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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 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:** Determination of spin-state of Fe in (Mg,Fe)(Si,Al)O3 at high pressures up to 130 GPa using HP-LT XMCD	**Experiment number**: ES-180
Beamline: ID12	**Date of experiment**: from: 26/11/2014 to: 03/12/2014	**Date of report**: 09/09/2015
Shifts: 18	**Local contact(s)**: Fabrice Wilhelm	*Received at ESRF:*

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Report:

The purpose of this proposal was to study the pressure-induced spin transition of iron silicate perovskite (Mg,Fe)(Si,Al)O_3. We expected to be able to measure the XMCD signal of the k-edge of Fe at low temperature and various pressures. We started out at ambient pressure conditions for obtaining a reference for the XMCD signal of the high-spin state. However, even without a diamond-anvil cell which would greatly decrease the signal due to the low transmission of ~7 keV x-rays through diamond, we were unable to obtain a reasonable signal, even after several hours of collection time. There were a few factors which contributed to the difficulties we faced: 1) The sample has a low Fe content (synthesized using 20% FeO), which results in a small absorption yield. 2) Samples were synthesized using a multi-anvil press, resulting in non-uniform and non-flat grains of about 20-30 μm in each direction (with X-ray beam diameter 30 μm). 3) Stability issues on the beamline which resulted in the beam drifting off the sample area during the measurement. Measuring the XMCD signal relies on subtracting the resulting differences of two opposing field directions between two XANES spectra of opposite polarizations, and, therefore, drift of the x-ray beam on the sample was producing a considerable undesirable effect on the measured signal and, thus, affecting repeatability and quality of the final data.

The beamline staff minimized the stabilization issues to the best extent possible, by removing any mechanical vibrations from the stages of the cryostat and the x-ray optics, by automatically scanning for the sample center every few short measurements, and by running each measurement multiple times for averaging. This still proved to be insufficient for the iron silicate perovskite sample, and it seems that the solution would be

to use a pelletized sample, produced by pressing multiple grains recovered from the multi-anvil synthesis into a pellet of ~100 μm diameter and ~50 μm uniform thickness.

In order to utilize the time for measuring the XMCD of Fe at high-pressure conditions, we decided to eventually measure an iron rich sample Fe_7C_3. This sample is ferromagnetic at ambient conditions (Tsuzuki et al. 1984) and is claimed to undergo two pressure-induced magnetic transitions (Chen et al. 2012; 2014), at around 7 and 53 GPa.

Our Fe_7C_3 samples were also recovered from a multi-anvil synthesis, and are therefore 20-30 μm in each direction. However, due to the high Fe content and due to the optimization efforts of the local contact we were able to obtain spectra with a reasonable signal at 6 GPa (295 K) and at 35 GPa (2 K) (see Fig. 1). The collection time for each spectrum was ~24 hours. We used local ESRF non-magnetic membrane cells, in the transmission mode. Pressure was measured offline using ruby fluorescence. Magnetic fields of ±1.5 T were used to measure the XMCD signal.

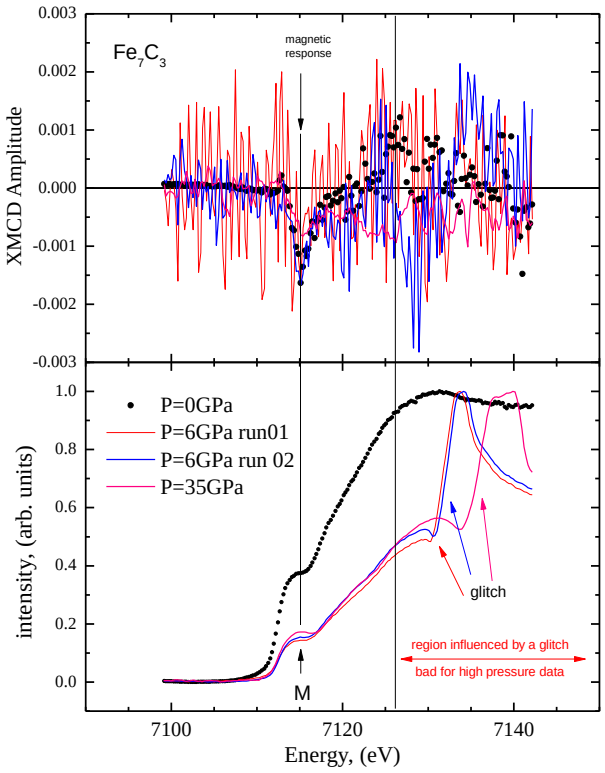

Figure 1: XANES (bottom) and XMCD (top) signal of Fe_7C_3 at 0 GPa (RT), 6 GPa (RT) and 35 GPa (2 K).

At 6 GPa we performed two runs, with the only difference being that in the 2nd run we optimized the sample position relative to the x-ray beam every few measurements. Figure 1 shows that this resulted in a spectrum of significantly higher quality, with a much better signal to noise ratio. We can also see that the XMCD signal at 6 GPa is very similar to our ambient pressure measurement. This is expected and goes well with observations of Chen et al. (2012; 2014). At 35 GPa and 2 K we still observe an XMCD signal at the same energy range, although with a lower intensity. This XMCD signal proves that the Fe still has a magnetic moment, and that the previously reported transition at room temperature high pressure conditions transforms Fe_7C_3 into a paramagnetic state with an ordering temperature below room temperature.

Another issue we faced was ‘glitches’ due to the diamond (spectral artifacts occurring due to strong diamond anvil diffraction). These artifacts affected a large energy range of the collected data at high pressure. We made several attempts to improve this situation (DAC rotation), but the glitches were not completely removed. Although the glitches were less of an issue at ambient pressure, at pressure of 35 GPa we had a strong parasitic signal from them affecting our signal in the energy range of our interest.

Further improvements to be made in future experiments include: 1) Collecting the data in the total fluorescence yield in back scattering geometry will help to avoid problems related to the sample surface and variations in effective thickness (see Fig. 2). 2) Using a partially perforated anvil will diminish effect of ‘glitches’. In the current run we were unable to do this, as our perforated anvils are not of the Boehler-Almax design required for the membrane cell provided by ESRF. Special diamond anvils need to be purchased for this purpose. 3) Pelletizing multiple grains of the recovered sample for the high-pressure experiments will minimize the effects due to instability.

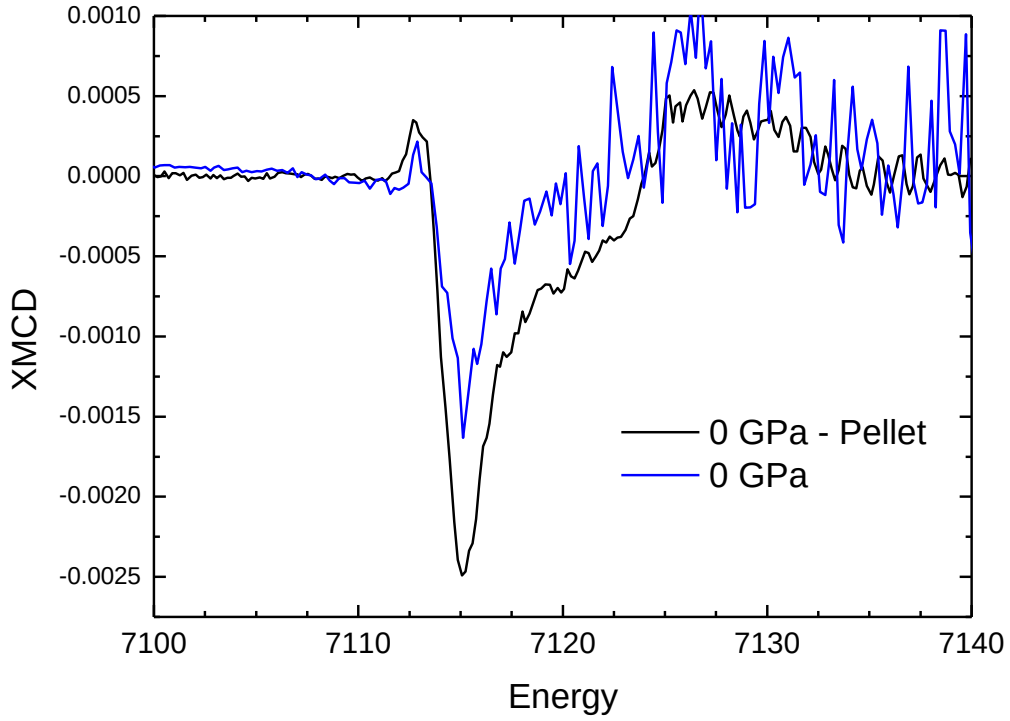

Figure 2: XMCD of Fe_7C_3 at 0 GPa (RT) collected in transmission mode (blue) and in total fluorescnece yield in back scattering geometry (black).

References:

Tsuzuki, A., Sago, S., Hirano, S.I., and Naka, S. (1984) High temperature and pressure preparation and properties of iron carbides Fe_7C_3 and Fe_3C. Journal of Materials Science, 19, 2513–2518.

Chen, B., Gao, L., Lavina, B., Dera, P., Alp, E.E., Zhao, J., and Li, J. (2012) Magneto-elastic coupling in compressed Fe_7C_3 supports carbon in Earth’s inner core. Geophysical Research Letters, 39, L18301

Chen, B., Li, Z., Zhang, D., Liu, J., Hu, M.Y., Zhao, J., Bi, W., Alp, E.E., Xiao, Y., Chow, P., and others (2014) Hidden carbon in Earth’s inner core revealed by shear softening in dense Fe_7C_3. Proceedings of the National Academy of Sciences, 111, 17755–17758.