

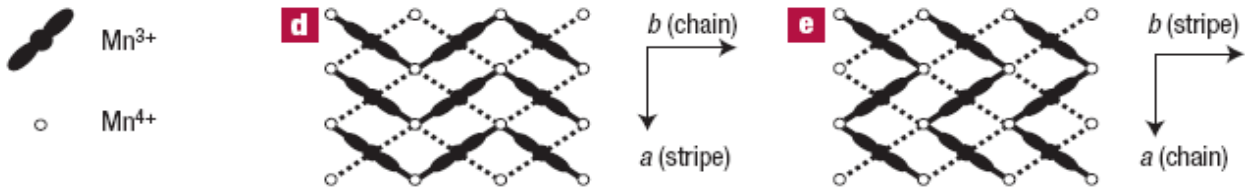


	<b>Experiment title:</b> Ferroelectricity driven by orbital order in multiferroic $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$	<b>Experiment number:</b> 28-01 814
<b>Beamline:</b> BM28	<b>Date of experiment:</b> from: 29 Aug 2007 to: 4 Sept 2007	<b>Date of report:</b> 19 Dec 2010
<b>Shifts:</b> 18	<b>Local contact(s):</b> D. Mannix	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): *Prof Andrew Boothroyd (Oxford University, UK) Miss Heather Lewtas (Oxford University, UK) *Dr Danny Mannix (XMaS CRG, ESRF, France)		

## Report:

The recent interest in multiferroic materials is driven by the possibility of the development of new smart spintronic materials, such as electric field manipulated magnetic data storage. X-ray Resonant Scattering can provide a powerful microscopic description of the mechanisms leading to the multiferroic state.  $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$  has attracted considerable scientific attention due to its ferroelectric state arising from charge and orbital ordering [1]. This effect may lead to the possibility of ferroelectric devices manipulated by small perturbations of orbital order. *The aim of this experiment was to initiate an investigation into the orbital and charge ordered degrees of freedom in  $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$  at the XMaS beamline.*

$\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$  undergoes several crystallographic and charge ordered phase transitions [1]. At 405K, it has the Amam space group, with  $a=5.410 \text{ \AA}$ ,  $b=5.462 \text{ \AA}$  and  $c=19.277 \text{ \AA}$ , which is charge disordered. At 365K the crystal structure becomes Pbnm, with  $a=5.412 \text{ \AA}$ ,  $b=10.921 \text{ \AA}$  and  $c=19.234 \text{ \AA}$  with charge order and orbital stripes along the a-axis. Below 295K, the space group becomes Am2m with  $a=10.812 \text{ \AA}$ ,  $b=5.475 \text{ \AA}$  and  $c=19.203 \text{ \AA}$  and with charge order and orbital stripes along the b-axis. In this phase, the 90-degree rotation of the orbital stripes drives the material ferroelectric, see **Fig. 1**.

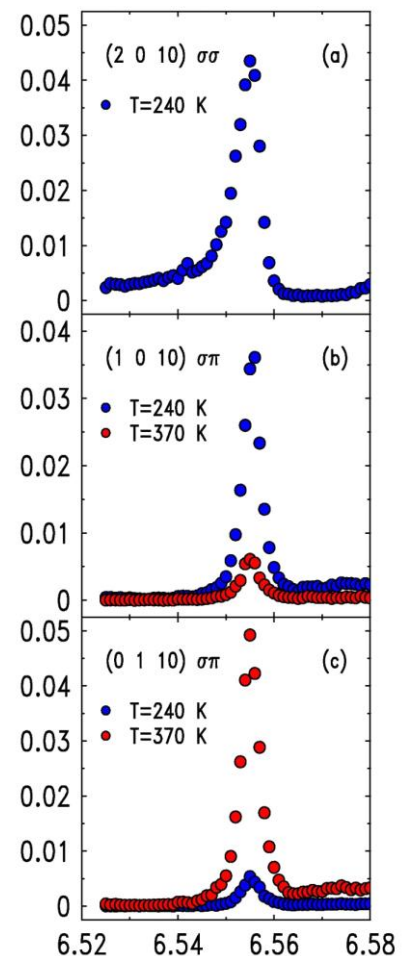


**Figure 1.** The charge and orbital stripes in  $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$  ref. [1]. (left) The high temperature charge ordered phase, with orbital stripes along the  $a$ -axis. (right) The low temperature charge ordered phase, with orbital stripes rotated by 90 degree, orientated along the  $b$  axis.

During this experiment we investigated the thermal evolution of the charge and orbital order in  $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$ . At 240K, with the incident photon energy tuned to the Mn K edge, we observed RXS at charge order Bragg positions such as  $(2, 0, 10)$  in the  $\sigma\sigma$  scattered polarization, as shown in **Fig. 2a**. Furthermore, these experiments have allowed us to investigate directly the orbital order at Bragg positions  $(1, 0, 10)$ , where we have observed the switching of the orbital stripes from the  $a$  axis to the  $b$  axis below and above 295K, as shown in **Figs. 2b&c**.

In a future experiment, we plan to build on these interesting results by measuring the azimuthal dependence of the charge and orbital peaks. This will enable us to understand better the origin of these peaks and, in the case of the orbital peaks, it will provide a check of the asymmetry of the scattering object (probably small Jahn-Teller distortions with the same symmetry as the  $d_{x^2/y^2}$  orbitals).

**Figure 2.** Energy scans of: (a) Charge Order peak  $(2, 0, 10)$  in the  $\sigma\sigma$  channel at the Mn K-edge. (b) the Orbital Order peak at  $(1, 0, 10)$  in the  $\sigma\pi$  channel at 240K and 370K. (c) The Orbital Order peak  $(0, 1, 10)$  in the  $\sigma\pi$  channel at 240K and 370K. Notice the switching of the orbital peaks from the  $a$  to  $b$  axes in figures (b) and (c).



## Reference

[1] Tokunaga *et al.* Nature Mat. **5**, 937 (2006); Keimer *et al.* Nature Mat. **5**, 933 (2006).