EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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 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:** **High pressure-low temperature Moessbauer study of magnetite across the structural transition and magnetic anomaly**	**Experiment number**: HC-3069
Beamline: ID18	**Date of experiment**: from: 11 to: 18 April 2017	**Date of report**: 06 June 2017
Shifts: 18	**Local contact(s)**: Dr. V. Cerantola	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

D.P.Kozlenko, S.E.Kichanov, E.V.Lukin

Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research,
141980 Dubna, Russian Federation

Report:

Studies of the pressure-induced phenomena in magnetite Fe_3O_4, the oldest known magnetic material, have a long and controversial history [1-7]. At ambient pressure, the crystal structure of magnetite is of the inverse spinel type with tetrahedral sites (T-) occupied by Fe^{3+} and octahedral sites (O-) occupied both by Fe^{2+} and Fe^{3+}. The antiferromagnetic exchange between the T- and O-sites aligns magnetic moments of iron along the [111] direction. At P ~ 20 GPa, a reconstructive phase transition to a high pressure polymorph, of the $CaTi_2O_4$ structural type, occurs [3, and refs. therein]. In addition, at P ~ 15-20 GPa, anomalous behaviour of the magnetic and electronic properties was established by several techniques including Mössbauer spectroscopy [4], combined X-ray magnetic circular dichroism and X-ray emission spectroscopy study [5]. The nature of these anomalies remains controversial. Possible scenarios include the inverse to normal spinel type transition [4,7], high spin to intermediate spin transition (HS-IS) in the octahedral sites occupied by Fe^{2+} [6], the enhanced delocalization of 3*d* electrons of iron atoms [7].

The important information clarifying nature of the magnetic and electronic states of Fe ions in different oxygen coordination in Fe_3O_4 and their evolution across the structural and magnetic anomalies region the can be obtained from high pressure – low temperature Moessbauer experiments. We should note that at present time no systematic Moessbauer studies of Fe_3O_4 at high pressure and low temperature were performed. Most of previous measurements were performed at ambient or elevated temperatures [2,4] and only scarce data sets at pressures P ~ 35 GPa well above the region of interest and few temperature points are available [8]. In order to provide a detailed insight into the microscopic mechanisms of the magnetic anomalies observed in Fe_3O_4, we performed high pressure – low temperature synchrotron Moessbauer experiments at ID-18 in the pressure range 0-40 GPa and temperature range 10-300 K.

The representative synchrotron Moessbauer spectra of Fe_3O_4 measured at P = 28 GPa and temperatures of 100 and 290 K are shown in Fig. 2. At low temperatures, they can be fitted by two sextets corresponding to the Fe ions in the tetrahedral and octahedral sites of the spinel structure. The typical values of the isomer shifts are 0.35 and 0.73 mm/s, hyperfine fields 48.4 and 48.0 T, quadrupole splittings -0.04 and 0.02 mm/s (T = 100 K). At elevated temperature T = 290 K, a broadening of the spectral lines and appearance

of the central line is detected. This observation corresponds to a phase transition to the orthorhombic high pressure phase with smaller magnetic ordering temperature and hyperfine fields, and larger quadrupole splittings for the two Fe ions sites (trigonal prismatic and octahedral), accompanying by a gradual spin crossover of the Fe^{2+} ions in octahedral sites from the high spin HS (S = 2) to the low spin LS (S = 0) state. Both cubic spinel and orthorhombic phases coexist at this temperature. At higher pressure, the temperature region of the orthorhombic phase stability is shifted to lower temperatures, while the spin crossover occurs only around the ambient temperature in the studied pressure range up to 40 GPa. The detailed data analysis is in progress.

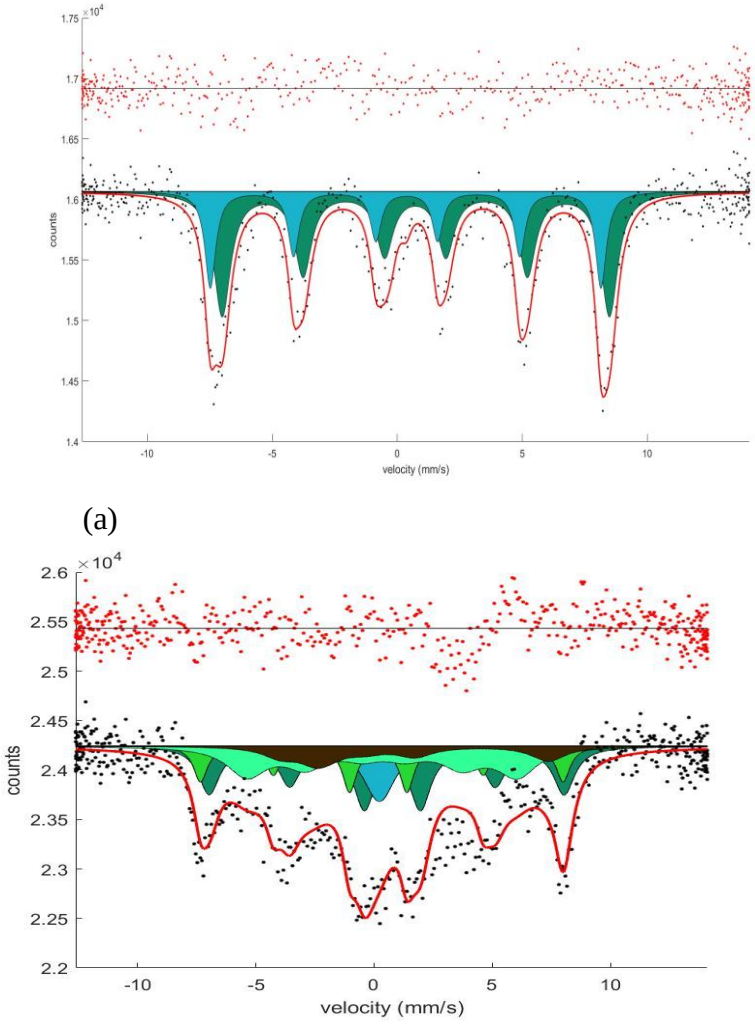

Figure 1. The representative synchrotron Moessbauer spectra of Fe_3O_4, measured at P = 28 GPa and T = 100 K (a) and 290 K (b).

1. H. K.Mao et al., J. Geophys. Res. 79, 1165-1170 (1974).
2. M. P.Pasternak, et al., Phys. Rev. B, 50, 6446-6449 (1994).
3. E. Bykova, et al., Nature Commun. 7, 10661 (2016).
4. M.P.Pasternak, et al., J. of Magn. Magn. Mater. 265, L107-L112 (2003).
5. Y.Ding, et al., Physical Review Letters, 100, 045508 (2008).
6. G.Kh.Rozenberg, et al., Physical Review B, 75, 020102 (2007).
7. K.Glazyrin, et al., Am. Mineralogist, 97**,** 128-133, (2012).
8. W.M.Xu et al., Phys Rev. B 70, 174106 (2004).