EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

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.

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.

ESRF	**Experiment title:** Microcrystal study of Fe3O4 below the Verwey transition	**Experiment number**: HE3133
Beamline: ID11	**Date of experiment**: from: 21/10/2009 to: 23/10/2009	**Date of report**: 28.2.2011
Shifts:	**Local contact(s)**: Jon Wright	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Jean-Paul Attfield, Centre for Science at Extreme Conditions, University of Edinburgh
Mark S Senn*, Centre for Science at Extreme Conditions, University of Edinburgh
Jon P Wright*, ESRF

Report:

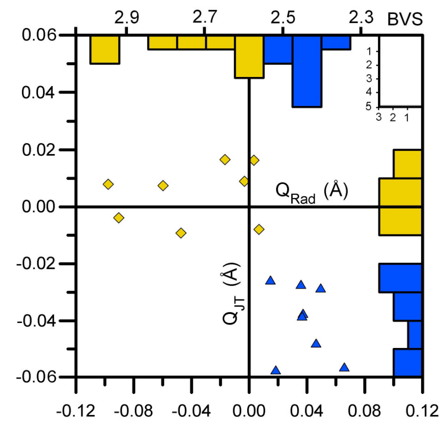
Magnetite (Fe_3O_4) is the oldest magnetic material known to man. The binary oxide is of particular theoretical interest on account of its low temperature transition (the Verwey transition) at ~ 120 K (T_v), which is believed to be as a result of charge ordering,[1] and gives rise to a multiferroic ground state. However, despite extensive study over the last 70 years since the discovery of the Verwey transition, the experimental determination of the structure of the low temperature phase has until now been withstanding.

Historically the solution of the structure by x-ray diffraction has been hampered due to the microtwinning which occurs below the T_v and the extinction and multiple scattering which makes reliable determination of the weak superstructure peaks problematic. By making use of the high brilliance at hard energies (75 keV) of the source at ID11 and by using a r ~ 20 μm grain of magnetite, we have been able to demonstrate that the problems conventionally hampering the structure determination by single crystal diffraction may be experimentally overcome (Figure 1).

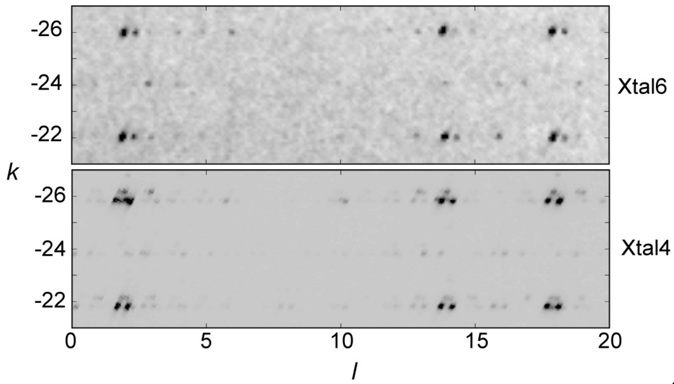
We were able to collect significant data on two different crystals and have hence been able to verify our structure for the ground state of magnetite independently. The data collected on one of the crystals (xtal6), comprising of 91, 433 unique reflections out to a resolution of 0.3 Å (Figure 2) has allowed us to make a completely anisotropic refinement of the 56 atom asymmetric unit of the space group Cc ($\sqrt{2}a$ x $\sqrt{2}a$ x $2a$) which correctly describes the low temperature structure.

Our results confirm the long proposed space group, and the conjecture Verwey made in 1939 of charge ordering. Additionally orbital ordering of the Fe^{2+} states is evidenced by the local distortion of the FeO_6 octahedra which is in good agreement with models proposed from electronic structure calculations.[2,3] However anomalous shortening of almost all Fe^{2+}-Fe^{3+} distances orthogonal to the $Fe^{2+}O_6$ Jahn-Teller short axis has been observed. These results along with charge transfer implied by the rather continuous BVS distribution imply that these three site distortions (trimerons, Figure 4) are the fundamental local ordering parameter rather than the charge or orbital ordering. Our findings are published in Nature and are supported by our electronic structure calculations which are published in Physical Review B.[4, 5]

(3)



(1)



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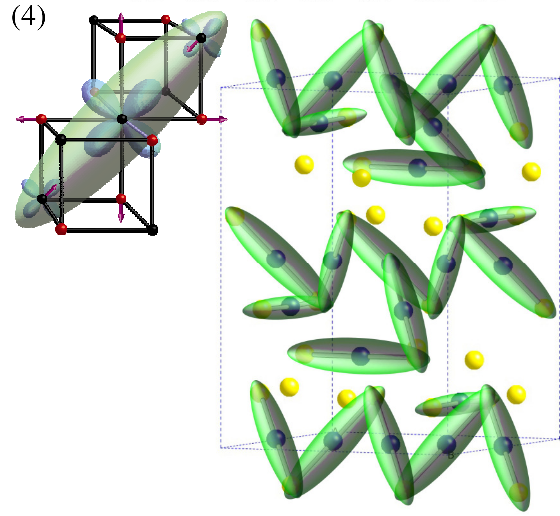

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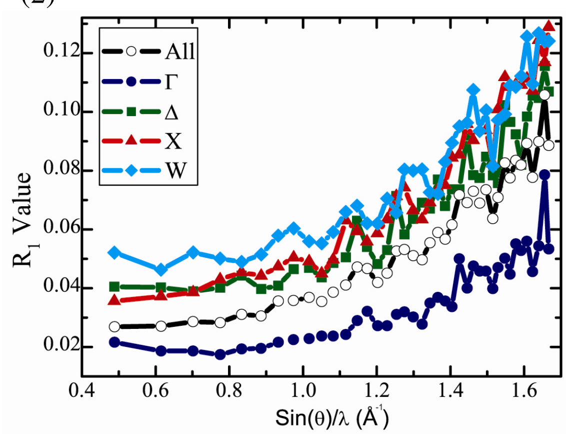

Figure 1: Reciprocal section from a r = 20 μm (Xtal6) and a r = 100 μm grain (Xtal4) measured at ID11showing that a near single domain of the Verwey structure of magnetite is obtained for the smaller grain with only a small degree of monoclinic twinning, while for the larger grain orthorhombic type twinning is also observed.
Figure 2: Fitting statistics for the final refinement (506 parmaters, 91,433 unique reflections) against Xtal6 data, as a function of resolution shell.
Figure 3: BVS and Jahn-Teller distortion correlation for Fe^{3+} (yellow) and Fe^{2+} (Blue) states evidencing charge ordering.
Figure 4: A trimeron - an orbitally ordered Fe^{2+} state that shares charge with two neighbouring sites, arrows indicates the distortions of iron (black) and oxygen (red) atom positions. The Jahn-Teller short Fe^{2+}-O bond is out of the plane of the page and coloured light blue. The cooperative arrangement of trimeron distortions within the Verwey structure. Fe^{2+}/Fe^{3+} states are shown as blue and yellow spheres respectively with trimerons represented as green ellipsoids

References:

[1] E. J. W. Verwey, *Nature*, 1939, **144**, 327-328.
[2] H. T. Jeng, G. Y. Guo and D. J. Huang, *Phys. Rev.* B, 2006, **74**, 195115.
[3] K. Yamauchi, T. Fukushima, and S. Picozzi, *Phys. Rev.* B, 2009, **79**, 212404.
[3] M. S. Senn, J. P. Wright, and J. P. Attfield, *Nature*, 2012, **481**, 173-176.
[4] M. S. Senn, I. Loa, J. P. Wright, and J. P. Attfield *Phys. Rev. B,* 2012, **85**, 125119.