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

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.

ESRF	**Experiment title:** The Verwey Structure of Magnetite under Pressure	**Experiment number**: HC1634
Beamline: ID09a	**Date of experiment**: from: 23/10/2014 to: 27/10/2014	**Date of report**: 01/09/2015
Shifts: 12	**Local contact(s)**: Michael Hanfland	*Received at ESRF:*

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Report:

Previously, we have shown that below the Verwey transition [1], magnetite (Fe3O4) adopts a complex arrangement of cooperative 'trimeron' distortion, in addition to charge- and orbital-ordering. [2] Previous powder diffraction results in diamond anvil cells had shown that this monoclinic-to-cubic transition is suppressed at higher pressures, above ~ 6 GPa (figure 1).[3]

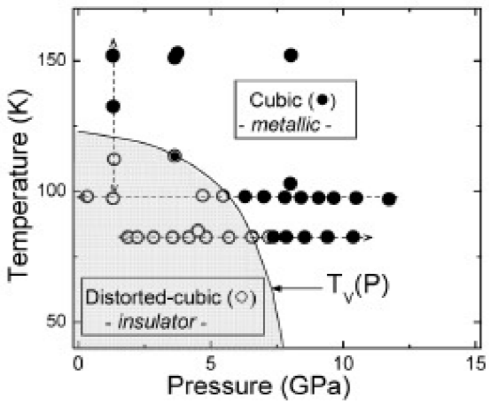
The aim of this experiment was to investigate the evolution of the structural distortions under pressure and temperature, using single crystal diffraction. Based on our experience of measuring the transition at ambient pressure (experiment HE3133 and [2]) it was apparent that this experiment would present considerable technical difficulties, due to both the limited rotation of the diamond cell (resulting in incomplete data sets) and significant twinning occurring during the transition.

During the experiment, three different crystals were loaded and measured under a range of temperatures and pressure. The first proved unsuitable for further data collections due to poor data quality on cooling through the Verwey transition. A wide range of pressure/temperature points were collected for the other two crystals; the first (crystal 1) was measured on cooling to 90 K, before increasing pressure in ~0.5 GPa increments to a maximum of 7.5 GPa. For comparison, pressure was applied to the final crystal (crystal 2) at a temperature above the transition (150 K) up to a maximum of ~5.5 GPa, before cooling through the transition. Once at 90 K, the pressure was again increased to 7.5 GPa. At all temperature/pressure points, data were collected with a range of X-ray fluxes to capture both strong and weak reflections.

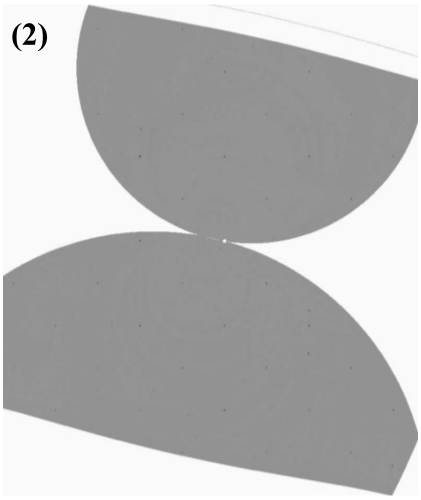
Initial results from the diffraction data closely agree with the phase diagram generated from powder diffraction data; crystal 1 shows the expected transition from cubic to monoclinic symmetry on cooling below ~120 K (figures 2 and 3), followed by a transition back to cubic symmetry at pressures above ~6.5 GPa. Crystal 2 shows supression of the transition temperature with pressure, 90 K < T_v < 110 K at 5.5 GPa. This crystal also shows a transition from monoclinic back to cubic symmetry between 5.6 GPa and 7.5 GPa at 90 K.

Currently, the significant crystal twinning present below the transition have prevented a full refinement of the crystal structure from these data. Work to simplify the structural model is on-going in order to make full use of the limited data, as are methods to systematically reject anomalous intensities.

(1)



(2)



(3)

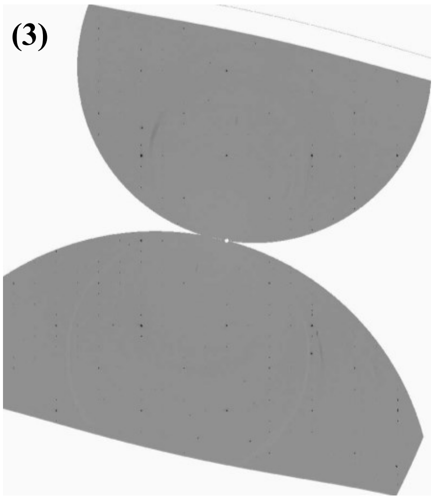


Figure 1: P-T diagram showing variation of Verwey transition temperature with pressure, from [3]. Our results confirm this analysis, adding additional data points.
Figure 2: Diffraction plane from crystal 1 at showing cubic symmetry.
Figure 3: Diffraction plane from crystal 1 at 90 K, clearly showing the development of monoclinic superstructure peaks.

References

[1] E. J. W. Verwey, Nature, 1939, **144**, 327-328.
[2] M. S. Senn, J. P. Wright, and J. P. Attfield, Nature, 2012, **481**, 173-176.
[3] G. Kh. Rozenberg et al., Phys. Rev. Lett. 2006, **96**, 045705.