EUROPEAN SYNCHROTRON RADIATION FACILITY

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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

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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 nature of the Fe^{3+} electronic state in $MFe^{3+}O_3$ (M = Al, B) above 50 GPa**	**Experiment number:** **HC-2174**
Beamline: ID18	**Date of experiment:** from: 10.11.2015 to: 17.11.2015	**Date of report:**
Shifts: 18	**Local contact(s): Daniel Merkel**	*Received at ESRF:*

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Report:

The interest in $MFe^{3+}O_3$ (M = Al, B) ferrites arises from our recent study of Fe_2O_3 hematite which revealed *a* novel type of Mott metal-insulator transition (MIT) characterized by a *site-selective* localization of the electrons [1]. This scenario contradicts the classical case of the MT, leading to an insulator to metal transition concurrent with a complete collapse of magnetism and an isostructural volume collapse, as it was observed for example in a very similar $GaFeO_3$ compound at ~50 GPa [2]. To further understand this new standpoint we have performed synchrotron MS (SMS) studies of other related ferric oxides: namely, the Al and B analogues of $GaFeO_3$ and $FeFeO_3$ up to 110 and 140 GPa, respectively. He was used as pressure medium.

Based on a preliminary analysis of the obtained SMS data and recently collected SXRD data we have established that $BFeO_3$ does not change the space group ($R\bar{3}c$) up to ~140 GPa, the highest pressure measured. Similar to previous observations [3], an isostructural volume decrease of ~8% was observed at around 55 GPa coinciding with the drastic change of the Al and B analogues of $GaFeO_3$ and $FeFeO_3$ up to 110 and 140 GPa, respectively. He was used as pressure medium.

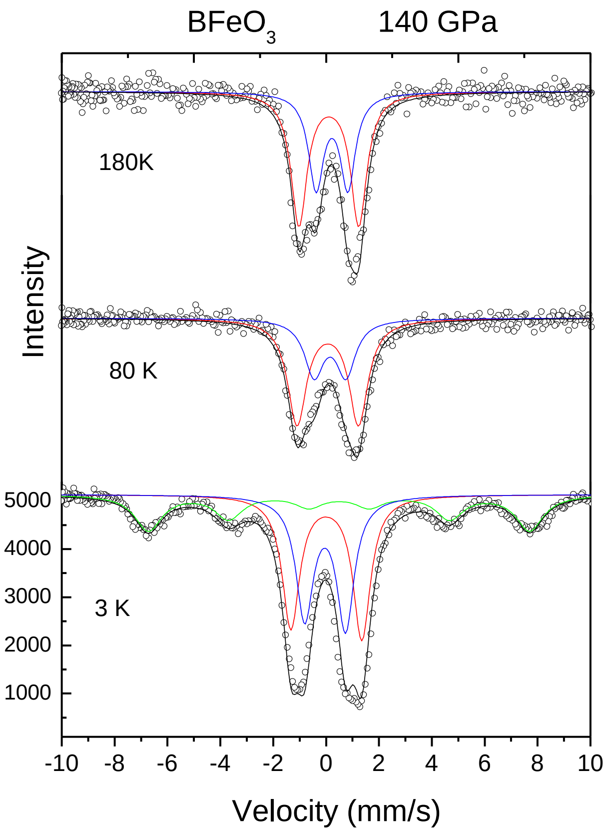

Fig. 1. Mössbauer spectra of $BFeO_3$ recorded at 140 GPa at various temperatures. Two components are clearly distinguished above 50 K. At temperatures below 50 K a new HS component appears (green one) with an abundance of ~30 %.

Based on a preliminary analysis of the obtained SMS data and recently collected SXRD data we have established that $BFeO_3$ does not change the space group ($R\bar{3}c$) up to ~140 GPa, the highest pressure measured. Similar to previous observations [3], an isostructural volume decrease of ~8% was observed at around 55 GPa coinciding with the drastic change of the magnetic properties. However, based on the obtained room temperature MS data we can conclude, that in $BFeO_3$ the corroborating magnetic and isostructural transition at ~55 GPa, which was explained previously as a transition to the low-spin (LS) state [4], in fact is the transition to a state characterized by two electronic sites (Fig. 1). The latter is especially hard to explain given the presence of only one Fe^{3+} structural position in $BFeO_3$. Furthermore, at temperatures below 50 K we observed the appearance of a high-spin (HS) component (Fig. 1), whose abundance does not change significantly with pressure and remains rather high, ~30%, even at 140 GPa. Meanwhile, the quadrupole split component shows no sign of a magnetic interaction down to 2.5 K (Fig. 1), which is not typical for a LS state.

Furthermore, our SMS measurements of $AlFeO_3$ (space group *Pna2₁*) also show a drastic change of the magnetic properties around 50 GPa corroborating with a first order isostructural transition. Also in the present case, Fe^{3+} demonstrates very unusual features above 50 GPa. Namely, the observed single MS component, whose parameters are typical for a nonmagnetic or low-spin (LS) state, partly transforms below 50 K to a high-spin (HS) state while the former component also does not show any sign of magnetic interactions down to 2.4 K (Fig. 2).

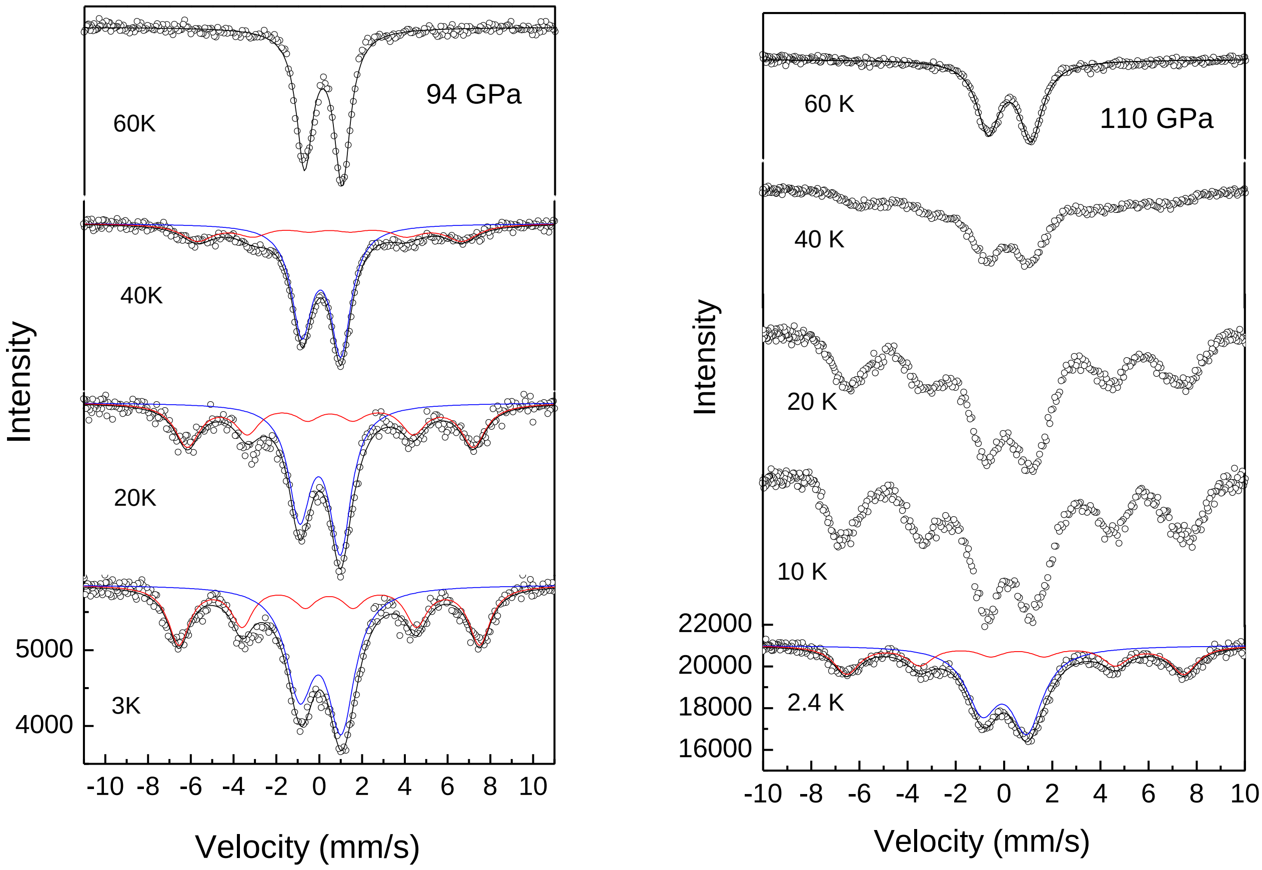

Fig. 2. Mössbauer spectra of $AlFeO_3$ recorded at 94 and 110 GPa, respectively, at various temperatures. Two components with different isomer shifts are clearly distinguished below 50 K: one – HS and another one – with no sign of a magnetic interaction down to 2.4 K (red and blue lines, respectively).

The absence of any sign of magnetic interactions at low temperature is associated usually with a breakdown of electronic correlation and an insulator-to-metal transition [5] but in the present case according to our $R(P,T)$ data and measurements [6], the materials remain semiconducting with a rather large energy gap. Such Fe^{3+} behavior *contradicts with all existing ideas and previous observation*s in other Fe-bearing compounds [5].

Moreover, our recent synchrotron XRD studies of $BFeO_3$ and $AlFeO_3$ performed at 89 and 118 GPa, respectively, revealed rather unusual V(T) behavior at low temperature. Namely, a strong continuous volume decrease below 50 K corroborating with the observed appearance of the HS state. Currently we are performing a theoretical analysis of the obtained data, which should help to understand the observed unusual phenomena.

References

1. E. Greenberg *et.al.*, to be published

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4. A. G. Gavrilyuk, I. A. Troyan, I. S. Lyubutin et al., JETP **100**, 688 (2005).

5. G. Kh. Rozenberg, W. Xu, M. P. Pasternak, *Z. Kristallogr.*: Crystalline Materials, **229**(3), 210 (2014).

6. I. A. Troyan, M. I. Eremets, A. G. Gavrilyuk et al., JETP Letters. **78**, 13 (2003).