Soft x-ray diffraction from lattice constrained orbital order in Pr(Sr$_{0.1}$Ca$_{0.9}$)$_2$Mn$_2$O$_7$

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Abstract. Controlling orbital occupancy is a fundamental prerequisite for orbitronics. It has been shown in the orthorhombic bilayer manganite Pr(Sr$_{0.1}$Ca$_{0.9}$)$_2$Mn$_2$O$_7$ that the direction of orbital order stripes can be influenced by controlling temperature or through inducing strain in the material. In this paper we have used resonant soft x-ray diffraction at the Mn L-edge to confirm the rotation of the orbital direction $T_{OO2}$ and furthermore prove that there is no change in the occupied orbital type, however the orbital rotation causes a switch from $3x^2-r^2$ to $3y^2-r^2$ on a single site. We find that unlike the tetragonal bilayer manganites, where an onset of A-type AFM quenches the orbital order, no such effect is found on the orbital order below $T_N$.

1. Introduction

Orbital order is a key ingredient in the transition metal oxides[1, 2, 3], however the control or even measurement of this order parameter has been elusive. Crystallographic distortions, in particular Jahn-Teller distortions appear to be ubiquitous in orbitally ordered materials, and many systems also contain magnetic and even charge order. This makes direct measurements of orbital order particularly difficult. Despite this, there is considerable interest in measuring, and possibly controlling, the orbital occupancy in a material[4].

In the material Pr(Sr$_{0.1}$Ca$_{0.9}$)$_2$Mn$_2$O$_7$, Tokunaga and co-workers have recently shown that the direction of orbital chains can be switched through a thermal transition[5], and more recently through applying uniaxial stress[6]. Like many layered manganites, Pr(Sr$_{0.1}$Ca$_{0.9}$)$_2$Mn$_2$O$_7$ possesses both long range magnetic and charge order, in addition to orbital order. Diffraction techniques are inherently wavevector sensitive and so, in principle, can selectively probe individual order parameters with unique periodicities. This is complicated by the concomitant nature of the Jahn-Teller distortions and orbital order[7]. Not only do these phenomena both occur with the same wavevector, but they also have the same transition temperatures. However, it was conclusively demonstrated by Castleton and Altarelli that orbital order and Jahn-Teller distortions can be disentangled through the resonant diffraction spectrum at the Mn L edges[8, 9].
Pr(Sr$_{0.1}$Ca$_{0.9}$)$_2$Mn$_2$O$_7$ crystallises in a orthorhombic lattice, and so unlike other tetragonal bilayer manganites[10], the $a$ and $b$ axes can be easily separated through diffraction, even on a twinned crystal. The crystal can be described in the $Amam$ spacegroup, with lattice parameters $a = 5.410$ Å, $b = 5.462$ Å and $c = 19.277$ Å at 405 K. Through the anisotropy of optical conductivity, Tokunaga and co-workers concluded that the orbital order formed with chains running along the $b$ axis below 350 K[5]. The orbital chains were constrained by the orthorhombic crystal lattice, whereas tetragonal bilayer manganites have shown orbital chains simultaneously along both $a$ and $b$ axes. Intriguingly below $\sim 325$ K the stripe direction of the orbital chains flips to lie along the $a$ axis. There is simultaneously a small crystallographic change, however the $b$ axis remains longer than the $a$ axis.

In this paper we describe the use of soft x-ray diffraction to observe the rotation of orbital stripes in Pr(Sr$_{0.1}$Ca$_{0.9}$)$_2$Mn$_2$O$_7$ using soft x-ray resonant diffraction at the Mn $L$ edges. The anisotropy of the stripes can be determined in each phase through azimuthal measurements, and the complex temperature dependence of the orbital order signals are explained.

2. Experimental Method
Soft x-ray diffraction measurements were undertaken at beamlines ID08 at the ESRF and I06 at Diamond Light Source (DLS). A sample of Pr(Sr$_{0.1}$Ca$_{0.9}$)$_2$Mn$_2$O$_7$ was prepared with the [100] face surface normal. Due to the similarity of the $a$ and $b$ lattice parameters of the orthorhombic crystal, a large degree of twinning was observed. Thus it was possible to observe scattering reflections in both the [100] and [010] directions simultaneously. The experiments were conducted under high vacuum conditions, using the soft x-ray diffraction endstation at ID08, and using the Daresbury soft x-ray diffractometer at DLS. A new sample mount was designed for use at DLS incorporating a piezo rotation device to enable azimuthal measurements.

3. Results and Discussion
At 330 K a diffraction signal was observed at a $2\theta$ angle of 121° corresponding to the (0,$\frac{1}{2}$,0) orbital order reflection (Fig. 1). This displayed a complex energy spectrum with split resonances at both the manganese $L_3$ and $L_2$ edges[11]. Reducing the temperature of the sample to 315 K revealed a double reflection, observed by two peaks in the $\theta$-$2\theta$ scan. The orthorhombic nature of the sample causes the $2\theta$ value of the ($\frac{1}{2}$,0,0) reflection to be slightly higher than that of the (0,$\frac{1}{2}$,0) reflection, however it is clear from the scan at 315 K that these two reflections can be resolved. The individual crystallographic domains of the twinned were sufficiently small such that no observable relative change in intensity of either reflection was observed when raster scanning the synchrotron x-ray beam over the sample. At DLS the x-ray beam was only of order 100 $\mu$m horizontally and 20 $\mu$m vertically. As the sample was cooled further, the original high temperature (0,$\frac{1}{2}$,0) disappears, and the $2\theta$ value of the ($\frac{1}{2}$,0,0) reflection increased due to thermal contraction of the sample. At 90 K there was a further transition where a step increase in the wavevector of the orbital order reflection was observed. Further investigation using single crystal high energy x-ray x-ray revealed this to be a structural transition, evident through a change in the lattice parameters [11]. This revealed that the orbital order reflection remains at the commensurate position, and the transition is purely structural, rather than a commensurate to incommensurate transition.

Figure 2 shows the relative intensities of the (0,$\frac{1}{2}$,0) and ($\frac{1}{2}$,0,0) reflections. This demonstrates the simultaneous presence of both orbital configurations between 280 K and 325 K. Although this might suggest the presence of a second order transition, as the crystal is twinned with many small domains, it is quite possible that within each domain the transition is of first order. The inset of Figure 1 shows a schematic of the orbital stripes in the $ab$ plane in both phases. Despite the reduction of intensity previously seen in the orbital signal in bilayer manganites[12], we
observe no change of intensity at $T_N$. In addition to the change in position of the orbital signal, there is a slight decrease in intensity at $T_S$.

Although the position of the $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, 0)$ reflections are sufficient to separate the two orbital configurations, it is possible to measure the anisotropy and therefore the direction of the orbital stripes through azimuthal measurements. The sample is rotated around the scattering vector, and the intensity of the reflection is measured while the Bragg condition is maintained. Figure 3 shows the variation of the intensity of these reflections. The expected intensity of the reflection has been calculated using the orbital model shown in the inset of Figure 2, and shows good agreement with the data.

4. Conclusion

Resonant soft x-ray diffraction has been used to observe the orbital transition in $\text{Pr(Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$. Using a highly twinned sample the observation of the $(0, \frac{1}{2}, 0)$ and

Figure 1. $\theta$-2$\theta$ scans showing the diffraction signals in the different orbital phases. All scans were measured at 652 eV. The inset shows the change in position of the reflection through the low temperature transition ($T_S$). The change in position of the reflection between 295 K and 100 K is due to thermal contraction, and reflects a gradual change of lattice parameter, rather than the abrupt change observed at 90 K.

Figure 2. Temperature dependence of the orbital order reflections measured while cooling. The $(0, \frac{1}{2}, 0)$ reflection appears at $T_{O01}$, with the $(\frac{1}{2}, 0, 0)$ reflection forming at $T_{O02}$. A further transition is observed at $T_S$. The orbital schematic insets show the orbital order configuration above and below $T_{O02}$. The data was measured at 652 eV at the Mn $L_3$ edge.
Figure 3. Anisotropy of the \((\frac{1}{2},0,0)\) and \((0,\frac{1}{2},0)\) orbital order reflections, measured by rotating the sample around the scattering vector. The solid line shows the calculated azimuthal dependence. Fitting errors of the peak intensity are within the symbol size.

\((\frac{1}{2},0,0)\) has been possible in a single sample. A strong resonant signal was seen, particularly in the low temperature phase, with each orbital reflection showing an azimuthal dependence in agreement with the orbital model. This conclusively demonstrates that orbital order exists in \(\text{Pr(Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7\) and the direction of the orbital chains can be switched through temperature control.

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