Unravelling structure and magnetism in strongly correlated systems

Doped $LaMnO_3$ compounds are a playground for the study of strong electronic correlations. Their remarkable properties under external magnetic field, such as the giant magneto-resistance in use in magnetic devices, is due to an intricate interplay between lattice, orbital and spin degrees of freedom. In this work we succeeded in decoupling the lattice and magnetic degrees of freedom leading to a new perspective on the fundamental processes that are in competition in these materials.

In $LaMnO_3$ (Lanthanum Manganite), the magnetic Mn atoms are in the charge state Mn^{3+}. This ion has four electrons in the 3d shell, with their spins parallel. The system spontaneously relaxes energy by distorting the cage containing the manganese (an octahedron of six oxygen atoms), splitting the highest occupied 3d orbital (the e_g energy level) by a mechanism called the "Jahn-Teller effect". This results in a cooperative Jahn-Teller distortion, i.e. a periodic, 3-Dimensional arrangement of distorted cages (see Fig. 1(a)) with associated orbital and magnetic orderings.

The underlying ordering of the atomic orbitals defines magnetic exchange pathways which give an overall antiferromagnetic structure (Fig. 1(b)). In the *ab* plane of the crystal lattice all the Mn's are ferromagnetically coupled: the Mn spins are parallel to each other. But neighbouring planes are antiferromagnetically coupled along the *c* axis (*z* in Fig. 1(b)).

It is well known that removing one electron to convert $3d^4$ to $3d^3$ induces the emergence of ferromagnetism in $LaMnO_3$. This has usually been done by replacing trivalent La by a divalent cation; in compensation, some of the $3d^4$ Mn^{3+} ions convert to the $3d^3$ charge state Mn^{4+}. There is no Jahn-Teller effect for the electronic configuration $3d^3$ (the e_g electronic level is unoccupied). Also, Mn $3d^3$ has a much smaller radius than Mn $3d^4$. Consequently, the emergence of a three-dimensional ferromagnetic component has been attributed to local changes in the symmetry of the octahedral cages, affecting the orbital ordering and the magnetic exchange pathways.

In our study we have doped $LaMnO_3$ with chromium, replacing some of the Mn^{3+} by Cr^{3+}. The Cr^{3+} ions have the same $3d^3$ configuration as Mn^{4+} but their ionic radius is closer to that of Mn^{3+}. We have found that, where a Cr $3d^3$ atom replaces a Mn $3d^4$ atom, the magnetic pathways change but, surprisingly, the nearby structure of distorted cages does not change.

We first proved by element-selective magnetic spectroscopies that there are in fact two ferromagnetic components emerging from the Cr doping. We found one from the host $3d^4$ Mn atoms, and a second one from the added $3d^3$ Cr atoms, each of these moments being proportional to the macroscopic ferromagnetism. Second finding, supported by *ab initio* calculations of the X-Ray spectra (see below): these two ferromagnetic components, were found to be antiparallel. It appears therefore that this doping with $3d^3$ atoms relaxes some of the antiferromagnetic coupling between the *ab* planes, producing the small overall ferromagnetic component.

We investigated the symmetry of the Mn and Cr cages using X-ray absorption near-edge spectroscopy at synchrotron facilities in France and Brazil. Unexpectedly, the spectra at the Mn and Cr X-ray K-edge were nearly identical in shape. This proves that the local electronic structure and therefore the structure of the oxygen cages are the same around the $3d^4$ ion Mn^{3+} and around the dispersed $3d^3$ ions Cr^{3+}. There is no significant reduction in the distortion, even though the Cr^{3+}, with its $3d^3$ configuration, does not have 3d level splitting.

Thus, the weakening of the antiferromagnetic Mn^{3+}-Mn^{3+} *c*-axis exchange pathway is not due to a restoration of the cage symmetry around the $3d^3$ ion. These conclusions contradict the theoretical model previously proposed for the emergence of ferromagnetism in doped $LaMnO_3$ compounds. We suggest a simple magnetic scheme compatible with our experimental results in Fig. 1(c).

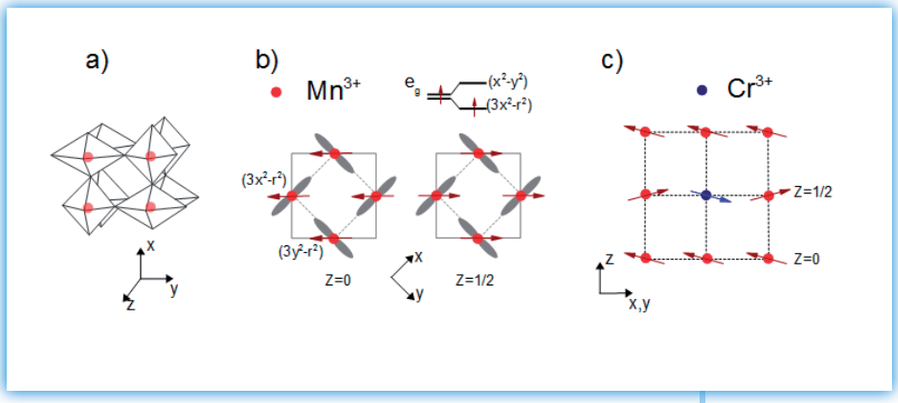

Fig. 1: (a) The 3D structural scheme of alternate, Jahn-Teller distorted MnO_6 cages in the orthorhombic crystal $LaMnO_3$. (b) Ordering of the e_g orbitals (represented in grey) and magnetic orderings (red arrows) in the ab plane for z =0 and z = c/2 (where z is the crystal c-axis). (c) Our proposed solution for the ferromagnetic ordering observed when an Mn is replaced by a Cr impurity.

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FURTHER READING

Emergence of ferromagnetism and Jahn-Teller distortion in $LaMn_{1-x}Cr_xO_3$.
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