

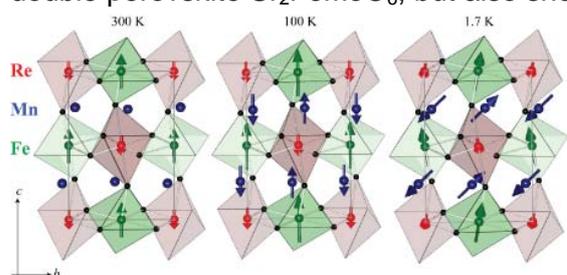
## New chemistry and physics in magnetic oxides

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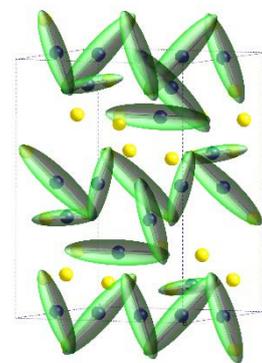
Early concepts of magnetism emerged from studies of magnetic minerals, notably magnetite ( $\text{Fe}_3\text{O}_4$ ). Today we know of many types of magnetism and magnetic materials, but transition metal oxides remain important as they are based on abundant, non-toxic elements and can offer large magnetisations at room temperature. They have also been investigated intensively for coupling of magnetism to other phenomena, for example, to electronic conductivity for spintronic materials; to ferroelectricity in multiferroics; and to lattice thermodynamics in magnetocalorics. This talk will present new chemical and physical aspects of spintronic oxides.

'Manganites' are manganese oxides such as  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  where mixing of large La and Sr cations at the A sites of the  $\text{ABO}_3$  perovskite structure induces ferromagnetism and electronic conductivity. High pressure has recently been used to synthesise new 'A-site manganites' with  $\text{Mn}^{2+}$  cations at the A-sites,<sup>1,2</sup> such as  $\text{Mn}_2\text{FeReO}_6$  which has a high Curie temperature of 520 K and similar ferrimagnetic and spin-polarised conducting properties to the much-studied magnetoresistive double perovskite  $\text{Sr}_2\text{FeMoO}_6$ , but also shows a novel switch from negative to large



positive magnetoresistances at low temperatures driven by  $\text{Mn}^{2+}$  spin ordering. Investigation of possible rare earth (R) analogues has led to discovery of a new 'double double perovskite' type  $\text{MnRMnSbO}_6$  ( $\text{R} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ) with simultaneous 1:1 cation order at both A and B sites.<sup>3</sup>

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is the original magnetic material and undergoes the complex Verwey structural distortion below 125 K. The nature of the ground state was unclear for over 70 years until determination of the full superstructure showed that  $\text{Fe}^{2+}/\text{Fe}^{3+}$  charge ordering occurs with a pronounced orbital ordering of  $\text{Fe}^{2+}$  states, but an unexpected localization of electrons in linear, three-Fe 'trimeron' units was also discovered.<sup>4</sup> Trimerons are examples of orbital molecules, weakly bonded clusters of transition metal ions within an orbitally ordered solid.<sup>5</sup> Recent studies have explored orbital molecule orders in other systems and also in natural magnetite.<sup>6</sup> The complexity of the magnetite superstructure has also led us to explore a simple ellipsoidal approach for analysing polyhedral distortions in coordination complexes.<sup>7</sup>



<sup>1</sup> A. M. Arévalo-López, G. M. McNally, J. P. Attfield, *Angew. Chem.* 2015, **54**, 12074.

<sup>2</sup> A. M. Arévalo-López, F. Stegemann, J. P. Attfield, *Chem. Comm.* 2016, **52**, 5558.

<sup>3</sup> E. Solana-Madruga, Á. M. Arévalo-López, A. J. Dos Santos-García, E. Urones-Garrote, D. Ávila-Brandé, R. Sáez-Puche, J. P. Attfield, *Angew. Chem.* 2016, **55**, 9340.

<sup>4</sup> M.S. Senn, J.P. Wright, J.P. Attfield, *Nature* 2012, **481**, 173.

<sup>5</sup> J. P. Attfield, *Applied Physics Letters Materials* 2015, **3**, 041510.

<sup>6</sup> G. Perversi, J. Cumby, E. Pachoud, J. P. Wright, J. P. Attfield, *Chem. Comm.* 2016, **52**, 4864.

<sup>7</sup> J. Cumby, J. P. Attfield, *Nature Comm.* 2017, DOI: 10.1038/ncomms14235.