ESRF	**Experiment title:** Structural and magnetic phase transitions induced by pressure studied by XMCD and XANES at Fe K-edge on pure Fe, Fe_2O_3 and Fe_3O_4 samples	**Experiment number**: He1617
Beam line: ID24	**Date of experiment**: from: 12/02/2004 to: 17/02/2004	**Date of report**: 19/02/2004
Shifts: A préciser	**Local contact(s)**: Olivier MATHON	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

François Baudelet *

Mattéo D'Astuto *

Jean-Paul Itié *

Pierre-Yves Plaçais *

Sakura Pascarelli *

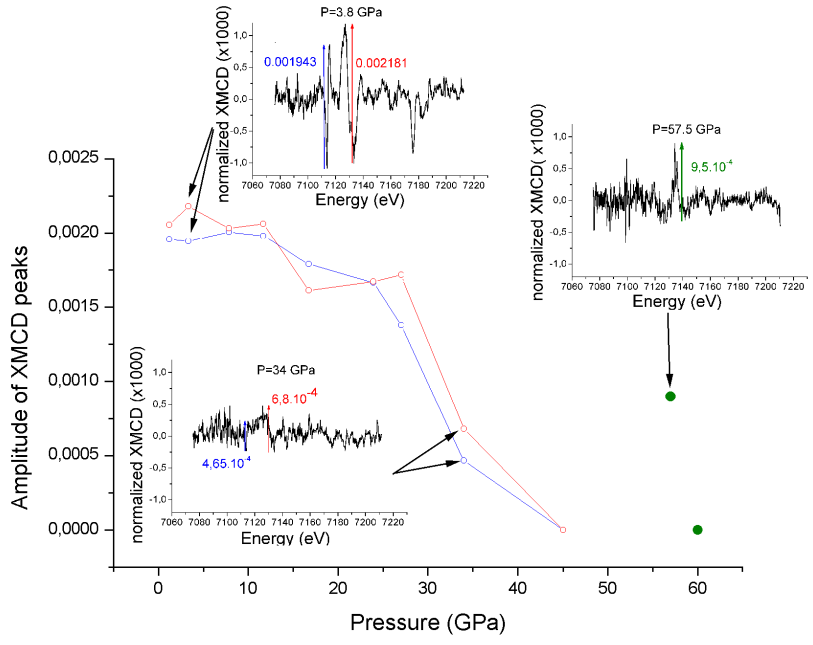
Report:

Maghemite

X-ray magnetic circular dichroism (XMCD) measurements on Fe K-edge have been performed on µm-sized maghemite (γ-Fe_2O_3) powder under high pressure (0 to 60 GPa) using a 200µm-diamond anvil cell. Pressure was measured using ruby fluorescence. This device allowed us to study the magnetic behaviour of iron sites during the phase transition from maghemite to antiferromagnetic hematite (α-Fe_2O_3), reported around 30 GPa in ref. [1], and the transition to the high pressure phase of hematite, between 50 and 75 GPa. Mössbauer spectroscopy [2] revealed the non–magnetic behaviour of this high pressure phase, and the onset of an "intermediate phase" during this transition.

XMCD spectra exhibit two peaks from 0 to 30 GPa, corresponding respectively to tetrahedral (lower energy peak) and octahedral (higher energy one) sites of iron

Figure 1: Evolution with pressure of the amplitude of the peaks in the XMCD spectra. Large green dots show the onset of a new type of signal at 57GPa. Inserts show three typical spectra obtained at various important pressure points.



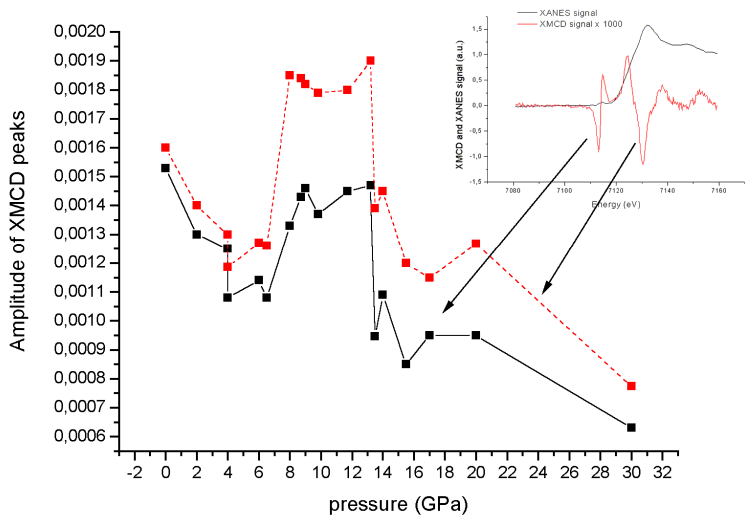
ions in maghemite. We observe a slow decrease of magnetization up to 30 GPa, and then an abrupt fall until complete vanishing at approximately 45 GPa, where hematite is expected to be the unique phase in the sample (see figure 1).
Further pressure increase brings an unexpected signal in the XMCD spectrum at 57 GPa. Its energy is the same as that of the negative part of the octahedral feature in lower pressure spectra, and its sign is inverted. It disappears at 60 GPa, which suggests that the transition ends around that pressure, and that the intermediate phase of the transition suggested by Pasternak et al. could be the source of this signal. Actually, though it has to be confirmed and further studied, that signal might be an evidence of a ferromagnetic order in the intermediate phase between hematite and the high pressure non-magnetic phase of Fe_2O_3.
Keeping in mind the strong structure similarity between Fe_2O_3 and Fe_3O_4, connections between the results of this experiment and the one reported just below on magnetite may be established.

[1] *Z. Wang, S.K. Saxena, Solid State Communications* ***123*** *(2002)*
[2] *M.P. Pasternak, G.K. Rozenberg et al., Physical Review Letters* ***82****, 4663 (1999)*

Magnetite

X-ray magnetic circular dichroism (XMCD) measurements on Fe K-edge have been performed on µm-sized magnetite (Fe_3O_4) powder under high pressure (0 to 30 GPa) using a 400µm-diamond anvil cell. Magnetite crystallizes in the inverse spinel structure in which tetrahedral A sites contain one-third of Fe^{3+} ions, while octahedral B sites contain the other Fe ions which are 50% Fe^{3+} and 50% Fe^{2+}. At a temperature T_V, the magnetite undergoes a crystallographic transition, the so-called Verwey transition.

Figure 2: Evolution with pressure of the amplitude of the peaks in the XMCD spectra Two events at 8 and 14 GPa are clearly seen.



The pressure of the insulator-metal transition reported in ref [3] is different from the result of Rozenberg and co-workers [4]. The authors of ref [3] report a disappearing of the Verwey transition at 8 GPa whereas those of ref [4] report the Verwey transition up to 16 GPa.
Magnetite XMCD spectra exhibit two peaks, corresponding respectively to octahedral and tetrahedral sites of iron ions, like in maghemite. We observe a decrease of magnetization with pressure from 0 to 6 GPa, and then an abrupt jump around 8 GPa. The intensity is then almost constant until an onset of vanishing at 14 GPa. These two events seen in the XMCD pressure dependence of magnetite at 8 and 14 GPa are probably in close relation with those described in resistivity measurements in ref. [3,4]. Change in XMCD amplitude can be attributed to variation of the 3d iron magnetic moment, or to variation of the exchange interaction of the excited 4p photoelectron with the 3d bands of neighbouring atoms. Both possibility are due to a modification of the overlap between the atomic orbital, which lead also to a change of conductivity.

[3] *S. Todo et al. J. Appl. Phys.* ***89****, 11 7347 (2001)*
[4] *G.K. Rozenberg, G.R. Hearne, and M.P. Pasternak, Phys. Rev.B* ***53****, 6482 (1996)*