Soft x-ray resonant diffraction study of magnetic and orbital correlations in a manganite near half-doping

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We have utilized the resonant x-ray diffraction technique at the Mn L-edge in order to directly compare magnetic and orbital correlations in the Mn sub-lattice of Pr\textsubscript{0.6}Ca\textsubscript{0.4}MnO\textsubscript{3}. The resonant line shape is measured below $T_{OO} \sim 240$ K at the orbital ordering wave vector $(0, \frac{1}{2}, 0)$, and below $T_N \sim 175$ K at the antiferromagnetic wave vector $(\frac{1}{2}, 0, 0)$. Comparing the width of the super-lattice peaks at the two wavevectors, we find that the correlation length of the magnetism exceeds that of the orbital order by nearly a factor of two. Furthermore, we observe a large ($\sim 3$ eV) shift in spectral weight between the magnetic and orbital line shapes, which cannot be explained within the classic Goodenough picture of a charge-ordered ground state. To explain the large shift, we calculate the resonant line shapes for orbital and magnetic diffraction based on a relaxed charge-ordered model.

In a number of manganites, including Pr\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3}, La\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3} and La\textsubscript{2-x}Sr\textsubscript{x}MnO\textsubscript{3}, the dynamics resulting in a charge-ordered, insulating state in the vicinity of half-doping are still not well understood. In his seminal work on exchange interactions in manganites, Goodenough considered charge and orbital order at half-doping as a precursor to the magnetic CE ground state\textsuperscript{1}. In this picture, charge ordering at $T_{CO}$ results in a checkerboard pattern of Mn\textsuperscript{3+} and Mn\textsuperscript{4+} sites (Figure 1). The Mn\textsuperscript{3+} sites each have one $e_g$ electron and are thus Jahn-Teller (JT) active, while the $e_g$ levels are empty on the Mn\textsuperscript{4+} sites. A cooperative JT distortion and orbital ordering of the Mn\textsuperscript{3+} sites at $T_{OO} = T_{CO}$ occurs concomitantly with the charge ordering. The in-plane JT distortions favor occupation of $3x^2 - r^2$ and $3y^2 - r^2$ orbitals on the Mn\textsuperscript{3+} sites, establishing a ferromagnetic exchange pathway along orbital zig-zag chains (dotted line in Figure 1). Magnetic CE ordering, defined by antiferromagnetically coupled ferromagnetic chains, occurs at $T_N \leq T_{OO}$.

Extensive neutron and x-ray scattering measurements support the Goodenough picture\textsuperscript{2,3,4,5,6}. However, this model makes definite predictions about the Mn ground state for which experimental confirmation is still lacking. One controversial issue is the degree to which the “Mn\textsuperscript{3+}” and “Mn\textsuperscript{4+}” sites are actually separated by unit valence. Indeed, a number of experimental results challenge the charge ordering model\textsuperscript{6,7}. Recent analysis of Mn K-edge resonant x-ray diffraction in Pr\textsubscript{0.6}Ca\textsubscript{0.4}MnO\textsubscript{3} suggests that the charge ordering is far from complete, but supports the presence of an orbitally ordered ground state\textsuperscript{7}. In addition, the Goodenough model predicts a strong coupling between the orbital and magnetic correlations within the Mn\textsuperscript{3+} sub-lattice. However, no single experimental technique has been able to directly compare magnetic and orbital correlations.

Recently, it has been demonstrated that resonant diffraction at the Mn L-edges may be utilized to study magnetic and orbital order in the manganites\textsuperscript{10,11,12}. The Mn L-edge resonances involve strong dipole transi-
tions from the 2p core levels to unoccupied states within the 3d band. The resonant enhancement of magnetic scattering at the Mn L-edge is significantly greater than at the K-edge.\textsuperscript{13} Furthermore, the structure of the resonant diffraction line shape provides a direct spectroscopy of the Mn 3d band in the presence of correlations.

In this letter, we present a resonant x-ray diffraction study of a near half-doped manganite at the Mn L-edge which permits the first direct comparison between magnetic and orbital correlations. Our data provide evidence against a charge ordering into distinct Mn\(^{3+}\) and Mn\(^{4+}\) sub-lattices in Pr\(_{0.6}\)Ca\(_{0.4}\)MnO\(_3\), and indicate a more complex ground state. First, we find that the magnetic correlations are significantly longer-ranged than the orbital correlations. Second, the spectral line shapes and the difference in intensity between magnetic and orbital scattering disagree with the ionic CE picture. Rather, we suggest that while the \(e_g\) electron is still localized, it is shared between neighboring lattice sites.\textsuperscript{14}

We have focused on twinned, single crystal Pr\(_{0.6}\)Ca\(_{0.4}\)MnO\(_3\), which has been described as a CE-type antiferromagnet.\textsuperscript{3} Pr\(_{0.6}\)Ca\(_{0.4}\)MnO\(_3\) exhibits charge/orbital order at \(T_{OO} = T_{CO} \approx 240 \text{ K}\) and long-range spin order at \(T_N \approx 170 \text{ K}\), which result in super-lattice reflections at \((0, \frac{1}{2}, 0)\) and \((\frac{1}{2}, 0, 0)\), respectively, with respect to the orthorhombic unit cell \((a = 5.41 \text{ Å}, b = 5.43 \text{ Å})\). The twinned crystal has both \([100]\) and \([010]\) oriented domains at the sample surface such that both \((\frac{1}{2}, 0, 0)\) and \((0, \frac{1}{2}, 0)\) reflections are accessible at the same scattering angle. At the Mn L-edges, which are \(\approx 650 \text{ eV}\) and lie in the soft x-ray regime, \(2\theta \approx 124^\circ\) for these reflections. Although the \((\frac{1}{2}, 0, 0)\) and \((0, \frac{1}{2}, 0)\) reflections are not resolved in momentum space, the magnetic and orbital scattering are clearly distinguished by different transition temperatures and correlation lengths.

The diffraction measurements were performed at the X1B undulator beamline at the National Synchrotron Light Source. The spectrometer is housed in an UHV chamber to reduce adsorption on the sample surface. A focusing gold diffraction grating selects the incident photon energy. Variable width slits before and after the grating determine the energy resolution, which is \(< 0.5 \text{ eV}\) (calculated) for the measurements shown here. The incident beam is \(\pi\)-polarized and diffraction occurs in the horizontal geometry. The sample is mounted to the cold finger of a He cryostat. The azimuth is fixed with the \(c\)-axis normal to the scattering plane.

Figure 2(a) shows the energy dependence of the diffracted intensity at \(Q = (\frac{1}{2}, 0, 0)/(0, \frac{1}{2}, 0)\) in the vicinity of the Mn \(L_{III}\) (2\(p_\pi \rightarrow 3d\)) and \(L_{II}\) (2\(p_\pi \rightarrow 3d\)) absorption edges. The scans were taken at 183 K, below \(T_{OO}\) but above \(T_N\), and at 100 K, below \(T_N\). A high temperature \((T = 240 \text{ K})\) spectrum has been subtracted from both spectra to remove the contribution from specular reflectivity and fluorescence. To emphasize the difference in the line shapes, the two curves are scaled to the same intensity at their respective maxima. As we discuss below, the peak in the 100 K spectrum \((\approx 60,000 \text{ counts/s})\) is actually 100 times more intense than that of the 183 K spectrum. The background subtraction is thus only significant for the orbital spectrum, for which it is approximately a 10% effect.

There is a dramatic shift in the resonant spectral weight upon warming through \(T_N\): Below \(T_N\) there is a sharp peak at 645.5 eV within the \(L_{III}\) region and smaller scattering within the \(L_{II}\). Above \(T_N\), the peak in the \(L_{III}\) occurs at 648.5 eV and the \(L_{II}\) and \(L_{II}\) scattering are nearly equal in intensity. Warming from 100 K to \(T_N\) results in no change in the line shape; only a decrease in intensity is observed. Similarly, above \(T_N\) the line shape remains constant, exhibiting an order-parameter like drop-off in intensity around 240 K. The inset to Figure 2(a) shows the temperature dependencies of the intensity measured at 645.5 eV and 648.5 eV. (The intensity of the 648.5 eV feature is only indicated above 180 K, as the contribution from the magnetic scattering dominates at lower temperatures.) The transition temperatures \(T_N = 175 \text{ K}\) and \(T_{OO} = 240 \text{ K}\) agree well with those measured in Ref.\textsuperscript{3} and comparison with neutron data on the same sample\textsuperscript{15} confirms that the resonant
diffraction intensity below $T_N$ is indeed sensitive to the magnetic ordering.

In Figure 2(b), we show the HWHM of the magnetic Bragg peak as a function of energy near the Mn $L$-edges. Away from the $L_{II}$ and $L_{III}$ edges, photoelectric absorption limits the penetration depth to $\sim 1000$ Å. Figure 2(b) indicates the further decrease in penetration depth as the incident energy is tuned through the Mn $L$-edges, resulting in a broadening of the magnetic peak. Comparing the absorption and the resonant diffraction spectra shows that the peak in the absorption coincides with the peak in the orbital spectrum. We note that the resonant line shapes in 2(a) are not corrected for absorption effects; however, calculations of the absorption away from the $L$-edge suggest that the change in absorption does not significantly affect the resonant line shapes.

This study permits the first direct comparison of magnetic and orbital correlations in a manganite. Figure 3 compares longitudinal momentum scans through the orbital and magnetic diffraction peaks at 645 and 648 eV. At both energies, the orbital peak is significantly broader than the magnetic peak, indicating that the difference in width results from differences in the magnetic and orbital correlation lengths and not absorption or extinction effects. We define the inverse correlation length, $\frac{1}{\xi} = HWHM$, where the HWHM of the peak is fit with a Lorentzian line shape. Analyzing the peaks at 645 eV, we find an orbital correlation length $\xi_{orb} = 375 \pm 40$ Å. The magnetic correlation length however, is more than a factor of two longer with $\xi_{mag} = 780 \pm 40$ Å.

In earlier $K$-edge resonance experiments on Pr$_{1-x}$Ca$_x$MnO$_3$, it was found that the orbital correlation length was $\sim 300$ Å for $x = 0.4$, in good agreement with our results, and $\sim 160$ Å for $x = 0.5$ [1]. Comparison with neutron scattering measurements, which showed similarly short-ranged magnetic correlations in the Mn$^{3+}$ sub-lattice, led to suggestions that the Mn$^{3+}$ magnetic and orbital correlation lengths were identical [2] [1]. These results supported the CE picture, since orbital domain walls create magnetic domain walls in the Mn$^{3+}$ sub-lattice. However, the $L$-edge resonant diffraction at $(\frac{1}{2}, 0, 0)$ is only sensitive to the Mn$^{3+}$ sites and clearly indicates longer range correlations between spins than orbitals within this sub-lattice. Furthermore, we confirmed that the discrepancy between magnetic and orbital correlation lengths is isotropic in the $ab$ plane by measuring transverse scans through the magnetic and orbital peaks. This measured difference between orbital and magnetic correlation lengths presents a direct challenge to the Goodenough picture of magnetic and orbital coupling.

A further challenge to the Goodenough picture lies in the comparison between the magnetic and orbital resonant diffraction line shapes and intensities. In the CE model, the magnetic and orbital scattering at $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, 0)$ result entirely from the Mn$^{3+}$ sub-lattice. However, a single atom picture cannot explain two of our key findings:

First, the magnetic scattering is significantly stronger than the orbital scattering. A larger population of $a$-oriented than $b$-oriented domains could favor magnetic scattering. In a separate experiment, we found that the orbital and magnetic spectra were maximized for different positions of the beam on the sample surface. By optimizing the beam position separately for the orbital and magnetic spectra, we found a ratio of magnetic to orbital peak intensities $\sim 25:1$. Other factors will also contribute to a smaller orbital scattering, such as the shorter in-plane correlation length and the greater absorption at the orbital peak energy.

Second, the orbital resonance line shape is peaked at energies where there is little spectral weight in the magnetic scattering. This is difficult to reconcile with a single atom picture, where the spectral weight for magnetic and orbital scattering is expected to be in the same energy range.

However, we find we can describe both the resonant line shapes and difference in intensities by assuming a more realistic ground state in which the $e_g$ electron is shared between neighboring sites,

$$|g\rangle = \alpha|3; 4\rangle + \beta|4; 3\rangle$$  \hspace{1cm} (1)

Here, $|i; j\rangle$ denotes $i$ electrons on the JT distorted site where the scattering takes place and $j$ electrons on a neighboring site along a ferromagnetic chain. (In the CE model depicted in Figure 1, $|g\rangle = |4; 3\rangle$.) The hopping parameter $t$ that couples the two configurations in Eqn. (1) is approximately of the order of 1-1.5 eV and is therefore significantly larger than the JT energy of 0.1-0.3 eV. We can therefore expect $\alpha \approx \beta$.

The inclusion of coupling to a neighboring site leads to two different (dipole allowed) intermediate states:

$$|n_1\rangle = \beta'|\mathbf{c}^5; 3\rangle - \alpha'|\mathbf{c}^4; 4\rangle$$ \hspace{1cm} (2)

$$|n_2\rangle = \alpha'|\mathbf{c}^5; 3\rangle + \beta'|\mathbf{c}^4; 4\rangle$$ \hspace{1cm} (3)

where $\mathbf{c}$ denotes a $2p$ core hole. Within an ionic picture, the energy difference $\Delta_1 = E_{|\mathbf{c}^5; 3\rangle} - E_{|\mathbf{c}^4; 4\rangle}$ is related to the Coulomb interactions between $3d$ electrons, $U_{dd}$, and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Longitudinal momentum scans above ($T = 183$ K, dark circles) and below ($T = 100$ K, open circles) $T_N$ at (a) 645 eV and (b) 648 eV.}
\end{figure}
between the 3d electrons and the 2p core hole, $U_{pd}$. Thus, $\Delta_1 = U_{dd} - U_{pd}$, which can be of the order of a few eV.

We will argue that the magnetic scattering is dominated by the $|3;4\rangle$ configuration of the ground state while the orbital scattering is dominated by the $|4;3\rangle$ configuration, and that the orbital scattering is dominated by transitions to the higher energy $|n_2\rangle$ intermediate state, while the magnetic scattering is dominated by transitions to the lower energy $|n_1\rangle$ intermediate state. Thus, the orbital scattering spectral weight is shifted to a higher energy than the magnetic scattering.

The ground-state configurations $|3;4\rangle$ and $|4;3\rangle$ make significantly different contributions to the orbital scattering. Contributions to orbital scattering occur in two ways. First, the JT distortions split the 3d intermediate states, leading to a finite orbital scattering on resonance. This effect occurs for both intermediate state configurations $|2;4;4\rangle$ and $|2;5;3\rangle$. However, as shown in Ref. [12], this effect is only important if the JT splitting is significantly larger than the core-hole lifetime broadening of 0.3-0.5 eV. A second and much stronger effect occurs if the lower $e_g$ level on the JT site is occupied in the ground state. Therefore, the $|4;3\rangle$ configuration makes the dominant contribution to the orbital scattering.

In contrast, there is no reason to assume that the magnetic scattering of the $|3;4\rangle$ and $|4;3\rangle$ configurations differ strongly in intensity (although their spectral line shapes can be different). However, it is straightforward to show that the ratio of scattering intensities for the two different intermediate states $|n_1\rangle$ and $|n_2\rangle$ is $r = [(\alpha \beta')/(\alpha \beta')]^4$. Assuming $\alpha \approx \beta$, $t = 1.1$ eV and a 3.5 eV splitting between $|n_1\rangle$ and $|n_2\rangle$, we obtain $r = 20$. This shows that the scattering through intermediate states $|n_2\rangle$, and therefore the orbital scattering, is about 20 times weaker than the magnetic scattering. Similarly, the magnetic scattering arising from $|n_2\rangle$ will also be significantly smaller than that from $|n_1\rangle$.

To quantify these arguments, we calculated the magnetic and orbital scattering in the ordered state by exact diagonalization of a Hamiltonian including the full $U_{pd}$ and $U_{dd}$ Coulomb interaction and the 2p and 3d spin-orbit coupling for the different configurations. We assumed an octahedral crystal field of 1.5 eV and a JT splitting of the $e_g$ orbitals of 0.1 eV.

The results are compared with the measured spectra in Figure 4, which shows the separate and combined contributions from the $|3;4\rangle$ and $|4;3\rangle$ configurations. Figure 4(a) shows the magnetic scattering, which is dominated by the $|3;4\rangle$ configuration. The $|4;3\rangle$ contribution is strongly reduced by the spectral weight effect described above. Figure 4(b) shows the orbital spectrum. It is dominated by the $|4;3\rangle$ configuration, which though reduced by the same spectral weight transfer compared to the magnetic scattering, still contributes more strongly than the $|3;4\rangle$ configuration to the orbital scattering.

We note that this model is preliminary and that a number of open questions remain. For example, the model cannot explain why the magnetic spectrum is strongest below the peak in the absorption. Nevertheless, we feel it is a step in the right direction and illustrates the quality of ground state information obtained with this technique.

In summary, we have measured the resonant line shape at the Mn $L$-edge in Pr$_{0.6}$Ca$_{0.4}$MnO$_3$, at $T_N < T < T_{OO}$ and at $T < T_N$. The comparison of the magnetic and orbital line shapes, in addition to theoretical calculations, strongly suggest that the Mn sites are highly mixed between the Mn$^{3+}$ and Mn$^{4+}$ formal oxidation states. Furthermore, we find that the magnetic correlations are longer ranged than the orbital correlations. These findings pose a direct challenge to the classic Goodenough picture of charge, orbital and magnetic order in half-doped manganites. The results presented here emphasize the sensitivity of resonant diffraction at the Mn $L$-edge to the ground state of the 3d electrons and encourage a new approach to theoretical calculations.

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