

Orbital and Spin Correlations in a Manganite Probed With Soft X-ray Resonant Diffraction

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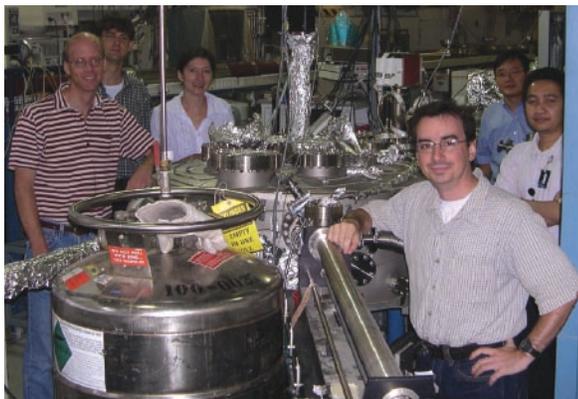
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Soft x-ray resonant diffraction was used to directly probe spin and orbital correlations in a near-half doped manganite. The diffraction was performed at the manganese (Mn) L_{II} and L_{III} absorption edges, providing a sensitive spectroscopy method for studying the Mn 3d states in the spin and orbitally ordered phases. These measurements suggest that the established “checkerboard” model for charge ordering of the Mn^{3+} and Mn^{4+} ions is too simplistic, and reveal a surprising discrepancy between the orbital and magnetic correlation lengths.

In doped manganites of the form $RE_{1-x}A_xMnO_3$ (where RE is a rare earth and A is a divalent element), the magnetic coupling between Mn sites depends on the overlap of the Mn 3d electron orbitals. Therefore, a complex behavior arises in these materials when the direction of the highest occupied Mn 3d orbital is itself a degree of freedom. For example, the Mn 3d orbitals can undergo long-range order, usually in association with cooperative distortions of the oxygen octahedra that surround the Mn sites. Understanding how the orbital physics drives the overall ground state necessitates a direct probe of both orbital and magnetic order.

We used resonant x-ray diffraction to directly probe the magnetic and orbital order in the near half-doped manganite $Pr_{0.6}Ca_{0.4}MnO_3$, for which the proposed spin, charge, and orbital ground state is shown in **Figure 1**. The incident energy at a magnetic, $(\frac{1}{2} 0 0)$, or orbital, $(0 \frac{1}{2} 0)$, Bragg peak was tuned through the Mn L_{II} and L_{III} atomic absorption edges (~ 650 eV). At the L-edges, core Mn $p_{1/2}$ and $p_{3/2}$ electrons are resonantly excited into unoccupied 3d levels, which enhances the Mn sites' contribution to the diffracted intensity. The strength of the $2p \rightarrow 3d$ resonance at a Mn site depends on the local charge distribution of the occupied 3d orbitals. This leads to a large contrast between the resonant scattering factors on sites 1 and 2 (**Figure 1**) and a large enhancement of the orbital $(0 \frac{1}{2} 0)$ Bragg peak. The resonance matrix element also depends on the direction of the spin in

the 3d levels, resulting in magnetic resonant scattering at the antiferromagnetic Bragg peak, $(\frac{1}{2} 0 0)$. The magnetic enhancement at the L-edges is truly enormous – off resonance, the magnetic scattering is too weak to be



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BEAMLINE X1B

Funding

Department of Energy, Division of Materials Science; The Netherlands Organization for Scientific Research (NWO) Spinoza program

Publication

K.J. Thomas, J.P. Hill, S. Grenier, Y.-J. Kim, P. Abbamonte, L. Venema, A. Rusydi, Y. Tomioka, Y. Tokura, D. F. McMorrow, G. Sawatzky, and M. van Veenendaal, "Soft X-ray Resonant Diffraction Study of Magnetic and Orbital Correlations in a Manganite Near Half-Doping," *Phys. Rev. Letts.*, **92**, 237204 (2004).

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observed in these materials – and thus provides a unique opportunity to directly compare the orbital and magnetic correlations in a manganite.

Figure 2a shows the orbital and magnetic resonant line shapes (energy scans at fixed Q). The features in the line shapes are the different excited states in the $3d$ band, which are probed with increasing incident energy. The 3 eV shift in spectral weight and the large difference in intensity between the orbital and magnetic spectra suggests that the checkerboard charge-ordered picture in **Figure 1** is too simple. Furthermore, longitudinal scans through the orbital and magnetic Bragg peaks show that the orbital peak is approximately two times wider than the magnetic peak (**Figure 2b**). This suggests that the orbital correlations are shorter-ranged than the magnetic correlations, a result that appears at odds with orbitally driven magnetic order.

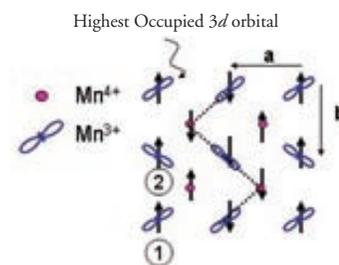


Figure 1. Schematic of the ground state exhibiting charge-orbital-magnetic order in $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, showing only the Mn sites in the Mn-O plane. In $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, the charge order is modeled as a checkerboard of Mn^{3+} and Mn^{4+} ions and only the Mn^{3+} ions have the orbital degree of freedom. (The symmetry of the highest occupied electron orbital is indicated by a blue lobe). The orbital zig-zag chains couple the Mn sites ferromagnetically along the chain and antiferromagnetically between the chains. The orbital order doubles the unit cell along b , leading to $(0 \frac{1}{2} 0)$ type reflections, while the spin order doubles the unit cell along a , leading to $(\frac{1}{2} 0 0)$ reflections.

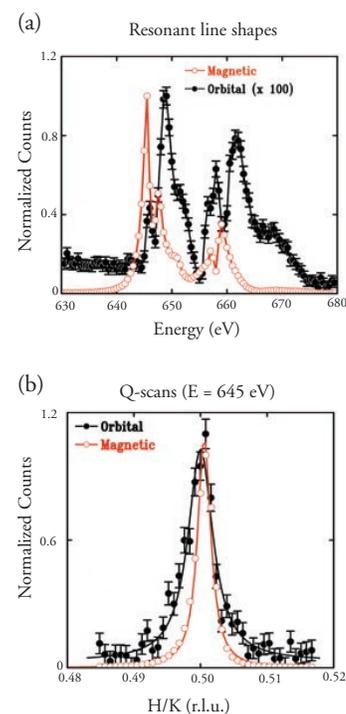


Figure 2. (a) Resonant diffraction line shapes at fixed Q at the orbital $(0 \frac{1}{2} 0)$ position (black curve) and the magnetic $(\frac{1}{2} 0 0)$ (red curve). Note that the magnetic resonant line shape is peaked ~ 3 eV below the orbital line shape. (b) Longitudinal Q scans through the magnetic and orbital Bragg peaks, at the same energy.