

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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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

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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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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.


Experiment title:

Resonant X-ray Study of the Total Ionic Separation in Charge Ordered Fe₂OBO₃

Experiment number:

HE2902

Beamline: ID20	Date of experiment: from: 3/12/2008 to: 9/12/2008	Date of report: 06/03/2009
Shifts:	Local contact(s): V. Scagnoli	<i>Received at ESRF:</i>

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Report:

Charge disproportionation and ordering has been the subject of a substantial number of studies in condensed matter physics, and represents a key concept in helping us understand a range of interesting phenomena. A variety of transition metal oxides display a degree of charge disproportionation at equivalent crystallographic sites, such as magnetoresistive manganites [1] and superconducting stripes in cuprates [2]; with the stripes' dynamic fluctuations being suggested as a mechanism for high temperature superconductivity [3].

The iron oxoborate material, Fe₂OBO₃, is an interesting transition metal compound, which appears to demonstrate the transition from charge disordered orthorhombic crystal to charge ordered monoclinic crystal upon cooling [4], with a CO structure which doubles the *a*-axis at low temperature. In Fe₂OBO₃ the CO transition occurs at 340 K, below which Mossbauer spectroscopy has revealed charge disproportionation in a partially localized structure, with non-integer charge separation of the iron atoms [5]. However, upon cooling below 270 K Mossbauer and bond-valence-sum studies have suggested that the system approaches near total ionic separation, and is the most explicit example of integer valence separation seen so far in any system [6]. These ions exist at four separate sites, which are unequally crystallographically distorted [5, 6]. Recent x-ray scattering experiments by the principal investigator [7] have shown that upon warming from the low temperature CO phase, with superlattice reflections present at commensurate (*n*/2 *k* *l*) type positions (i.e. with *n*, *k*, *l* integers), the reflections move to incommensurate positions along the *c*-axis in the high temperature CO phase.

In our study at ID20, we began by selecting a suitable crystal of iron oxyborate, which grows in the form of needles measuring 0.2mm x 0.1mm x several cm. The crystals grow along the *a*-axis, with clean facets in the [0 1 1] and [0 0 1] directions. After reducing the size of the sample, so as to be comparable to the incident x-ray the sample was mounted with the [0 0 1] direction surface normal. After establishing a UB matrix, we then identified the incommensurate reflections at room temperature, before cooling the sample into the incommensurate region. However, we found that cooling too rapidly inhibits the development of long range

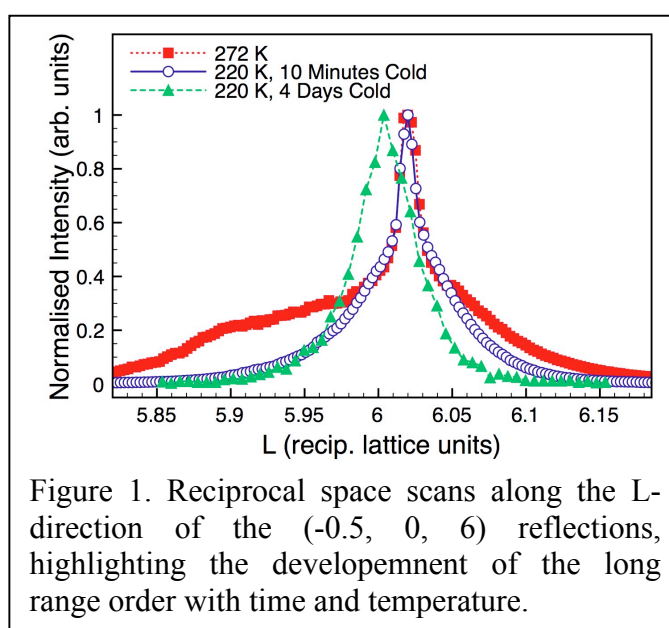


Figure 1. Reciprocal space scans along the L-direction of the (-0.5, 0, 6) reflections, highlighting the development of the long range order with time and temperature.

However, we found that cooling too rapidly inhibits the development of long range

commensurate order. After returning to room temperature and cooling slowly, we observed the development of the commensurate $(-0.5, 0, 6)$ reflection at around 275 K, Figure 1. However, it is only with additional cooling, and time, that the reflection becomes fully commensurate, with no diffuse background.

In this study we only examined the commensurate phase, and revealed that at least two different kinds of reflections exist at these positions. In the un-rotated σ - σ channel we observed reflections that showed small resonant features amid the usual absorption profile, and reflections that showed a strong resonance, Figure 2. Such a strong resonance with little non-resonant contribution is indicative of a strong charge order, with little contribution from any associated lattice distortion. Surprisingly we also observed some reflections solely in the σ - π channel; a scattering process that does not originate from pure charge order. The only mechanisms which may produce such an effect are magnetic scattering and Templeton (ATS) scattering. However, the system does not become magnetically ordered until 155 K [10] and Templeton reflections are limited to integer indices of the crystallographic structure. One additional possibility is the existence of Templeton scattering through the presence of a small additional lattice distortion: which is often associated with orbital order [11, 12].

By utilizing the phase plate available only on ID20 we were able to perform full polarization analysis, revealing that signal expected to originate from charge order shows a dramatic conversion of a large proportion of the scattered signal to non-linearly polarised light, Figure 3. We are currently in the process of analysing and explaining this phenomenon, however, in order to do so, we must extend our study into the, as yet unstudied, incommensurate phase. We also observed a Templeton reflection at the $(0\ 0\ 7)$ position, confirming that some distortion away from the known structure must be present, as such Templeton reflections from iron sites are forbidden in the known $P2_1/c$ structure.

By utilising the full polarisation analysis studies taken of the $(-0.5\ 0\ 6)$, $(0\ 0\ 7)$ and $(1.5\ -2\ 6)$ reflections and a large range of energy scans in both the rotated and unrotated polarisation channels, we intend to employ theoretical fitting using the FDMNES code to understand the nature of long range order in the commensurate phase of iron oxyborate; as previously demonstrated in such materials as magnetite [13].

References

- [1] Mori S, Chen C H and Cheong S -W, *Nature* **392** 473-476 (1998) [2] Tranquada J M *et al.*, *Nature* **375** 561-563 (1995) [3] Salkola M I, Emery V J, and Kivelson S A, *Phys. Rev. Lett.* **77** 155-158 (1996) [4] Attfield J P *et al.* *J. Mater. Chem.*, **9** 205-209 (1999) [5] Douvalis A P *et al.*, *J. Phys.: Condens. Matter*, **12** 177-188 (2000) [6] Angst M *et al.*, *Phys. Rev. Lett.*, **99**, 086403 (2007) [7] Angst M *et al.*, *Phys. Rev. Lett.*, **99**, 256402 (2007) [10] Attfield J. P. *et al.* *J. Mater. Chem.*, **9**, 205 (1999) [11] Lorenzo J. E. *et al.* *PRL* **101**, 226401 (2008) [12] Bland S R *et al.*, Unpublished [13] Nazarenko E *et al.* *Phys. Rev. Lett.* **97**, 056403 (2006)

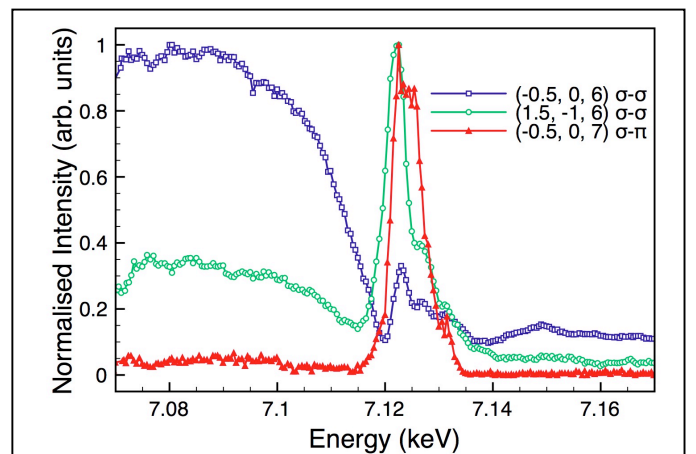


Figure 2. Energy spectra of several superlattice reflections in Fe_2OBO_3 , measured on ID20, at 220 K (within the commensurate phase). The $(-0.5, 0, 7)$ reflection is only present in the rotated σ - π channel.

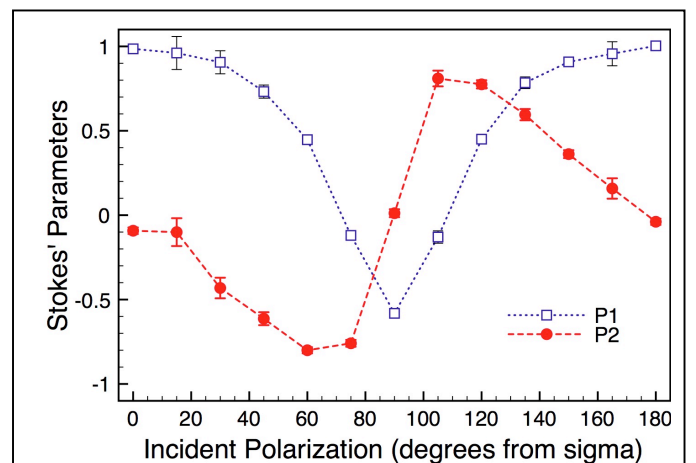


Figure 3. The result of a full polarisation analysis on the commensurate $(-0.5, 0, 6)$ reflection at 220K [10]. A pure charge order signal is expected to drop to a P1 value of -1, which is clearly not achieved.