

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://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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.

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.

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: Low Temperature structure of off-stoichiometric magnetites	Experiment number: HC1452
Beamline: ID11	Date of experiment: 29/10/14 – 31/10/14 and 8/10/15 – 10/02/15	Date of report: 01/09/14
Shifts: 12	Local contact(s): Jon P. Wright	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Prof J. Paul Attfield, Centre for Science at Extreme Conditions, University of Edinburgh *Dr. Elise Pachoud, Centre for Science at Extreme Conditions, University of Edinburgh *Dr. James Cumby, Centre for Science at Extreme Conditions, University of Edinburgh Dr. Mark Senn, Centre for Science at Extreme Conditions, University of Edinburgh Dr Jon P. Wright, ESRF Giuditta Perversi, Centre for Science at Extreme Conditions, University of Edinburgh		

Report:

This experiment aimed to study the effect of non-stoichiometry on the Verwey [1] structure of magnetite, $\text{Fe}_{3(1-\delta)}\text{O}_4$. Previous studies by Honig et al. [2] had concluded that the charge-ordered Verwey structure is very sensitive to chemical perturbation, the transition temperature decreasing with increasing iron deficiency. However, no detailed structural analyses had previously been reported for systematically non-stoichiometric samples. The goal of this experiment was to apply the knowledge and techniques we have developed while measuring stoichiometric magnetite (HE3133 and [3]) to this difficult problem.

A large number of microcrystals were screened during the experiment, initially to find good-quality cubic crystals, but more importantly to obtain crystals with the smallest number of twin domains on cooling through the cubic-to-monoclinic transition. Once a good quality crystal was obtained, the transition temperature was determined from wide angle diffraction images, measured while varying temperature. This procedure also served to later calibrate the cryostream temperature against SQUID magnetometry data. Following this screening, highly-redundant datasets were collected for a number of crystals; $3\delta = 0.001, 0.009$ and 0.012 . In addition, it was also possible to perform measurements on a sample of naturally-occurring magnetite.

From the high quality datasets, it has been possible to perform an unconstrained structural refinement for all samples, the results of which are detailed below.

Natural Sample

Analysis of data from a naturally-occurring sample of Fe_3O_4 has shown that a Verwey-like transition does occur, at a temperature (119 K) slightly below that of synthetically-pure magnetite (123 K) (figure 1). This is consistent with a small amount of chemical doping ($\sim 1\%$) as determined from elemental analysis. The crystallographic structure of the sample below the transition temperature is very similar to that of pure Fe_3O_4 , showing very slight deviations due to doping. This work is currently being prepared for submission to Earth and Planetary Science Letters, and is the first direct structural evidence that the charge-ordered Verwey phase is likely to exist in non-terrestrial magnetite.

Non-stoichiometric Samples

Of the samples measured, only one ($3\delta = 0.012$) shows a significant difference in Verwey transition temperature from the pure, stoichiometric sample; the other two samples show crystallographic structures very similar to the $3\delta = 0$ model and the natural sample (above). Despite the large value of δ , the sample continues to show a Verwey-like crystallographic structure, forming the same monoclinic Cc supercell; from variable temperature diffraction images (figure 2) the transition temperature is determined as 103 K.

Refinement of a structural model for $3\delta = 0.012$ finds subtle changes from the $3\delta = 0$ structure, suggesting a reduction in overall charge separation between Fe^{2+} and Fe^{3+} sites. Analysis of the complex and correlated structural changes observed are still ongoing, and will benefit from comparison with samples of even greater non-stoichiometry.

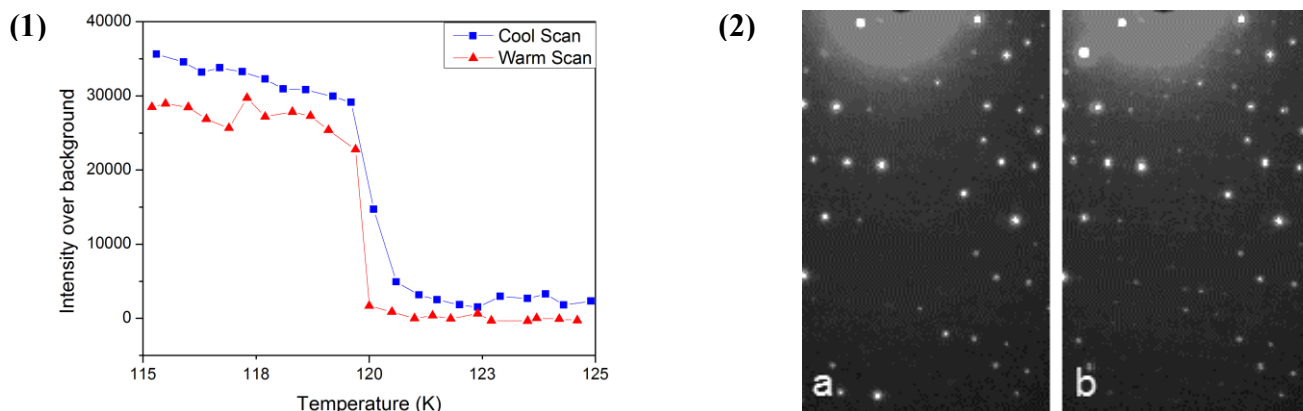


Figure 1: Changes in intensity of a superstructure peak in a natural magnetite sample, indicative of the cubic ($Fd-3m$) to monoclinic (Cc) transition.

Figure 2: Consecutive detector images for $3\delta = 0.012$ on cooling through the Verwey transition ($T_v = 103$ K), showing development of Cc superstructure peaks.

References

- [1] E. J. W. Verwey, Nature, 1939, **144**, 327-328.
- [2] J. M. Honig, J. Alloys Compds. 1995, **229**, 24-39.
- [3] M. S. Senn, J. P. Wright, and J. P. Attfield, Nature, 2012, **481**, 173-176.