

# Orbital order in manganites

Combined neutron and X-ray diffraction has revealed a new type of electronic behaviour in an important class of magnetic materials

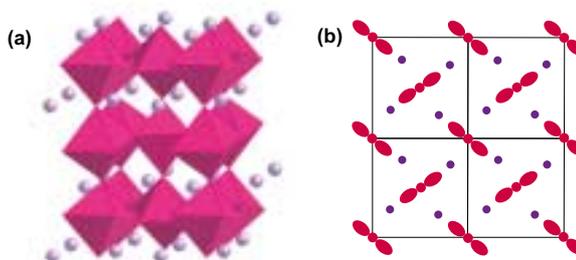
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**C**ompounds called manganites – derived from a structure consisting of a rare-earth element such as lanthanum combined with manganese and oxygen ( $\text{LaMnO}_3$ ) – have caused great excitement in the past decade because they show a huge change 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.

The key to this CMR effect is the manganites' complex electronic and magnetic structure, which depend subtly on how the outer 'd' electrons of the manganese atoms are arranged in their orbitals. In the parent lanthanum manganite, the triply-charged manganese atom ( $\text{Mn}^{3+}$ ) is bound to six neighbouring oxygen atoms in an octahedral shape (figure 1a). The  $\text{Mn}^{3+}$  ion has one electron involved in bonding; it occupies one of two possible d orbitals, which are geometrically different and are associated with differing bond lengths. The octahedral structure is thus actually slightly distorted. The lanthanum ions, also triply charged ( $\text{La}^{3+}$ ), sit between layers of manganese-oxygen octahedra.

If a percentage of the lanthanum ions is replaced with doubly-charged metal ions such as strontium ( $\text{Sr}^{2+}$ ), the electrons redistribute to give some  $\text{Mn}^{4+}$  ions with an empty d orbital (a hole). This 'hole-doping' allows the remaining 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.

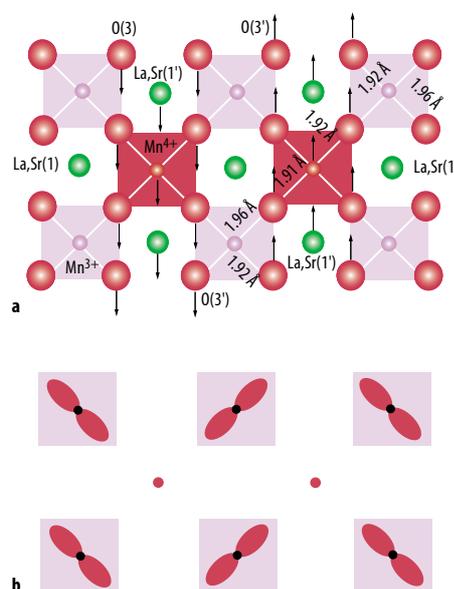
Using a combination of X-ray and neutron diffraction, we investigated the interplay between the ordering of the spins, the charge and the orbital occupancy in the 50 per-cent hole-doped, layered manganite ( $\text{LaSr}_2\text{Mn}_2\text{O}_7$ ). Neutron studies enabled us to measure the manganese-oxygen bond lengths, which indicated which d orbitals were occupied. We found that this compound has equal numbers of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions arranged alternately, and a 'staggered' arrangement of bonding orbitals (figure 2) below 225K. At 170K this charge-orbital order 'melts' as antiferromagnetic order sets in.



**Figure 1**  
(a) The structure of lanthanum manganite;  
(b) the staggered ordering of d orbitals

## An unusual transition

More recently, we have investigated the orbital ordering further, in the parent lanthanum manganite over a range of temperatures. The bonding d orbitals are again arranged in an alternate staggered pattern within each plane of manganese-oxygen octahedra (figure 1b), but unlike in  $\text{LaSr}_2\text{Mn}_2\text{O}_7$ , all the manganese ions are  $\text{Mn}^{3+}$  and have a bonding d orbital. The octahedra are distorted giving three different bond lengths. The compound retains this structure up to 750K – when something dramatic happens. The distortion disappears, the staggered arrangement of orbitals is lost, and the solid material abruptly contracts in volume. Such a transition in a solid, which depends purely on changes in the electronic arrangement, is rather unusual. We think that in the high-temperature, orbitally disordered state all the octahedra pack together more efficiently. This is similar to what happens when ice melts into water, although in that case the contraction is due to the water molecules losing positional order. ■



**Figure 2**  
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  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions (a) and the ordering of the bonding orbitals (b)