ESRF	**Experiment title:** **High pressure phase transitions in $RFeO_3$ (R = Sm, Fe) by single crystal and powder diffraction**	**Experiment number**: HC-2153
Beamline: ID27	**Date of experiment**: from: 09/09/2015 to: 12/09/2015	**Date of report**: 06/02/2016
Shifts: 12	**Local contact(s)**: Mohamed Mezouar	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Luxembourg Institute of Science and Technology, 41, rue du Brill, L-4422 BELVAUX

Mael Guennou*, Jens Kreisel

CNRS - UJF - Institut Néel 25 rue des Martyrs F-38042 GRENOBLE Cedex 09

Pierre Bouvier**

Universidade do Porto - IFIMUP Dept de Fisica Rua do Campo Alegre 687 PT - 4150 PORTO

Abilio Almeida*

Report:

1) Technical aspects

In accordance with the proposal, both single crystal (for $SmFeO_3$) and powder experiments (for $SmFeO_3$ and $TbFeO_3$) were carried out. XRD was performed in diamond-anvil cells with helium as pressure-transmitting medium.

For $SmFeO_3$: The powder experiment was carried out safely up to 50 GPa, and data were acquired in small pressure steps (0.5 to 1 GPa) upon compression. Upon decompression, data points could collected down to 25 GPa only before the gasket opened, so that the decompression could not be fully monitored. The single crystal experiment was carried out up to 53.3 GPa. The original crystal was untwinned, as it had been assumed from optical inspection. Data were only recorded on the increasing pressure run, both in the low-pressure and in the high-pressure phase. The cell was then disconnected and kept at high pressure for further experiment in our lab, so that no data was recorded upon decompression.

For $TbFeO_3$: The experiment was carried out up to 53 GPa in small pressure steps. Upon decompression, the gasket broke at 44 GPa.

2) Results obtained

We review below the objectives stated in the proposal and the corresponding results. Mind that analysis is not completed and that those preliminary results should be taken with great care.

1- Confirmation of the presence of an IM transition in $TbFeO_3$ and $SmFeO_3$ compounds and its crystallographic characterization.

→ We confirm the phase transition in both cases, at 41 and 46 GPa for $SmFeO_3$ and $TbFeO_3$ respectively. Phase coexistence at the transition is seen in a limited pressure range (~2 GPa for $SmFeO_3$, ~4 GPa for $TbFeO_3$). The transition in $SmFeO_3$ is found to be reversible, with a small hysteresis of a couple of GPa at

most. We could not check reversibility for the $TbFeO_3$ because of the gasket rupture. The crystal structures of the high-pressure phases are not conclusively identified yet, but some reasonable candidates have been found and it seems clear that the transitions are not isostructural, in contradiction with the common belief and in agreement with the original motivation of the proposal.

2- Characterization of any possible phase transition occurring before the IM Transition (expected at 25 GPa for $TbFeO_3$), probably related to changes in tilt systems.

→ No such change is observed for $SmFeO_3$. For $TbFeO_3$, we observe a kink in the evolution of the lattice constants around 22 GPa, which might be related to the peak splitting observed in high-pressure Raman spectroscopy, and indicate a tiny structural change at this pressure. However, this will have to be analysed more carefully.

3- Detailed description of the compression mechanism, in both phases, through the pressure-dependence of the spontaneous strains and, if the data quality allows for it, microscopic parameters (atomic positions, bond lengths, tilt angles).

→ The lattice constants and the evolution of the spontaneous strain has been determined for both compounds on the whole stability range of the orthorhombic *Pnma* phase. They show a remarkably different behaviour. All strains decrease nearly linearly for $SmFeO_3$. In contrast, for $TbFeO_3$, they show non-monotonous behaviour, and decrease slightly before increasing again at some intermediate pressure, while the total strain increases slightly. At first sight, this seems in line with the overall picture sketched in [1], i.e. a confirmation of the rules for the evolution of tilts under pressure modelled by the valence bond method, which does predict changes in behaviour in the orthoferrites series. However, a change in behaviour with pressure in a single compound would be remarkable, but this will have to be confirmed in the detailed analysis.

3) Perspectives

Future detailed analysis includes:

- Rietveld refinements of the powder patterns, as far as possible. It is probable that at some pressure, Rietveld refinement won't be possible anymore because of peak broadening caused by intergrain stresses.
- Strain analysis from the lattice parameters, and interpretation in the framework of Landau's formalism.
- Identification of the crystal sructure of the high-pressure phases in both cases.

Publication is not yet in preparation, but given the quality of the data obtained, and according to past experience, it makes little doubt that these XRD results, together with our high-pressure Raman data, will be published in a decent journal.

[1] Zhao *et al.*, Acta Cryst. B**60**, 263 (2004)