| ESRF | **Experiment title:** Soft X-ray diffraction of orbital rotations | **Experiment number**: HE 2677 |
|---|---|---|
| **Beamline**: ID08 | **Date of experiment**: from: 30th April 2008 to: 5th May 2008 | **Date of report**: 25th Sept 2008 |
| **Shifts:** 18 | **Local contact(s)**: Dr. Julio CRIGINSKI CEZAR | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

Prof. Peter D. Hatton

Dr. Thomas Beale

Mr Stewart Bland

**Report:**

This aim of this experiment was to observe the orbital rotation in $Pr(Sr_{0.1}Ca_{0.9})_2Mn_2O_7$ using soft x-ray diffraction. In the main this experiment was highly successful; a strong resonant signal was observed at the (0,0.5,0) positions which was then seen to move to the (0.5,0,0) position below the orbital transition. High resolution energy spectra were taken of these resonances, showing a highly complex Mn L edge resonance.

There were a few minor experimental issues. Initially the Keitheley currently anplyfier was very noisy, which made it very difficult to locate the reflection. When this current amplyfier was replaced by a different current amplifier / v to f, the signal to noise ratio on the reflection increased by around two orders of magnitude.

Secondly, a failiure in one of the in-vacuum sample translation stages prevented us from taking azimuths of the reflections. For this reason we have delayed publishing the results until this could be undertaken. These measurements have now been taken at Diamond, and the work will be submitted for publication shortly. The next page shows the first page of the paper to be submitted, of which a draft is completed.

# Thermally induced rotation of $3d$ orbital stripes in $Pr(Sr_{0.1}Ca_{0.9})_2Mn_2O_7$

T. A. W. Beale,[1] S. R. Bland,[1] R. D. Johnson,[1] P. D. Hatton,[1,*]
J. C. Cezar,[2] S. S. Dhesi,[3] D. Prabhakaran,[4] and A. T. Boothroyd[4]

[1]*Department of Physics, University of Durham, Rochester Building, South Road, Durham, DH1 3LE, United Kingdom.*
[2]*European Synchrotron Radiation Facility, Boîte Postal 220, F-38043 Grenoble Cedex, France*
[3]*Diamond Light Source Ltd, Harwell Science and Innovation Campus, Diamond House, Chilton, Didcot, Oxfordshire OX11 0DE, United Kingdom*
[4]*Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, United Kingdom.*

(Dated: September 24, 2008)

Experimental results of resonant soft x-ray diffraction from orbital reflections in $Pr(Sr_{0.1}Ca_{0.9})_2Mn_2O_7$ are presented. Diffraction signals are observed at $(0, \frac{1}{2}, 0)$ above 300 K and $(\frac{1}{2}, 0, 0)$ below 300 K, corresponding to orbital stripes along the $a$-axis and $b$-axis respectively. The previously observed transition at 300 K is evidence of a rotation of the orientation of the $3d$ orbital stripes. Large resonances of the orbital signals are observed at the Mn $L$ edges, showing a complex structure indicative of a weakly Jahn-Teller distorted system. A second transition is seen at ∼85 K. Both these transitions are strongly first order, displaying hysteretic behaviour.

PACS numbers: 78.70.Ck, 75.47.Lx, 75.50.Ee, 75.60.Ch,

The application of the semicovalent exchange theory to the manganite series[1] initiated the drive to observe and understand the charge and orbital ordering and their complex interaction with magnetic order[2–4]. Recently this research has developed to investigate the possibilities of controlling and exploiting these order parameters, developing the fields of spintronics and orbitronics[5]. The mediation of the orbital state has been pioneered through applying strain to tetragonal $La_{1-x}(Sr,Ca)_xMnO_3$ thin films, coupling the Jahn-Teller distortions to the uniaxial strain[6,7]. This causes a preferential occupancy of the mangenese $3d$ orbitals in a single direction.

In this communication we observe the thermal switching of occupied orbitals in $Pr(Sr_{0.1}Ca_{0.9})_2Mn_2O_7$ using soft x-ray diffraction at the Mn $L_{2,3}$ edges. This means we are directly sensitive to Mn $3d$ electron orbitals through the resonant enhancement of the $2p \rightarrow 3d$ dipole transition. Unlike many manganites, $Pr(Sr_{0.1}Ca_{0.9})_2Mn_2O_7$ crystalizes into the orthorhombic spacegroup, $Amam$, with lattice parameters $a = 5.410$ Å, $b = 5.462$ Å, $c = 19.277$ Å at 405 K. This orthorhombic lattice, above the orbital order transition, has been shown to confine the formation of the orbital order to a single stripe direction[8–10]. Through investigations of the anisotropic optical response, supported by electron and x-ray diffraction measurements, it was concluded that the lone $e_g$ electron orbitals of the $Mn^{3+}$ ions order into stripes along the $a$-axis below $T_{OO1}$, 370 K (Figure 1). As the system is cooled below $T_{OO2}$, 300 K, these orbital stripes re-orientate such that the stripes now run along the $b$-axis. Although there is a small structural change both at $T_{OO1}$ and $T_{OO2}$ the system remains orthorhombic throughout.

Below the onset of orbital order ($T_{OO1}$), the space group is more properly described as $Pbnm$, followed by a further transition to $Am2m$ at $T_{OO2}$. However, for clarity throughout the paper we will refer to the orbital reflections as indexed in the $Amam$ spacegroup.

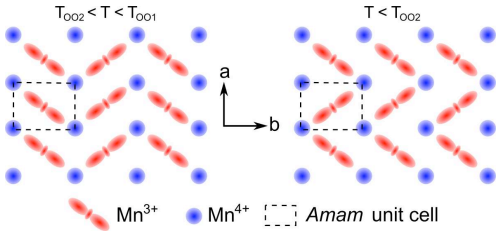


FIG. 1: Schematic of the orbital stripes running along the $a$-axis below $T_{OO1}$, and along the $b$-axis below $T_{OO2}$. Note that the structure is orthorhombic, above $T_{OO1}$, facilitating preferential stripe directions.

Samples of $Pr(Sr_{0.1}Ca_{0.9})_2Mn_2O_7$ were grown at the University of Oxford using the floating zone technique[11,12]. Small high quality samples were selected and prealigned with a rotating anode x-ray source. Two such samples, aligned with the indistinguishable (at low resolution) $a$-,$b$-axis surface normal, were polished to a mirror-like surface with 0.25 $\mu$m diamond suspension. Prior to the soft x-ray diffraction experiment these samples were studied with non-resonant (9.26 keV) high resolution x-ray diffraction at BM28, ESRF. This showed both samples to be twinned, through a 90° rotation, with reflections from each domain being approximately equal. Raster scanning the samples did not preferentially select either domain, suggesting that the domains were much smaller than the incident x-ray beam (100 × 300 $\mu$m). The sample giving the cleanest diffraction signal was then mounted in the in-vacuum six circle x-ray diffractometer on beamline ID08, ESRF. Diffraction measurements were undertaken using a horizontally polarized x-ray beam, provided by a single APPLE II undulator with an energy