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Revealing Electronic Crystals

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The interactions among valence electrons lie at the heart of much of today's condensed-matter experimental and theoretical research. Most of the key types of interactions can be found in one class of materials – manganites. Moreover, in manganites, these interactions cause the charges and orbitals to "crystallize" – that is to form regular patterns in the solid, allowing crystallographic studies of the electronic structure that results from the interactions. The determination of an electronic crystal is an experimental challenge, however, specifically in cases with a very low density of valence electrons. Using a technique called resonant x-ray diffraction, it was possible, first, to reveal the ordering of the orbitals and, second, to propose a crystallographic structure in which the ordered electrons are "dressed" with a distortion of the surrounding atomic structure.

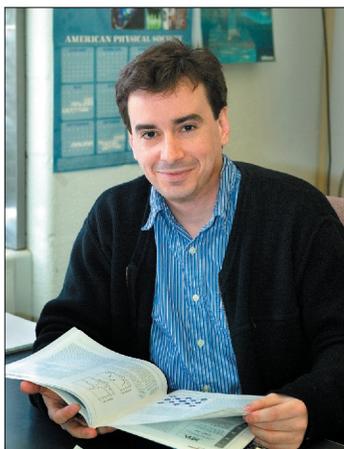
Determining precisely which electronic orderings take place in 3d oxide crystals may help refine some concepts for many interacting electrons. To that aim, manganites provide an ideal test-bed for these ideas. The manganese atom has all of the electronic degrees of freedom: its charge changes with the amount of hole doping and it has a large magnetic moment that can give rise to ferro- or antiferro-magnetic ordering. The Mn 3d valence orbital is also a degree of freedom; It is very anisotropic (**Figure 1**), and can align in different directions from site to site, a phenomenon known as orbital ordering. As is the case for magnetic ordering, one may observe ferro or antiferro orbital ordering. Further, because the magnetic structure depends on the relative orientations of the orbitals, manganites show many interrelated charge, orbital, and magnetic orderings. However, typically, orbital ordering concerns one electron out of a

hundred in the unit cell, and even lower densities, within larger unit cells, are of great interest in order to study the theoretical models in low-density conditions. Observing such orderings with traditional techniques is extremely challenging.

To study such orbital ordering, the main challenge to overcome is the low sensitivity of conventional x-ray or electron techniques. In fact, the standard crystallographic methods are hard-pressed to refine the positions of all the atoms in

the superstructure, much less the direction of the electronic orbitals. However, one may gain a huge increase in sensitivity if x-rays of a very particular energy are used in diffraction experiments – a phenomenon known as "resonant scattering." In resonant scattering, the energy of the incident x-ray is tuned to the energy of the photoelectric transition, so that the photoelectron doesn't leave the crystal but rather "visits" the valence orbitals of the excited Mn atom. If this valence electron has a different orientation from site to site, then one can observe a superstructure reflection, which corresponds to the orbital ordering. This is the "orbital order reflection."

Using this technique at NSLS beamline X22C and at the Swiss Light Source SIM beamline, we have determined the orbital ordering in manganites with large unit cells. We measured the orbital order reflections at the Mn K(L)-edges at X22C



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(SIM) and retrieved all the information on the electronic structure that is embedded in the dependence of the reflections with the energy of the photoelectric transition, the "spectrum" of the reflection. After numerical and tensorial analyses of the resonant scattering, we found a pattern in which the valence orbitals are antiferro-ordered and as far from each other as possible. Two conflicting models were evaluated,

and we could unambiguously determine that one of them, the so-called "Wigner-crystal model" was correct. We also showed that some valence orbitals are accompanied by a typical local distortion of the ligands (the oxygens). This distortion helps to trap the electron, increasing the resistivity. In fact, we also have found that the resonant spectra are extremely sensitive to the displacements of the

atoms. This is because the *atomic* structure determines the *electronic* structures, as is well known by users of the EXAFS technique. Finally, we proposed a crystallographic structure that could be used as an initial guess for a conventional crystallographic refinement, with the x-ray resonant spectra providing *non-arbitrary* constraints, in particular, on the space group.

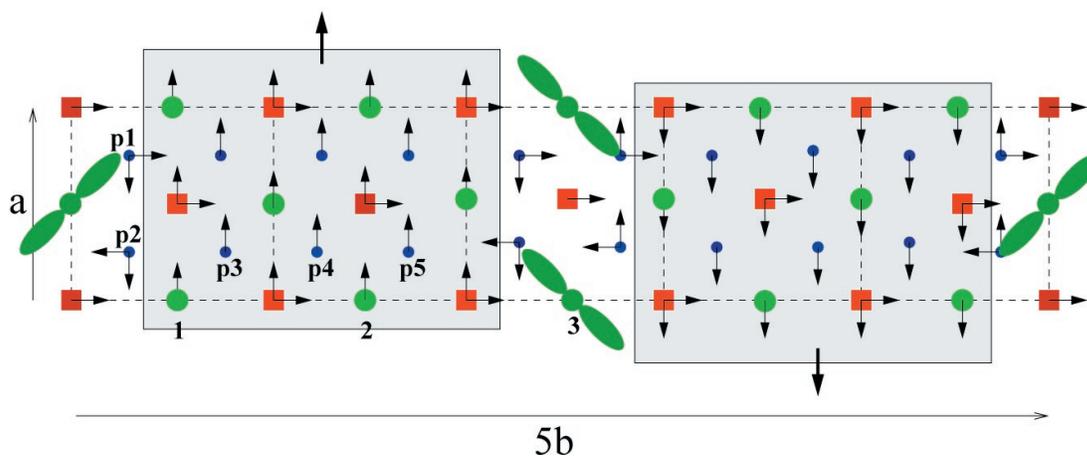


Figure 1. Orbital and atomic structures proposed from the study of the resonant x-ray diffraction data. In green, the Mn atoms. For a few of them, an extra valence electron gives an anisotropy, and these exhibit orbital ordering. Other atoms are oxygens and cations (Bi, Ca). Arrows are displacements from a non-ordered structure.