EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: *https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Microscopic Understanding of the Ferroelectric Mechanism in $BaMnF_4$	**Experiment number**: HC1767
Beamline:	**Date of experiment**: from: 06/05/15 to: 10/05/15	**Date of report**:
Shifts:	**Local contact(s)**: Jon Wright	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Mark Senn*
Warwick University, UK

Jon Wright*
ESRF

Report:

<u>Proposal Summary:</u>

The aim of this project is to develop a microscopic understanding of the driving forces responsible for the incommensurate ferroelectric phase transition in $BaMnF_4$. $BaMnF_4$ is not only important in its own right as a ferroelectric, with a T_N very close to room temperature (250 K), but its mechanism has potentially far-reaching implications on how we understand many other improper ferroelectrics and multiferroic materials. The ordered phase contains many weak superstructure peaks spanning 5 orders of magnitude. We propose to collect complete single crystal data sets containing these weak superstructure peaks to very high Q using a microcrystal and making use of the high brilliance and high energy of ID11 – the approach we used to solve the Verwey structure of magnetite.

<u>Scientific background of the Proposal:</u>

Proper ferroelectrics refer to a class of materials that develop a spontaneous electric polarisation below a transition temperature where the polarisation itself may be considered as the primary order parameter of the phase transition. As the physical property is a direct manifestation of the order parameter it is intuitive to conceive how the physical property might be tuned or enhance. Improper ferroelectrics on the other hand are a growing group of materials where the polarisation forms only a secondary order parameter of the phase transition. This group of materials provide substantially greater challenges in understanding the relationship between the order parameter(s) and physical property, and sound microscopic understanding requires an accurate knowledge of the atomic structure. Surprisingly, the microscopic mechanism of relatively few materials exhibiting improper ferroelectricity have been elucidated, and as such this represents a large bottle neck to the systematic development of new ferroelectrics with enhanced magnitudes of response.

Recently Benedek and Fennie[1] have proposed a new mechanism for ferroelectricity in the Ruddlesden-Popper (RP) compounds involving two order parameters both which have a non-zero propagation vector (and hence by symmetry arguments none of these single order parameters any induce ferroelectricity). We have recently performed a detail crystallographic study of these RP phases (under review) and our findings broadly support the picture of Benedek and Fennie and show how octahedral tilting and rotations may give rise to a ferroelectric polarisation.

In $BaMnF_4$, the local coordination environment has many similarities with the RP phases, consisting of interconnected corner sharing $Mn(F/O)_6$ octahedra. Despite the fact that crystallographic studies of these materials have been performed on several occasions [2,3] the order parameters for the ferroelectric phase transition have yet to be identified and a microscopic understanding of the mechanism is withstanding. At 250K this material undergoes an incommensurate phase transition with propagation vector [~0.2, 1/2, 1/2] below which it develops a spontaneous polarisation. The evolution of the propagation vector and particularly the intensity of the superstructure peaks are of great interest if the microscopic mechanism of this material is to be elucidated.

We have also recently shown[4] that an effective strategy for reliably extracting the intensity of weak superstructure peaks is to work at high resolutions ($\sin(\theta)/\lambda$) where the relative intensity of superstructure to structure peaks increases. Additionally, the use of microcrystals coupled to the high brilliance at high energies on ID11 will allow us to mitigate the effects of twining, multiple scattering and extinction on the data. We propose to use a similar approach here to elucidate the atomic structure of $BaMnF_4$

Results obtained during beamtime:

During our beamtime on ID11 data was collected primarily on two crystallites of approximately 50 microns. At 80 keV these were both found to scatter out to about 0.3-0.4 A. Data was collected for these crystals at 2-4 different phi orientations as a function of temperature from 300 down to 90 K. In total 8 temperature points were collected one each crystal (1 above and 7 below the phase incommensurate transition). Reliable structure refinements above the phase transition could be achieved with R1 < 3%. All data below the phase transition (270 K) was integrated with two propagation vectors k1 = (½ ½ 0.4) and k_2 = (½ -½ 0.4) which are inequivalent due the centring of the parent cell ($Cmc2_1$ 4.237Å x 15.170 Å x 6.021 Å). In total the hkl5 files contained ~ ¼ of million reflections. These reflections comprise primarily of satellite reflection (hklm) for m = 1,2 and 3 although a substantial numbers of higher order m = 4 and 5 with I >3sigma can be observed in certain planes (See Figure 1). This clear observation of higher order reflections points to a more anharmonic nature of the incommensurate phase than has been previously supposed. The significance of this results is that this phase transition is coupled to the multiferroic properties that develop below T_N. Our analysis of this high quality data and the high order satellite reflection is ongoing.

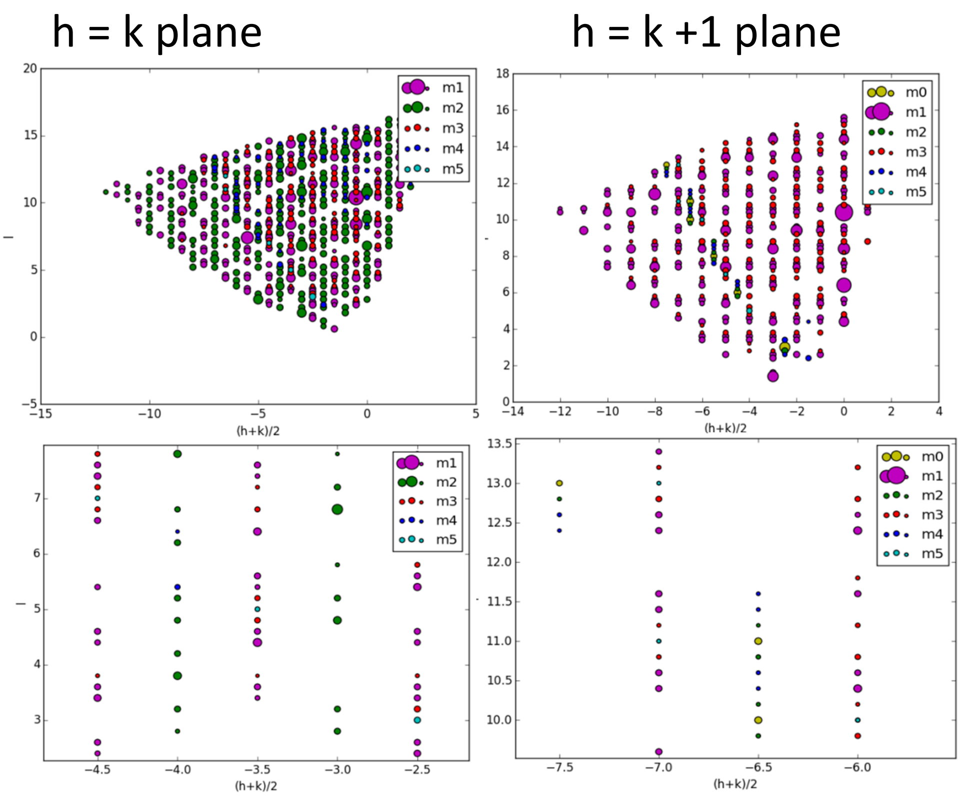

Figure 1: Plots of incommensurate satellite reflections with at 90K dataset of $BaMnF_4$. Only satellites for which $I > 3\sigma$ are plotted, with the area of the makers being proportional I/σ. While lower order satellite reflections dominate these plots, a significant number of higher order reflections (m = 4 and 5) are observed in the different planes.

<u>References</u>

[1] N. Benedek and C. Fennie, *Phys. Rev. Lett.* **106**(2011), 107204
[2] Ph. Sciau, J. Lapasset, D. Grebille and J. F. Berar, Acta. Cryst. A **B44**(1988), 108-116
[3] J. M. Posse, A. Grzechnik and K. Friese, Acta Cryst. **B65** (2009), 576–586
[4] Mark S. Senn, Jon P. Wright and J. Paul Attfield. *Nature* **481** (2012), 173-176.