ESRF	**Experiment title:** **Pressure Effects on the Magnetization of a Magnetic Iron Sulphide**	**Experiment number**: HE 1619
Beamline: ID24	**Date of experiment**: from: 04-feb-04 to: 10-feb-04	**Date of report**: 29-fev-04 *Received at ESRF:*
Shifts: 15	**Local contact(s)**: O. Mathon	

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Report:

We wanted to study the disappearance of the magnetization in monoclinic pyrrhotite (Fe_7S_8) at high pressure by following the evolution of the **x-ray magnetic circular dichroism at Fe K-edge** as a function of pressure. Two hypothesis exist concerning this magnetic phase transition: it could be either a high spin to low spin transition or a modification of the density of states of the Fermi level.

Pyrrhotite: a magnetic iron sulphide with lacunary structure

Pyrrhotite is an iron sulphide stemming from troilite (FeS). Its formula is $Fe_{1-x}S_x$ with $0 < x \leq 0.125$. For $x < 0.125$, pyrrhotite has a hexagonal structure and is antiferromagnetic. For $x = 0.125$, pyrrhotite (Fe_7S_8) has a monoclinic structure and presents iron vacancies. These vacancies are organized [Bertaut, 1953] in such a way that monoclinic pyrrhotite is ferrimagnetic. TEM studies [Li, 1996] have shown that its structure is formed by a stack of lacunary planes containing either sulphur or iron atoms. The planes containing sulphur atoms are full. Among the planes containing iron atoms, one over two is full whereas the other contains three atoms over four. All the iron ions (only Fe^{2+}) are in octahedral sites and it is the organization of this lacunary structure that generates the ferrimagnetism of Fe_7S_8. The Curie temperature is 578 K.

Having a highly anisotropic magnetic structure, Fe_7S_8 plays an important role in paleomagnetism. Paleomagnetism gives information about the magnetic history of the Earth and of other planets. Knowing the behaviour of magnetic minerals depending on temperature and pressure is necessary to understand the measurements of natural remanent magnetization and to correlate them to the conditions of formation of rocks and to their evolution. Fe_7S_8 could be at the root of the magnetic field measured on Mars. Indeed, Martian basalts are iron-rich and the core of Mars shows a high sulphide concentration [Fei, 1995]. Fe_7S_8 is also mentionned in the interpretation of some Earth magnetic anomalies [Quidelleur, 1992].

Even though it exists only two magnetic iron sulphides (Fe_7S_8 and Fe_3S_4), the magnetic phase diagrams of these sulphides are not known.

Behaviour of pyrrhotite under pressure

Previous results

Mössbauer spectroscopy at room temperature have shown that Fe_7S_8 becomes paramagnetic above 1.6 GPa [Vaughan, 1973]. This transition could be due to a high spin – low spin transition of Fe^{2+}. This could imply local variations of the Fe-S distances. It could also be explained by a change in the behaviour of the electrons because of the reduction of the interatomic distances. Electrons, that are localized at room pressure, should be delocalised at higher pressure. Otherwise, Fe_7S_8 presents a crystallographic transition above 3.6 GPa.

We performed **susceptibility measurements** as a function of pressure in collaboration with S. Gilder (IPG, Paris) [Gilder, 2002]. They show a progressive disappearance of magnetization: half of the saturation magnetization is lost between 0 and 0.9 GPa.

XMCD measurements at the Fe K-edge under pressure

The experiments have been carried out on ID24, on a synthetic sample, at room temperature and at pressures lying between room pressure and 5 GPa. The magnetic field was 0.5 T.

We managed to measure the dichroic signal in the anvil cell at atmospheric pressure as it is shown on fig.1. This signal is weak (3.10^{-4} of the absorption signal) because it is the resulting magnetization of moments coupled antiferromagnetically (roughly 4 in a direction, 3 in the opposite direction).

For higher pressures the signals were too noisy to conclude. Indeed, besides the weakness of the signals, we were confronted to spectroscopic difficulties and to the strong absorption of the diamonds of the anvil cell at these energies. We are considering the use of hollowed diamonds and means to obtain more homogeneous samples.

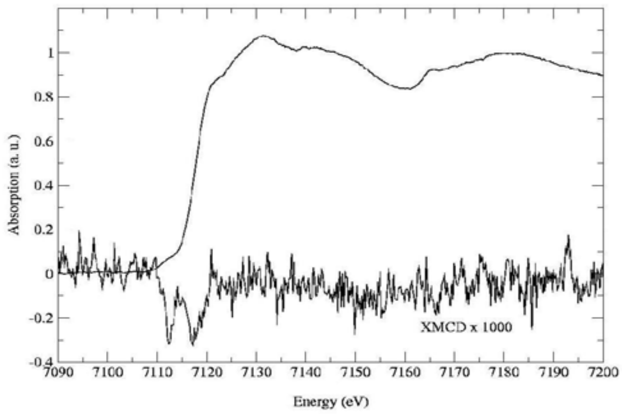

Fig. 1: Absorption and XMCD spectra of at atmospheric pressure in the anvil cell.

References

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