

Understanding colossal magnetoresistance

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Neutron studies are helping researchers explore a recently-discovered electronic effect that will lead to new devices

The complex manganites are derived from a structure consisting of a rare-earth element such as lanthanum combined with manganese and oxygen (LaMnO_3). These electrically conducting compounds have caused great excitement in the past decade because they show a huge change in resistivity when a magnetic field is applied. This colossal magnetoresistance (CMR) effect could be the key to the next generation of magnetic memory devices, magnetic-field sensors, or transistors.

Like their chemical cousins, the high-temperature superconductors (see p.14), they possess complicated electronic structures. Yet unravelling their behaviour – over a range of temperatures or in magnetic fields – is essential to understanding CMR and finding suitable CMR materials for commercial application.

Hidden electron orbitals

Our contribution to this active research area has been to investigate, in these materials, an attribute of electronic structure that has hitherto been difficult to probe experimentally – the electron orbitals. Electrons involved in chemical bonding have three defining properties laid down by quantum mechanics, their charge, spin and orbital. The orbital refers to the shape of the volume that the electron is likely to occupy (the electron cloud). In transition metals such as manganese, it is the outer 'd' orbitals that are involved in bonding and give heavy metal compounds their electronic and structural characteristics.

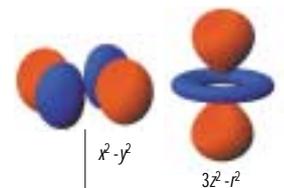
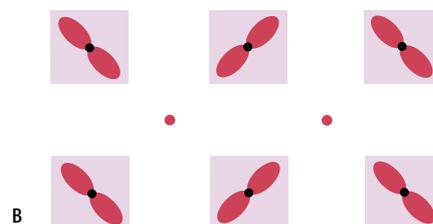
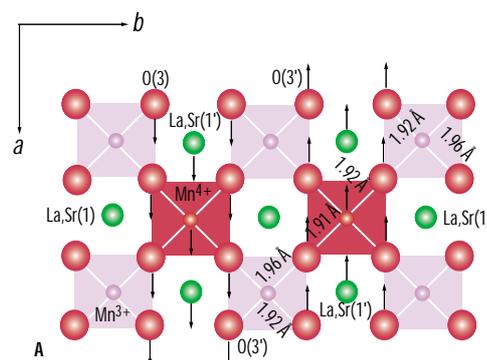
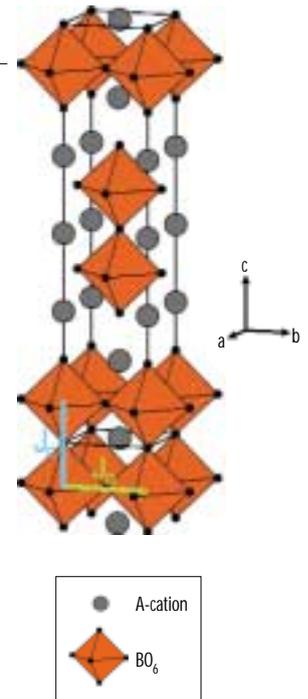
In the CMR manganites, the manganese atom is triply charged (Mn^{3+}) and is bound to six neighbouring oxygen atoms in an octahedral shape as shown in Figure 1. Mn^{3+} has one d electron involved in bonding. This 'valence' electron occupies one of two possible d orbitals, as shown in Figure 2. These orbitals are thought to be significant in CMR. Each can mix, or 'hybridise' with the oxygen orbitals to form bonding orbitals; each is geometrically different and is associated with differing bond lengths.

The lanthanum ions, which are also triply charged (La^{3+}), sit between the layers of the manganese-oxygen octahedra. If a percentage of the lanthanum ions is replaced with metal ions such as strontium (Sr^{2+}) which are doubly charged, then there is a redistribution of electrons resulting in the formation of some Mn^{4+} ions,

now with an empty d orbital (a hole). This is called 'hole-doping' and allows the remaining valence electrons to hop from manganese to manganese atom so that the material conducts like a metal. Furthermore, when the 30 or 40 per-cent hole-doped manganite is cooled below a certain temperature, the spins of these electrons align so that the material becomes ferromagnetic. It is this that increases the resistivity of the material because the aligned electrons scatter oppositely-aligned electrons trying to pass through.

Using a combination of X-ray and neutron diffraction, we investigated the interplay between the ordering of the spins, the charge and the orbital occupancy in the 50 per-cent hole-doped manganite ($\text{LaSr}_2\text{MnO}_7$). Neutron studies enabled us to measure the manganese-oxygen bond lengths, which indicated which d orbitals were occupied. We found that this compound has equal numbers of Mn^{3+} and Mn^{4+} ions arranged alternately, and a 'staggered' arrangement of bonding orbitals (see Figure 3) below 225K. At 170K this charge-orbital order 'melts' as antiferromagnetic order (spins alternately aligned) sets in. ■

1 The structure of lanthanum strontium manganite



3

The structure of 50 per-cent hole-doped lanthanum strontium manganite ($\text{LaSr}_2\text{Mn}_2\text{O}_7$), at a temperature of 165K, looking down through the manganese-oxygen octahedra. Neutron diffraction allowed us to determine the position of both manganese and oxygen atoms and thus the Mn–O bond distances. This revealed the ordering of the Mn^{3+} and Mn^{4+} ions (A) and the ordering of the hybridised orbitals (B)