Soft x-ray resonant diffraction in transition metal oxides

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ABSTRACT

We discuss recent soft x-ray resonant diffraction studies of magnetic and structural correlations in manganites and cobaltates. In half-doped manganites, the resonant enhancement of super-lattice diffraction peaks resulting from orbital and magnetic order is utilized to make a direct comparison of orbital and spin correlations. The main finding is that the correlation length associated with magnetic order exceeds that of the orbital order by of order a factor of two - a result which appears at odds with orbitally driven magnetic exchange pathways. Similar resonant diffraction measurements at the Co L-edge were performed to study the oxygen-doped cobaltate $\text{Bi}_2\text{Sr}_2\text{CoO}_{6+\delta}$, in which we find a surprising incommensurate antiferromagnetic order.

1. INTRODUCTION

X-ray resonant diffraction and scattering are techniques which utilize the strong enhancement of the atomic scattering factor near an absorption edge to study subtle structural and electronic re-arrangements, as well as magnetic order^{1,2}. The enhancement arises from the virtual excitation of a core electron into an unoccupied state of the resonant ion and then the subsequent decay of that electron back into its initial state. This process contributes to the coherent scattering and gives rise to an energy dependent scattering factor $f = f(Q) + f'(E) + if''(E)$, where $f(Q)$ is the Q-dependent form factor from Thomson scattering and f' and f'' are the anomalous scattering factors, which vary rapidly only in the vicinity of the absorption edge. Depending on the particular absorption edge, the anomalous scattering factors are sensitive to chemical shifts which result from different valence states, structural distortions and/or the spin polarization of the valence electrons. Thus, super-lattice reflections which result from small charge reorganizations, structural shifts or magnetic order can be significantly enhanced near resonance.

Beyond the intensity enhancement of diffraction peaks, several aspects make this technique attractive for studying novel materials. One is the element specificity, which allows the separation of one element's contribution to the scattering factor from all of the other atoms in the unit cell. For example, in magnetic materials with more than one magnetic ion, the partition of the magnetic moment onto different chemical sites can be extracted from resonant scattering and absorption measurements. The second point is that the excited electron "feels" the electronic and magnetic environment of the valence states. Thus, scanning the energy through the resonance at the diffraction peak provides a spectroscopy of the unoccupied states projected onto the resonating ion.

The majority of synchrotron beam lines operate in the energy range of 5-30 keV, which branches the K-edges of 3d transition metals and the L-edges of the rare earths. (K and L denote core electron states with atomic numbers $n = 1$ and 2, respectively). To reach the strong dipole resonances into the important 3d electronic states of transition metal oxides, it is necessary to use soft x-rays (200-1000 eV). The penetration depth at these energies is considerably reduced

compared to hard x-rays: $\sim 1000 \text{ \AA}$ with soft x-rays compared to $\sim 1\text{-}10 \text{ }\mu\text{m}$ with hard x-rays. As a result, soft x-ray diffraction measurements must be performed in high vacuum in order to maintain a clean surface. L-edge diffraction measurements provide considerable sensitivity to the electronic and magnetic correlations found in many transition metal oxides, and recent experiments include the investigation of hole doping in High T_c cuprate superlattices, hole crystallization in cuprate ladders, orbital and spin order in manganites, and spin and charge ordering in nickelates.³⁻¹⁰ The limitation, or perhaps better said, frustration, is that working in the soft x-ray regime severely limits the accessible Q-space. Starting from titanium to copper, the smallest measurable periodicity is between 13.7 and $6.7 \text{ \AA}$. While there are a number of transition metal materials which can be probed, the true calling of this technique will likely be artificially structured materials.

Here, we discuss two interesting applications of the resonant x-ray diffraction technique in $3d$ transition metal oxide materials. The first is the near half-doped manganite $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ (PCMO), which is described by a charge, orbital and spin ordered ground state. The diffraction peaks resulting from orbital and spin order are dramatically enhanced at the Mn L-edges, permitting a direct comparison of the correlations associated with the coupled magnetic and orbital ordering. The second material discussed is the insulating cobaltate, $\text{Bi}_2\text{Sr}_2\text{CoO}_6$ (BSCoO), which has been described as a mixed phase ferromagnetic and antiferromagnet.

2. EXPERIMENTAL TECHNIQUE

Resonant diffraction measurements were performed using the scattering chamber at the X1B beamline at the NSLS.¹¹ The diffractometer, which permits full rotation of the sample and detector angles and a limited range of sample tilts is housed inside of a high vacuum chamber. A diffraction grating (600 or 1200 lines/mm) is used to monochromatize the beam. Vertical slits after the monochromator limit the energy resolution to $\sim 0.5 - 1 \text{ eV}$. Baffles before the sample are used to mask the beam, typically to $1 \text{ mm} \times 1 \text{ mm}$. The detector resolution is fixed by a square aperture and there is no polarization analysis.

The samples are mounted with a thin layer of glue onto a copper block which is inserted and clamped into the cold finger using a load lock arm. Temperature control from $20 - 300 \text{ K}$ is achieved using a continuous flow of He through the cold finger. The scattering geometry is shown schematically in Figure 1. Scattering is in the horizontal direction and the incident x-ray beam is primarily π -polarized (electric field in the plane of scattering).

Both the manganite and cobaltate single crystals were grown by the floating zone-technique. For the manganite experiments, the crystals were oriented and polished with the smallest grit size of $0.1 \text{ }\mu\text{m}$. The cobaltate $\text{Bi}_2\text{Sr}_2\text{CoO}_{6+\delta}$ samples were not polished, as they cleaved easily into rectangular platelets with a surface normal along the desired reciprocal lattice direction. (The samples were cleaved *ex-situ*.) The cleaved cobaltates yield better fluorescence spectra than the polished manganites; however, the specular reflection makes a strong contribution to the scattering in the cobaltate. In general, we find it is easier to work with a crystal with a small (~ 1 degree) separation between the specular and Bragg reflections. We use the $(0,0,2)$ Bragg reflection to line up the cobaltate and the specular reflection and measured miscut to line up the manganites.

Figure 1 Scattering geometry for the resonant diffraction measurements. Azimuthal dependence of the scattering is probed by rotating the sample in the plane perpendicular to Q .

The principle measurements are as follows: At a fixed energy near resonance, we measure longitudinal and transverse Q-scans through the super-lattice reflection as in a standard diffraction measurement. Bragg reflections are also measured as a function of energy at fixed Q. These resonant diffraction energy line shapes essentially map out the energy dependence of the diffracted intensity in the vicinity of the absorption edge. While detailed calculations are required to interpret the line shape, this type of measurement essentially provides a spectroscopy of the unoccupied states projected onto the resonating ion. Measurements are also made as a function of temperature, from ~ 50 K to 300 K and azimuthal angle, where an azimuthal rotation consists of rotating the sample about the Q-vector. The azimuthal dependence of the scattering arises from the different selection rules that are satisfied depending on the orientation of the dipole electric field with respect to the crystallographic axes.

3. ORBITAL AND SPIN ORDER IN HALF-DOPED MANGANITES

A number of half-doped manganites, such as $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 < x < 0.7$), $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ exhibit an insulating ground state which is described by charge, orbital and antiferromagnetic order. This behavior contrasts, and may compete, with the stabilization of a conducting, ferromagnetic ground state that is observed in manganites such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Characterizing and understanding the origin of the insulating, ordered phase near half-doping has therefore received considerable theoretical and experimental attention.

The formal Mn valence at $x=0.5$ (half-doping) is 3.5. In the insulating manganites considered here, a transition occurs at $T_{\text{CO}} \sim 250$ K, which is described as a checkerboard ordering of Mn^{3+} and Mn^{4+} sites. Although significant experimental evidence and recent calculations suggest that the charge difference between the two sublattices is much less than 1¹¹⁻¹⁴, it is convenient to use this language to describe the ground state. With only one e_g electron, the Mn^{3+} site is Jahn-Teller active and the surrounding oxygen orbitals distort to lift the electronic degeneracy. The distortions are correlated in the lattice and form a pattern of stretched and contracted oxygen octahedra around the Mn^{3+} sites. Since the Mn 3d valence electron orbitals reflect the symmetry of the surrounding oxygen octahedron, the Jahn-Teller distortions are cooperative with Mn 3d orbital order. The pattern of the Mn orbital order at half-doping is indicated schematically in Figure 2. Orbital order occurs at the same temperature as the charge order.

Historically, the charge and orbitally ordered state indicated in Figure 2 was predicted to explain the pattern of spin order observed with neutrons.^{15,16} The magnetic order is described by ferromagnetic zig-zag chains and antiferromagnetic coupling between the chains, as indicated in Figure 2. Experimentally, antiferromagnetic order occurs at or below the charge-orbital ordering transition temperature, consistent with a picture in which the magnetic exchange pathways are driven by the overlap of adjacent Mn electron orbitals.

Structural studies of a number of manganites were consistent with this picture: small motions of the oxygen sites lead to symmetry breaking and new reflections at $T_{\text{CO}}/T_{\text{OO}}$. Resonant diffraction measurements at the Mn K-edge provided a greater sensitivity to the super-lattice reflections associated with charge and orbital order.^{11,13,17-20} A full analysis of the azimuthal and polarization dependence of these reflections suggested that the resonance at the charge order reflection resulted from a purely structural distinction between the so-called Mn^{3+} and Mn^{4+} sites and was not consistent with a difference in valence of 1 between the two sub-lattices.^{11,13} However, in [11], it was argued that the orbital ordering reflection is consistent with the orbital symmetries indicated in Figure 2.

Figure 2. Schematic of the ground state of half-doped charge/orbital ordered manganites, reproduced from Ref. [8]. The symmetry of the Mn 3d valence electrons is shown. The plus and minus signs indicate spin directions.

Calculations showed that the K-edge orbital order diffraction peak is overwhelmingly more sensitive to the oxygen distortion than the 3d electrons.²¹ Greater sensitivity to the 3d electrons could be achieved by performing a resonant diffraction measurement of the orbital order at the Mn L-edge, which involves strong dipole resonances from 2p to 3d. In a theoretical paper, Castleton and Altarelli calculated the resonant energy line shape of the orbital order diffraction peak (that is, the energy dependence of the diffraction peak at fixed Q) as a function of increasing JT distortion.²² The calculations showed that it is possible to distinguish the contributions to the resonant diffraction which arise from the structural distortion from the contribution due to the electronic orbital order.

In addition to directly probing the orbital order, L-edge resonant diffraction permits a direct comparison of the orbital and magnetic correlations in the ground state. While at the K-edge, magnetic scattering is too weak to measure in manganites, the resonant magnetic exchange scattering at the L-edge is quite large. This is a result of the large spin-orbit coupling of the 2p core electrons and the strong exchange effects in the 3d states.²

The spin and orbital correlations in half-doped manganites constitute an interesting example of coupled order parameters and one can ask how the correlations and dynamics in one phase, e.g. orbital order, influence the same properties in the magnetic phase. Of particular interest is the observation of short-range orbital order. Short-range orbital order has been attributed to the formation of orbital domains, in a so-called orbital glass state. The microscopic origin of the domains, which could arise from strain or cationic disorder, is however, unclear.

To investigate the coupling between magnetic and orbital orders, we used the resonant enhancement at the Mn L-edges to compare magnetic and orbital diffraction peaks in several half-doped, pseudo-cubic manganites which exhibit the ground state shown in Figure 2. Here, we will focus on the previously reported results from $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, in which both the magnetic and orbital diffraction peaks are accessible with soft x-rays.⁸ The accessible magnetic and orbital reflections are $Q = (1/2, 0, 0)$ and $Q = (0, 1/2, 0)$, respectively, where the reflections are indexed to the orthorhombic unit cell with $a = 5.43$, $b = 5.45$ Å and $c = 7.65$ (Pbnm structure). In this sample, orbital order occurs at $T_{\text{OO}} \sim 240$ K and antiferromagnetic order occurs at $T_N \sim 160$ K. The charge order reflections, which also appear at T_{CO} , are not accessible at the Mn L-edge.

The high degree of twinning in these pseudo-cubic manganites means that both [100] and [010] oriented domains are present in nearly equal quantities on a crystal face prepared with "[100]" orientation. This is confirmed by a comparison of the (2,0,0) and (0,2,0) Bragg reflections with hard x-rays. The twinning can actually be viewed as an advantage for these soft x-ray experiments, since a [100]/[010] face permits measurement of both magnetic, $Q = (1/2, 0, 0)$, and orbital, $Q = (0, 1/2, 0)$, super-lattice diffraction peaks using the same polished surface. Since $a \sim b$, $|Q_{\text{mag}}| \sim |Q_{\text{orb}}|$, the two reflections are not easily resolved in angle. Thus, at the same Bragg angle, we measure a superposition of the magnetic and orbital diffraction when $T < T_N$ and both orbital and magnetic order exist. However, it is possible to distinguish the orbital and magnetic diffraction by temperature, energy dependence and azimuthal dependence. In particular, the c-axis for the crystal is well defined and we can optimize orbital and magnetic diffraction at two distinct azimuths: c-axis perpendicular to the scattering plane and c-axis in the scattering plane.

3.1. Diffraction Results

Figure 3 shows longitudinal Q-scans along $Q = (1/2, 0, 0)/(0, 1/2, 0)$ measured at 100 K ($T < T_N$) and 183 K ($T_N < T < T_{\text{OO}}$), with the c-axis perpendicular to the scattering plane. The peaks are measured at 645 eV (Fig. 3a) and 648 eV (Fig. 3b), which correspond to energies below and at the peak of the absorption, respectively. At this azimuthal angle (c perpendicular to the scattering plane), the intensity of the antiferromagnetic diffraction peak is optimized, but the orbital diffraction peak is quite weak. In fact, the intensity of the magnetic peak is ~ 100 times stronger than the orbital peak. As a result, in this azimuthal configuration, the magnetic scattering overwhelmingly dominates at low temperatures and we will refer to the peak below T_N as the magnetic peak and above T_N as the orbital peak.

Focusing on the longitudinal scans at 645 eV in Figure 3a, the orbital peak is approximately a factor of two broader than the magnetic peak, suggesting that the orbital order is shorter ranged than the magnetic order. Note that both scans constitute longitudinal scans which are measured at the same energy and scattering angle and therefore the same experimental resolution. At 648 eV (Figure 3b), the maximum in the absorption, both peaks are broadened due to the decreased penetration depth. However, the increase in width is most pronounced for the magnetic peak. This suggests that the width of the magnetic peak is resolution limited, while the orbital peak width is dominated by intrinsic short-range order.

Figure 4 shows energy scans at fixed Q through the magnetic ($T < T_N$) and orbital ($T_N < T < T_{\text{OO}}$) diffraction peaks. The two line shapes are dramatically different, with the maximum intensity of the orbital peak occurring ~ 2.5 eV above

Figure 3. Longitudinal Q-scans through the magnetic (100 K) and orbital (183 K) Bragg reflections at (a) 645 eV and (b) 648 eV. (a) is reproduced from [8].

the peak in the magnetic scattering spectrum. As T increases toward T_N , the line shape stays constant; above T_N , the line shape changes to reflect pure orbital diffraction. Warming from T_N to T_{OO} , the line shape stays constant in shape.

Since the orbital order scattering is weak compared to the magnetic scattering at this azimuth, the nature of the orbital order upon cooling through T_N is inconclusive. By rotating the sample 90 degrees to bring the c -axis into the scattering plane, we find that the orbital scattering is significantly enhanced and the magnetic scattering almost completely depressed, a result consistent with the picture of the orbital ordering described in [11]. The resonant diffraction line shape remains essentially unchanged below and above T_N and there is only a small decrease in intensity in the diffraction peak upon warming through T_N . Figure 5 shows longitudinal Q-scans measured at 648 eV below and above T_N . The difference between the two longitudinal Q scans is the small contribution from the magnetic diffraction peak, which is approximately a factor of four weaker than the orbital diffraction peak. The inset shows a plot of the magnetic diffraction peak (the difference between the scans at 100 and 160 K) and the orbital peak at 160 K; the magnetic peak occurs at a slightly higher Q than the orbital peak, consistent with $a < b$ and is narrower than the orbital diffraction peak. This is an important result, since it shows that the orbital diffraction peak stays broad even below T_N .

Figure 4. Energy scans at fixed Q through the magnetic (100 K) and orbital (183 K) diffraction peaks. Reproduced from Ref. [8]. function of temperature, even below T_N .

We note that these measurements have also been performed on $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, which exhibit similar charge, orbital and magnetically ordered ground states. In these materials, magnetic scattering is forbidden at $Q = (1/2, 0, 0)$ because the spins stack antiferromagnetically along the c-axis.²³ As a result, we are able to measure orbital order diffraction above and below T_N . We find that the orbital order diffraction peak width remains constant upon cooling below T_N .²⁴

We now address the question of the different peak widths associated with the magnetic and orbital order. One possibility is that the ordered domains are anisotropic. That is, long-range magnetic and orbital order along a and short range order along b. There are several arguments against this picture. The first is the observation that transverse scans through the orbital and magnetic peaks show a similar discrepancy in width. A second point is that K-edge measurements of the orbital order show fairly isotropic correlation lengths along a, b and c.²⁵

3.2. Future experiments

Of considerable interest would be the ability to measure signatures of the orbital order on the oxygen sites. Band structure calculations and soft x-ray absorption measurements suggest that the holes lie predominantly on the oxygen sites and that the oxygen sites are strongly hybridized with the Mn sites.^{14,26} A good candidate for such an experiment is $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$, $x > 0.5$. Resonant diffraction measurements of BCMO reveal superlattice reflections resulting from orbital and charge order similar to those found in the half-doped manganites. However, the unit cell is larger than that depicted in Figure 2 to accommodate the extra Mn^{4+} sites and the smallest orbital order Q vector is therefore accessible at the O K-edge ($E \sim 540$ eV).

The strong diffraction at the orbital order reflection also opens the door to performing coherent diffraction measurements. Misaligned orbital domains will diffract x-rays with different phases resulting in texture, or "speckle" in the diffracted intensity. Although in practice a real-space reconstruction from the speckle pattern is difficult even for simple structures²⁵, analysis of the changes (or absence of changes) in the speckle pattern with temperature, external field or time provide important information about the domain structure and its fundamental dynamics.

Measurements of the speckle pattern in the orbital and charge order diffraction peaks have previously been measured at the Mn K-edge.²⁶ These measurements showed that the speckle pattern associated with charge order remained static on the time scale of a few minutes. However, there was insufficient intensity at the orbital diffraction peak to say conclusively if the orbital domains remained static. Preliminary measurements suggest that the resonant enhancement of the orbital order diffraction peak available at the Mn L-edge permits a better signal to noise, on smaller time scales, than the measurements in [27].²⁸ In particular, it may be possible to get close enough to the region of critical scattering to see dynamics in the orbital domains.

Figure 5. Longitudinal Q -scans in the azimuth where the c-axis is in the scattering plane. The difference between the 100 K and 160 K peaks is the small amount of magnetic signal at this azimuth. Inset: The difference peak (100 K - 160 K) and the 160 K peak.

4. INCOMMENSURATE MAGNETIC ORDER IN $\text{Bi}_2\text{Sr}_2\text{CoO}_{6+\delta}$

$\text{Bi}_2\text{Sr}_2\text{CoO}_{6+\delta}$ (BSCoO) is a cobaltate derived from the high T_c cuprate $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$.³⁰ Though similar in structure to its high T_c precursor, BSCoO is an insulator at all temperatures that exhibits dramatic changes in its magnetic properties as a function of the oxygen content, δ .³¹ Based on thermogravimetric analysis and the known structure, the range of δ is $0.25 < \delta < 0.5$.³² Taking a simple ionic picture of the Co sites and assuming every oxygen introduces two holes, this range corresponds to an equal mixture of Co^{2+} and Co^{3+} ($\delta = 0.25$) and all Co^{3+} ($\delta = 0.5$). The magnetic correlations in the Co-O plane evolve from antiferromagnetic (AF) at $\delta \sim 0.5$ to ferromagnetic (FM) at $\delta \sim 0.25$. At zero-field, magnetic order in the $\delta = 0.25$ phase gives rise to neutron diffraction peaks at $(0,0,l)$, $l = \text{odd integer}$ due to an antiferromagnetic coupling between the layers. In the $\delta = 0.5$ phase and at zero field, there are AF diffraction peaks at (h,k,l) positions with h,l even and k odd or k,l even and h odd. In [31], it was suggested that BSCoO exhibits phase separation into ferromagnetic, $\delta = 0.25$ and antiferromagnetic, $\delta = 0.5$ regions at intermediate δ . Furthermore, the two phases appear to be coupled at intermediate δ : Both phases have the same transition temperature and aligning the spins in adjacent layers in the ferromagnetic phase changes the stacking in the antiferromagnetic phase. This is indicated schematically in Figure 6. The field necessary to align the layers, H_c , varies with δ , ranging from < 100 G at $\delta \sim 0.25$ and increasing to 2.5 T at $\delta \sim 0.5$. The spins are oriented along the a -axis for both phases.

To investigate the nature of the ferromagnetic phase at low field, we looked for magnetic resonant diffraction in the vicinity of $Q = (0,0,1)$ at the Co L_{II} and L_{III} edges in a BSCoO sample with a transition temperature ~ 250 K ($\delta \sim 0.45$). At this intermediate δ , both the FM and AF phases are present and have the same transition temperature. However, we can only reach the lowest Q reflection in the $\delta = 0.25$ phase at the Co L -edges. A freshly cleaved sample of BSCoO was mounted with a c -axis normal and the b -axis perpendicular to the scattering plane. A room temperature fluorescence scan near the Co L_{III} and L_{II} showed clear peaks at 778 eV and 793 eV.

While neutron scattering measurements indicate broad peaks at $(0,0,l)$, $l = \text{odd integer}$ positions, these higher resolution x-ray diffraction measurements reveal magnetic diffraction peaks at incommensurate positions along H and L . Figure 7 (left panel) shows H scans at $Q = (0,0,1.04)$ below (50 K) and near (230 K) the magnetic phase transition. The sharp peak at $H=0$ is the contribution from the specular scattering is present both below and above the magnetic phase transition; the broad wings with peaks at $h = 0.006$ and $h = -0.009$ indicate magnetic ordering with an

Figure 6. Schematic of the inter-plane stacking in the ferromagnetic and antiferromagnetic phases. Only the spins on the Co sites are shown. Application of the field changes the stacking from (a) to (b). Reproduced from [31].

Figure 7. (Left panel) Incommensurate magnetic diffraction peaks at 777 eV, below and near the phase transition temperature. The inset shows the temperature dependence of the intensity at the two peaks in the H-scan. (Right panel) Energy scans at fixed Q. The signal in the scan at $Q = (0.01, 0, 1.15)$ is dominated by the fluorescence.

incommensurate wavevector. The temperature dependence of the peaks at $Q = (0.006, 0, 1.04)$ and $Q = (-0.009, 0, 1.04)$ is shown in the inset. These incommensurate peaks disappear off resonance, leaving only the specular rod: the right panel of Figure 7 shows the energy dependence at fixed Q at the magnetic peak position ($Q = (0.01, 0, 1.04)$) and at a Q away from the peak ($Q = (0.01, 0, 1.15)$).

The observation of such a small incommensurability depends on the high resolution available with an x-ray experiment. For example, similar discrepancy between neutron diffraction and x-ray diffraction peaks was found in the cuprate $\text{PrBa}_2\text{Cu}_2\text{O}_{6.92}$.^{33,34} While further measurements are needed to understand the nature of the incommensurate magnetic scattering, it seems likely that it may be related to the mixed phase nature of these materials. In order to satisfy the magnetic interaction at the boundaries of the ferromagnetic phase, a long wavelength modulation of the spins may occur. Studying the evolution of the magnetic diffraction with δ would likely yield more insight into the origins of the incommensurability.

5. CONCLUSIONS

Resonant diffraction provides a high level of sensitivity to the valence electrons of correlated ions in a material. As the interesting physics in a number of transition metal oxides involves correlations - magnetic, electronic and structural - between the valence electrons, resonant diffraction at the transition metal L-edges has and will continue to provide new insight into these materials.

In manganites, resonant diffraction at the Mn L-edge permits an essential comparison between the electronic orbital ordering and spin correlations. The resonant energy line shapes of magnetic and orbital order diffraction peaks provide a sensitive map of the electronic structure. One outgrowth of these measurements is that these "maps" can be used to track the evolution of magnetic and orbital correlations in the presence of a perturbation, such as temperature, field, carrier concentration or strain. This means of tracking orbital and spin correlations may serve as a useful tool to understand the effects of nanoscaling and artificial device structures based on manganites. The comparison of magnetic and orbital diffraction peaks indicates that the magnetic correlation length exceeds the orbital correlation length by close to a factor of two. Importantly, we find that the orbital diffraction is not affected by the onset of magnetic order. Finally, the strong enhancement of the orbital diffraction at the Mn L-edges opens the possibility for the study of dynamics of the orbital domains using coherent resonant diffraction.

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