ESRF	**Experiment title:** STRUCTURAL ASPECTS OF THE HIGH-SPIN $\rightarrow$ LOW-SPIN CROSSOVER INDUCED BY HIGH-PRESSURE IN SELECTIVE Fe(III)-OXIDES.	**Experiment number**: HS-926
Beamline: ID30	**Date of experiment**: from: 9-June-99 to: 15-June-99	**Date of report**: 26-Aug-99
Shifts: 18	**Local contact(s)**: Stefan Carlson	*Received at ESRF:*

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Report:

1 – Pressure-Induced transformations in *R*FeO_3 perovskites (*R* = Pr, La). The *Mott* insulators *R*FeO_3 (*R = rear-earth)* perovskites are isostructural with the ortho-nickelates, which undergo a temperature driven insulator-metal (IM) transition at temperature T_{MI} that steeply decrease with increasing size of rare-earth ion [1]. Though this temperature-driven phenomena has been observed only with *R*NiO_3, we have recently selected the Pr-and La-orthoferrite, to investigate the structural aspects of the basic phenomena of *d-d correlation breakdown* resulting from very high static pressures.

The XRD studies using the TAU miniature DAC in the angle-dispersive mode have shown that in the range 30 - 55 GPa the low-pressure (*LP*) orthorhombic perovskite phase undergoes a first-order phase transition to a new high-pressure (*HP*) phase. Diffraction patterns of the $PrFeO_3$ *HP* phase could be attributed to the same orthorhombic perovskite structure but with a reduced ***c***-axis; for $LaFeO_3$ the structural transition near 30 GPa attributed to the transition to a tetragonal phase. The transition was accompanied by a ~2%

volume decrease and a precipitous drop of the resistance explained as due to an accelerated gap-closure. Further increase of pressure up to 126 GPa for $PrFeO_3$ and to 103 GPa for $LaFeO_3$ does not reveal any additional structural changes and is accompanied by a sluggish IM transition which is uncompleted to 130 GPa. Mössbauer studies (MS) pertinent to the *HP* phase documented for the first time the complex properties of the precursor state of the magnetic oxides at the IM transition, such as the onset of a high spin-low spin (HS-LS) crossover and following appearance of paramagnetic state near the IM transition. To elucidate the nature of the discussed electronic and magnetic transformations a further XRD studies to higher pressures beyond that in which IM transition occurs is necessary

1. J. B. Torrance, P. Lacorre, A. I. Nazzal et al., Phys. Rev. **B45**, 8209 (1992).

2 - High-Pressure Studies of Iron Halides. The pressure-induced Mott transition phenomena is characterized by the concurrency of insulator-metal transition and the collapse of the magnetic moment in the absence of a structural phase transition. One main issue is to investigate the pressure region close to the Mott transition where present Mott-Hubbard models [1] predict the onset of *a metal with moments* prior to the total collapse of the magnetic moment. Our studies with FeI_2 indeed support such a model showing that the transition from antiferromagnetic insulator to a normal metal is realised in two steps: at ~20 GPa FeI_2 undergoes an isostructural phase transition to paramagnetic metal state. This transition is accompanied by a small volume expansion of the lattice when electron localization occurs. Another electronic transition at ~28 GPa from paramagnetic to normal metal is not accompanied by an appreciable structural change.

In the case of $FeCl_2$ the consequence of structural transformations is different from FeI_2. The structural phase transition from *LP* CdI_2-type phase to a new *HP* phase takes place at ~30 GPa, which is accompanied by significant change of magnetic structure. MS observes additional sluggish transition to a diamagnetic state at the range 42-60 GPa. This transition could be consistent to an onset of HS-LS crossover or to a *Mott* transition resulting in a metallic nonmagnetic state. Further XRD and resistivity studies to pressures ~60 GPa could elucidate the nature of this transition.