Advanced resonant soft x-ray diffraction to study ordering phenomena in magnetic materials

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Abstract. Here we present recent advances in the resonant soft x-ray diffraction technique and present a review of recent experiments in the field. Our review is focused on the study of charge and orbital phenomena occurring in manganites systems. It is shown how resonant diffraction can access directly the 3d shell of Mn by tuning the x-ray energy to the Mn L\textsubscript{2,3} edges. Similarly, by tuning the energy to the oxygen K edge, empty oxygen 2p states can be probed. It is shown how the technique probes corresponding atomic multipoles, the monopole (charge), the magnetic dipole, and the orbital (electronic quadrupole) of the open valence shell.

1. Introduction
The interaction between electronic and magnetic degrees of freedom has been intensively studied in oxides in recent years. These interactions result in interesting macroscopic effects such as high-temperature superconductivity, colossal magneto-resistance and multiferroicity. In some of these systems, the charge, magnetic, orbital and the structural degrees of freedom are strongly coupled. X-ray probes have strongly contributed to the understanding of such couplings in recent years. One of the evolving techniques is resonant diffraction which provides direct access to ordering phenomena of the electronic and magnetic sublattices. Since the early work on Ho metal,[1] the technique rapidly developed into a powerful tool in the study of charge, magnetic and orbital ordering phenomena in materials. In particular, resonant magnetic scattering is widely used in studies of multiferroic materials, such as the RMnO\textsubscript{3} [2-7] and RMn\textsubscript{2}O\textsubscript{5} [8-12] families.

Here we are concerned mainly with the ordering of charge and orbitals. Resonant diffraction studies started with the claim of direct observation of orbital order at the Mn K edge about a decade ago [13,14]. Subsequent theoretical calculations [15] challenged this interpretation. These calculations predict that at the K edge, the probed splitting of 4p states is dominated by the effect of the oxygen 2p Mn-4p overlap caused by the Jahn-Teller distortion. These experimental studies represent the first measurement of an electric quadrupole moment of Mn 4p type states in this strongly correlated electron system. It has soon after been pointed out by theoretical calculations[16], that the Mn L\textsubscript{2,3} edge contains a much more detailed view of the orbital order, which was soon confirmed by first experiments. [17,18] Here we review more recent work, made possible by the use of different incoming x-ray polarizations and analysis of the polarization of the scattered x-rays as well as by rotation of the sample around the Bragg wave vector (azimuthal angle scans). Moreover, an example is given showing what type of information can be retrieved by the study of the energy dependence of reflections, even on polycrystalline samples.
2. Concepts of resonant diffraction
In this report we concentrate on the electric-electric dipole transition, which is in many cases a good approximation for resonant diffraction in the soft x-ray regime. A theoretical review can be found in [19], and extension to other transitions have recently been discussed elsewhere [20]. The structure factor for resonant diffraction can be written in the form

\[ F(E) \propto \sum_{k,Q,q} (-1)^{Q} H_{Q}^{k} D_{Q}^{k} \sum_{d} \langle T_{q}^{k} \rangle \, e^{i\mathbf{d} \cdot \mathbf{\tau}} \]  

(1)

where \( \mathbf{d} \) is the position of the resonant ions in the unit cell, \( \mathbf{\tau} \) the studied reciprocal lattice vector and \( \langle T_{q}^{k} \rangle \) represents an atomic multipole moment of rank \( k \) and projection \( q \) in the local axis system of the resonant ion. \( D_{Q}^{k} \) represents an axis transformation of the operators from the local site system to the experimental setup and \( H_{Q}^{k} \) contains the dependence on the x-ray polarization. The resulting tensor of rank \( k \) represents now atomic multipoles of the probed valence shell with \( k=0 \) charge (monopole), \( k=1 \) the magnetic dipole and \( k=2 \) the electronic quadrupole. The resonance is reflected by the energy dependence of \( \langle T_{q}^{k} \rangle \)

\[ \langle T_{q}^{k} \rangle \propto \sum_{n} \frac{\langle \mathbf{g}\mathbf{O}\mathbf{h} \rangle \langle \mathbf{n}\mathbf{O}\mathbf{g} \rangle}{E_{\mathbf{n}} - E_{\mathbf{k}} - \hbar \omega + i\Gamma} \]  

(2)

where the sum over \( n \) reflects the sum over all probed intermediate states in the resonant process. The resonant enhancement of the magnetic and electronic contrast is directly related to the denominator, which makes the expectation values for the atomic multipoles large when the energy of the x-rays approach the absorption edges. However, as the intermediate states contain a hole in the core state, the intermediate states have to be considered with this hole, making them more atomic like. The presence of the core hole leads to a complex energy spectra even for a single electronic quadrupole of the Mn 3d shell due to the occurrence of multiplet structure (see fig. 1).

Figure 1. Orbital \((\frac{1}{4} \frac{1}{4} 0)\) reflection of \( \text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_{4} \) taken at 160K at the Mn L\(_{2,3}\) edges in \( \pi \) incident polarization in the vicinity of the Mn L\(_{2,3}\) edges, representing the energy splitting of the multiplets.

3. Polarization (analysis) and azimuthal angle dependence
Most soft x-ray diffraction studies are concerned primarily with the measurement of a Bragg reflection and its energy, temperature, and (in the case of incommensurate structures) momentum dependence. In some cases, x-rays with two different linear incoming polarizations were used. Very few studies used the freedom to rotate the sample around the scattering wave vector (azimuthal scan) to explore the behavior of the internal moments and their symmetry properties [21-24], as is now standard for
resonant hard x-ray Bragg diffraction [25]. Studies using polarization analysis of scattered radiation are even more rare [21,23].

Polarization of the scattered radiation is performed using a graded C/W multilayer, with details in Ref. [26]. The information obtainable with polarized radiation contains the orientation of the orbitals at the resonant sites. Resonant diffraction with linear polarized x-rays tests directly the local symmetry of the resonant ion sampled by the structure factor of the probed reflection. For a simple checkerboard type orbital order, as is commonly assumed to occur in half doped manganites, the azimuth angle ($\Psi$) dependence of the orbital reflection is simply two fold symmetric and is proportional to a $\sin^2(\Psi)$ term with a single electric quadrupole $T_{2}^{2}$. This symmetry of the azimuthal angle dependence, as shown in Figure 2, is simple because the probed orbital reflection (1/4 1/4 0) is along a high-symmetry direction. Note that for these long x-ray wave lengths, there is only one orbital reflection accessible at the Mn L_2,3 edges. In addition, due to the 2 fold local axis at the Mn for this orbital ordering, we expect scattering only in the rotated polarization channels, as experimentally verified in Figure 3.

Figure 2. Azimuthal angle dependence of the orbital (1/4 1/4 0) reflection taken at 160K with $\pi$ incident radiation of La$_{0.5}$Sr$_{1.5}$MnO$_{4}$ [21] above the antiferromagnetic transition temperature. The individual energy positions has been chosen to reflect different spectral features shown in Figure 1.

Figure 3. Energy dependence of the orbital (1/4 1/4 0) reflection in the four standard polarization channels of La$_{0.5}$Sr$_{1.5}$MnO$_{4}$ [26] in the antiferromagnetic transition temperature (left 40K and right 60K).
Testing the local symmetry of the Mn ions has significant impact on the possible ordering schemes in manganites such as the Zener-polaron or ferroelectric phases as well as for possible magnetic structures, which may break the symmetry of the Mn 3d states. Theoretical calculations have shown that depending on the magnetic moment direction of the Mn$^{3+}$ ions, there might be a considerable contribution to scattering in the non-rotated polarization channels $\sigma-\sigma$ and $\pi-\pi$. \[27\] where $\pi$ and $\sigma$ are vectors that define x-ray polarization as in and perpendicular to the scattering plane, respectively. The absence of scattering in these channels has therefore impact on the magnetic moment orientation of the Mn ions. More recently, the polarization dependence of the models such as the Zener-polaron has been calculated,\[28\] which would lead again to significant deviations in both the azimuthal angle dependence as well as to substantial contributions in the unrotated polarization channels. This would also be reflected by unequal intensities of the orbital reflection for $\pi$ and $\sigma$ incident radiation, without an analysis of the polarization of the outgoing radiation. Such a change in intensity is caused by the loss of inversion symmetry at the Mn sites, as the electron is shared by two Mn ions forming a dimer (Zener-polaron). This is neither observed in simple perovskite (R/T)MnO$_3$ (R=Bi, Nd, Pr) and (T=Sr, Ca) systems \[29,30\] nor in A-site ordered manganites for all studied dopings.\[28\]

4. Oxygen K edge

To gain more information of the interaction of the Mn with the oxygen, the x-ray energy can be tuned to the oxygen K edge. Providing that the doping level (Ca concentration) is significantly large (and the ordering wave vector sufficiently small), the orbital order reflection will lie in the Ewald sphere and can be studied. This has been performed for 2/3 doping in the Bi/CaMnO$_3$ system, where strong reflection was observed at 528 eV. \[31\] This reflection has a single peak (single harmonic oscillator) shape as a function of energy, indicative of a significant fraction of unoccupied oxygen 2p states. Previously, the occurrence of such a narrow spectral shape of a superlattice reflection has also been found in cuprates \[32\] and magnetite, \[33\] where it was interpreted as either caused by a charge order at the oxygen or a charge and orbital order of the Fe-O subsystem. However, the required dependence on the polarization with respect to a given setting has not been performed to establish an orbital or charge scattering origin of the reflection. For the case of the manganites discussed here, the reflection had a strong azimuthal dependence and had equal intensities for both incident polarization channels. This is only compatible with an orbital origin. It shows that the reflection is caused by unoccupied oxygen 2p states which are aspheric, reflecting an electric quadrupole moment at the oxygen. This can be understood in terms of overlap of Mn 3d states with the oxygen 2p states inducing an orbital order at the oxygen sites as illustrated by band structure calculation presented in Ref. \[34\].
For the occurrence of charge order with the periodicity of a probed superlattice reflection, the reflection must usually fulfill three minimal requirements: A) The reflection must be space group allowed, indicated by non zero intensity away from the absorption edge. Note that the space group is often unknown. B) Despite resonant charge reflection is often accompanied by an orbital (aspherical) contribution, the intensity should be considerably stronger in the $\sigma$ than in the $\pi$ incidence channels, when no polarization analysis is used. C) When an azimuthal angle dependence is observed, there should be a clear non-zero intensity at all azimuthal angles. This has been observed in 1/8 doped LaMnO$_3$,[31] where the data has been interpreted as caused by a charge order of different planes along the c-axis, leading also to a charge difference at the oxygen. An example of a stronger signal in the $\sigma$–$\sigma'$ channel is exemplified in figure 4 for this system. [26] We would like to note that the direct measurement of the charge order in the soft x-ray regime remains a challenge, because it is a difficult task to separate the aspheric orbital contributions from the spherical charge.

5. Experiments on polycrystalline materials

Very recently, resonant soft x-ray diffraction has been successfully applied to study polycrystalline materials. Due to the very large enhancement of the signals at the L$_{2,3}$ edges for 3d ions and the K edge of oxygen, magnetic and orbital order reflection have been observed in nickelates and manganites, respectively.[28,30,35,36] These observations have become possible due to the use of an in vacuum CCD camera with high sensitivity and the possibility of collecting a larger part of the Debye Scherrer ring of a resonant powder reflection, as shown in Fig. 5. These experiments have been performed out of focus, with a spot size of approximately 2 x 2 mm, to obtain a reasonable averaging over powder grains. The probed volume is very small, in particular due to the very limited penetration depth at resonance in the order of only 1000 Å. This limitation has the advantage that the resonant reflection is significantly broadened along $q$, allowing to get intensity on the CCD camera also from grains slightly misaligned in theta (rocking curve) angle. This effect leads to a broadening of intensity on the camera, but helps to obtain a reasonable powder averaging.
The type of information which can be retrieved for these experiments are based on the energy, polarization, momentum transfer $q$ and temperature dependence. From the energy dependence of the orbital reflection of A-site ordered half doped SmBaMn$_2$O$_6$ (see fig 5a) it was concluded that the orbital order is of $x^2-y^2$ type. This is in contrast to that found for the layered La$_{0.5}$Sr$_{1.5}$MnO$_4$, which would be of $3z^2-r^2$ type. Moreover, an unusual temperature dependence of the orbital reflection was found in La$_{0.5}$Sr$_{1.5}$MnO$_4$, which was interpreted in terms of a different temperature evolution of Jahn-Teller distortion and the electronic quadrupoles (orbitals). [37] The independence of the intensity of the orbital reflection on the incoming x-ray polarization has been used to argue for the absence of Zener-Polaron formation for the RBaMn$_2$O$_6$ system for a large region of the doping range. [28] Such arguments excludes also other models based on a charge localization on the Mn-O bonds. Moreover, the momentum dependence of the orbital reflection was found to be linear as a function of doping. The temperature dependence at half doping could resolve the origin of the orbital restacking transition, whereas for higher doping it shows an anomalous melting transition of the orbitals, not associated with the onset of magnetic order.

Conclusions
Here we have presented recent progress in the use and applicability of the resonant soft x-ray diffraction technique. The examples given here on the studies of charge and orbital ordering in manganites show that the technique can lead to important conclusions on the electronic ground states properties of the Mn-O network. It shows that both the incoming x-ray polarization and the polarization of the scattered radiation imply stringent constrains on the symmetry of the Mn 3d and oxygen 2p electronic states. It also shows that experiments can be performed on polycrystalline materials, allowing easier access to many interesting materials, with order in the charge, magnetic or orbital degrees of freedom.

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