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| | Experiment title: Superexchange in Magnetic Iron Sulphides | Experiment number: HE1663 |
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Report:

We wanted to determine the role played by antiferromagnetic Fe-S-Fe superexchange compared to ferromagnetic Fe-Fe exchange in the magnetization of iron sulphides by performing **XMCD measurements at the iron and sulphur K-edges** on the ID12 beamline.

Aims of the experiment and scientific background

Iron sulphides in paleomagnetism

The study of rock magnetization gives information about the magnetic history of the Earth and of other planets. Paleomagnetism, in association with other methods, allows to date precisely several geological events thanks to the reversals of the Earth magnetic field that occurred along the time on a scale of several hundreds of thousands of years. These reversals are at the root of the anomalies observed on the remanent magnetizations measured on the Earth lithosphere.

Monoclinic pyrrhotite (Fe_7S_8) and greigite (Fe_3S_4) are the only ferrimagnetic iron sulphide minerals, the other iron sulphides exhibiting antiferromagnetism or van Wleck paramagnetism. Fe_7S_8 , which shows a strong anisotropy, plays an important role in the interpretation of some magnetic anomalies observed on the Earth. It could also be responsible for magnetic anomalies recently discovered on Mars. Fe_3S_4 results either from biological synthesis (inside or around living organisms) or from inorganic hydrothermal synthesis. Since its magnetic properties are very close to those of magnetite (Fe_3O_4), the presence of Fe_3S_4 often alters the interpretation of paleomagnetic measurements.

The two ferrimagnetic iron sulphides

Fe_7S_8 has a monoclinic crystal structure with iron vacancies. All iron atoms are in octahedral sites and the net magnetic moment is due to the organisation of the iron vacancies in the structure [Bertaut, 1953], [Li, 1996]. Fe-Fe distances are rather small (2.9\AA vs 2.49\AA in bcc iron and 3.49\AA in greigite) yielding possible ferromagnetic exchange.

Fe_3S_4 is a thiospinel, equivalent to Fe_3O_4 in the sulphide family. However, the magnetic properties of Fe_3S_4 are very different from those of Fe_3O_4 . The saturation magnetization is $1.5\mu\text{B}$ per formula unit in Fe_3S_4 vs 4.1 in Fe_3O_4 , the easy-magnetization axis is $[100]$ in Fe_3S_4 vs $[111]$ in Fe_3O_4 and no Verwey transition has ever been observed in Fe_3S_4 [Dunlop, 1997]. Fe^{2+} and Fe^{3+} are distributed among antiferromagnetically coupled tetrahedral and octahedral sites and the net magnetization of Fe_3S_4 is the result of these non-entirely compensated antiferromagnetic couplings.

Results

Pyrrhotite

At the **iron K edge**, the spectra (presented on fig.1) are the result of one hundred spectra acquired by reversing both the magnetic field and the beam polarization. The peak to peak intensity of the dichroic signal is 0.03% of the isotropic signal. These very encouraging results can be seen as preliminary results before a study of the variation of the dichroic signal under pressure.

At the **sulphur K edge**, the spectra (presented on fig.2) were obtained by reversing both the beam polarization and the magnetic field. They result from an acquisition of one hundred spectra. We used the EMPHU undulator in order to reverse the beam polarization for each point. In order to be sure that the weak signal is not spurious, we also recorded the evolution of the intensity of the dichroic signal when varying the magnetic field between $+2$ and -2T (hysteresis loop). The peak to peak intensity of the dichroic signal, normalized to 100% circular polarization, is 0.1% of the isotropic signal. The existence of the dichroic signal shows that the sulphur atoms are magnetically polarized. We are now working on the development of the appropriate theoretical framework to give a quantitative interpretation to this observation.

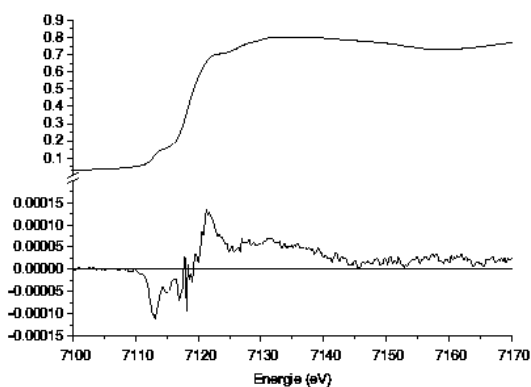


Fig.1: absorption and dichroic signal at the iron K-edge on pyrrhotite

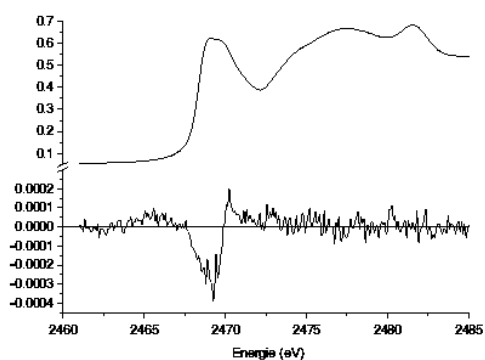


Fig.2: absorption and dichroic signal at the sulphur K-edge on pyrrhotite

Greigite

In order to have reference spectra, we collected data on an other thiospinel: FeCr_2S_4 . The spectra recorded at the **iron K-edge** on greigite, compared to that obtained on FeCr_2S_4 , showed that greigite contains only Fe^{3+} in tetrahedral sites. The contribution of the octahedral sites, and their population, cannot be observed at the Fe K-edge. These very promising results ask for more beamtime, when the experimental findings are analysed.

References

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