914(4)$, $x_{O(2)} = -0.2831(3)$, $y_{O(2)} = 0.2819(3)$, $z_{O(2)} = 0.0363(2)$; Mn/Rh–O(1) = 1.9956(5) × 2, Mn/Rh–O(2) = 1.989(2) × 2, 2.001(2) Å × 2. At 1.7 K, $a = 5.54476(9)$, $b = 5.5191(1)$, $c = 7.8161(2)$ Å

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