ESRF	**Experiment title: THE STRUCTURAL PHASE TRANSITION IN HEMATITE AND *R*FeO_3 UPON A HIGH-SPIN → LOW-SPIN CROSSOVER INDUCED BY HIGH-PRESSURE.**	**Experiment number**: HS-757
Beamline: ID30	**Date of experiment**: from: 10-Nov-98 to: 13-Nov-98	**Date of report**: 18-Feb-99
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Report:

1 - High-Pressure Structure of Fe_2O_3. The high-pressure (HP) form of hematite has been the subject of extensive investigation primarily because of its significance to earth sciences. Early HP experiments have shown that at 50 GPa Fe_2O_3 undergoes a structural phase transformation to a considerably denser structure, with a volume decrease of ~ 10% [1]. This phase could be equivalently assigned to a *distorted* corundum (Rh_2O_3 II-type) or orthorhombic perovskite structure. Based on HP Mössbauer studies (MS) it was concluded that the HP phase is characterized by iron ions of **two** different valences. This incited Suzuki *et al.* [1] to favor the perovskite option to the HP phase with formula ABO_3 where *A* and *B* stand for different iron charge states.

The highest pressures of all previous XRD measurements (~ 60 GPa) showed the coexistence of the low and high pressure phases. We extended our XRD studies to pressures of 80 GPa, using the TAU miniature DAC in the angle-dispersive mode.

Diffraction peaks corresponding to the HP phase first appeared at ~ 45 GPa and of a pure HP phase at P > 70 GPa. Diffraction peaks of the HP-phase could be indexed exactly to the *distorted* corundum structure with. space group *Pbna*. This structure with formula A_2O_3 can be assigned only in case of a single cation position. This is in full agreement with the recent obtained Mössbauer data revealing a single MS component at P>72 GPa [2].

1. T. Suzuki, T. Yagi, A. Akimoto, A. Ito, S. Morimoto, and S. Syono, in *Solid State Physics under Pressure* p. 149, KTK Scient. Publ., Tokyo (1985); J. Staun Olsen, C. S. G. Cousins, L. Gerward, H. Jhans,, and B. J. Sheldon, *Physica Scripta* **43**, 327 (1991).
2. M. P. Pasternak, G. Kh. Rozenberg, G. Yu. Machavariani, O. Naaman, R. D. Taylor, and R. Jeanloz, *Phys. Rev. Lett*. **82**, 4663 (1999).

2 - High-Pressure Structure of $PrFeO_3$ perovskite. The $R FeO_3$ (*R = rear-earth)* perovskites are isostructural with the ortho-nickelates. They are *Mott* insulators, which driven by temperature, undergo a metal-insulator transition with the concurrent loss of the Ni^{3+} moments [1]. Though this temperature-driven phenomena has been observed only with $R NiO_3$, we have recently selected the Pr-orthoferrite, to investigate the structural aspects of the basic phenomena of *d-d correlation breakdown* resulting from very high static pressures.

The XRD studies of $PrFeO_3$ performed to ~ 52 GPa, have shown that at ~30 GPa the low-pressure orthorhombic perovskite phase (space group *Pbnm*) starts undergoing a first order phase transition to a new high pressure (HP) phase. The diffraction patterns of the pure HP phase recorded at 52 GPa could be tentatively attributed to the same orthorhombic perovskite structure but with a reduced ***c*-**axis. The first-order phase transition is accompanied by a ~2% volume decrease and a precipitous drop, by more than four orders of magnitude, of the resistance explained as due to an accelerated gap-closure. Further pressure increase causes a sluggish metallization process with an incipient metallic state at ~130 GPa as well as a a *spin-crossover* process, from a high to a low-spin Fe^{3+}. To elucidate the nature of these electronic and magnetic transformations a further XRD studies to higher pressures is necessary.