s6.m21.o1 **Diffraction Probes of Charge and Orbital Ordering: from Perovskites to Geometrically Frustrated Systems.** Paolo G. Radaelli, *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, UK. E-mail: p.g.radaelli@rl.ac.uk*

Keywords: Charge and Orbital Ordering; Metal-Insulator Transitions; Neutron and X-ray diffraction

The concept of charge and orbital ordering (CO-OO) in oxides first emerged in the thirties with the work of Verwey, and was later employed by Goodenough and Anderson to interpret diffraction results on perovskites and spinels. In early works, CO and OO were inferred from lattice distortions and magnetic ordering schemes; more recently, better diffraction instrumentation has provided direct evidence of atomic displacements that could be interpreted as arising from CO-OO. However, as these probes became more quantitative, and new techniques to probe CO-OO, such as x-ray absorption and resonant diffraction, became available, previous results and, in some cases, the very concept of CO-OO were challenged. I will review some past and recent results on the manganese perovskites and on spinel oxides and sulphides. "Long-range-ordered polaron" phases are ubiquitous in manganites, and have long been interpreted as due to CO-OO. Understanding these phases is crucial, because the short-range version of the polaron correlations is though to be at the very basis of the CMR phenomenon. Our early work on $La_{0.5}Ca_{0.5}MnO_3$ [1] evidenced a displacement pattern, which could be interpreted as due to CO, albeit with a reduced charge disproportionation. This result has later been challenged based on single-crystal neutron diffraction data, but very recent results indicate that the two interpretations could be reconciled in the context of a more complex phase diagram. CO in magnetite (Fe_3O_4) is also a controversial subject. We have recently presented evidence of a weak CO modulation based on x-ray and neutron diffraction data [2], but modulations of the Fe^{3+} ionic radius are clearly a secondary effect in the context of much stronger polaronic distortions. These and other results have prompted us to study compounds where CO and OO do not obey the classical ionic picture of valence fluctuations. Systems displaying coupled metal-insulator and structural transitions, accompanied by anomalies in the magnetic susceptibility, are prime candidates to display this behaviour. When this occurs on a geometrically frustrated lattice, very unusual crystal deformations are produced. In mixed valence $CuIr_2S_4$, bond-centred Ir^{3+}/Ir^{4+} CO is accompanied by strong spin-lattice dimerization, whilst the symmetry is strongly reduced from cubic to triclinic [3]. $MgTi_2O_4$ displays related phenomenology, but in a single-valence system without CO. We have shown that in $MgTi_2O_4$ spin-lattice dimerization produces a chiral deformation of the structure, associated with ordering of the t_{2g} orbitals.

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s6.m21.o2 **Resonant X-Ray Diffraction on Manganites.** Stephane Grenier,[a] K. Jessica Thomas,[a] Valery Kiryukhin[b] and John P. Hill[a], [a]*Dept. of Physics, Brookhaven National Laboratory, USA and* [b]*Dept. of Physics, Rutgers, State University of New Jersey, USA, E-mail: grenier@bnl.gov*

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In the last few years, resonant x-ray diffraction (RXD) has succesfully been applied to the investigation of charge, orbital and magnetic ordering in a number of materials. Specifically, RXD allows the mapping of the near-Fermi unoccupied levels projected on the resonant atoms. In *3d* metal oxides, the density distribution of the lowest unoccupied electronic levels, the partially filled *3d* and the empty *4p* bands, are sensitive to the crystal field and strong correlations as to the Hund coupling and the Coulomb repulsion. These levels reflect the orbital occupancy on the metal, its magnetic moment and its surrounding atomic structure. Hence, the sensitivity of the RXD technique stems from the x-ray resonance process by which a core electron is promoted to these empty near-Fermi levels. In addition, one probes the long-range order of these unoccupied states with the diffraction, that is RXD combines spectroscopic information with that of a scattering experiment. At the Mn *K*-edge (for which the resonant process corresponds to the transition $1s \rightarrow 4p$), the RXD analysis has been performed on several perovskite manganites in order to investigate the pattern of charge ordering and of the inequivalent Mn crystallographic sites as a function of hole dopings. As the *4p* levels extend to the nearest oxygen layers, RXD spectra revealed the dramatic contrast enhancement in the x-ray scattering factors between Mn sitting in inequivalent oxygen octahedra. The analysis of our data supports previous crystallographic refinements for manganites with half and higher doping where a checkerboard pattern of inequivalent Mn atoms and a Wigner-crystal pattern were found respectively [1,2,3,4]. The patterns of distorted and undistorted octahedra *support* the existence of an ordering of the *3d* orbitals but, surprisingly, no evidence of charge ordering has been found - directly - from the *K*-edge RXD data. In order to gain more direct insight into the *3d* band, we performed the Mn *L*-edge RXD experiments ($2p \rightarrow 3d$) on a manganite near half-doping that was expected to show charge and orbital ordering and the CE-type antiferromagnetic order. The resonant scattering from the orbital ordering and the antiferromagnetic ordering were found and compared [5]. We found that the coherence lengths of the magnetic and the orbital ordering were different and that a model with orbital ordering and without charge ordering is necessary to the refinement of the data with first principle RXD calculations. All these observations open new questions and pose a direct challenge to our original understanding of the manganites within the framework suggested by Goodenough in the 50's [6].

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