

XMCD at Fe $L_{2,3}$ edges, Fe and S K edges on Fe_7S_8

Isabelle Letard · Philippe Saintavrit ·
Catherine Deudon

Received: 29 August 2006 / Accepted: 13 November 2006 / Published online: 12 December 2006
© Springer-Verlag 2006

Abstract Pyrrhotite (Fe_7S_8) is a natural iron sulphide that can participate in rock magnetisation. Its electronic structure is not yet surely described. X-ray magnetic circular dichroism (XMCD) at Fe $L_{2,3}$ edges on Fe_7S_8 , coupled with multiplet calculations, shows that iron is present only as Fe^{2+} in this magnetic iron sulphide. It reveals a strong magnetic orbital moment. XMCD at Fe and S K edges shows the quite strong polarization of both Fe and S in Fe_7S_8 .

Keywords Iron sulphide · XMCD · Pyrrhotite

Introduction

Pyrrhotite Fe_7S_8 is one of the few magnetic iron sulphides. The electronic and magnetic structure of this lacunary sulphide is still debated. XMCD at Fe $L_{2,3}$ edges joined to simulation gives access to the oxidation state of iron and to its geometric environment. We have enriched this study with XMCD measurements at Fe and S K edges in order to observe the magnetic polarization carried by these atoms.

The structure and magnetic properties of pyrrhotite are presented in Sect. 2. The results obtained at iron

$L_{2,3}$ edges, iron K edge and sulphur K edge are presented in the three following sections and discussed in the last one.

Fe_7S_8 : a magnetic lacunary iron sulphide

Pyrrhotite's formula is $Fe_{1-x}S$ with $0 < x \leq 0.125$. For $x = 0$, the mineral FeS receives the name of troilite. Pyrrhotite is a ferrimagnetic mineral that can be found in magmatic or metamorphic rocks as well as in sediments (Dunlop and Özdemir 1997). Pyrrhotite has been used in paleomagnetic studies as an indicator for the reversals of the Earth magnetic field (Quidelleur et al. 1992).

Crystallographic structure

Pyrrhotite structure derives from that of troilite FeS. FeS has a hexagonal structure similar to that of nicolite NiAs but with a superstructure (Vaughan and Craig 1978).

$Fe_{1-x}S$ with $x < 0.125$ has a hexagonal structure. The deficiency of iron compared to sulphur is resolved by the presence of vacancies on the cation sites. When $x = 0.125$, there are two polymorphs for Fe_7S_8 : the 3C Fe_7S_8 and the 4C Fe_7S_8 phases (Keller-Besrest and Collin 1982). The 3C phase is a high temperature hexagonal phase that can only be present at room temperature as a metastable state. The 4C phase is the stable phase at room temperature. It is a monoclinic and ferrimagnetic phase. The monoclinic network originates from a slight distortion: the β angle is equal to 90.4° instead of 90° for hexagonal network. In the 4C pyrrhotite, the vacancies are organised with a 4c

I. Letard (✉)
ESRF, Mailbox S21, BP220, 38 043 Grenoble Cédex, France
e-mail: letard@esrf.fr

P. Saintavrit
Institut de Minéralogie et de Physique des Milieux
Condensés, CNRS & UPMC, Paris, France

C. Deudon
Institut des Matériaux de Nantes, Nantes cédex 3, France

periodicity compared to the NiAs structure. In all these structures, iron occupies distorted octahedral sites.

The structure was first described by (Bertaut 1953) and recently confirmed by transmission electron microscopy (Li and Franzen 1996). The 4C pyrrhotite is composed of a stacking of (**a**, **b**) planes. Among these planes, one out of two is full (i.e. all the iron sites of the associated FeS structure are occupied) and the other one is lacunary (i.e. only three iron sites out of four are occupied). The cation vacancies are ordered in a periodical way along the **c** axis.

The fact that Fe₇S₈ contains both Fe³⁺ and Fe²⁺ ions or only Fe²⁺ ions is still debated. Indeed, the charge balance seems easier to obtain with the two oxidation states (e.g. 5 Fe²⁺, 2 Fe³⁺ and 8 S²⁻) (Bertaut 1953; Chikazumi 1997) but Mössbauer spectroscopy measurements did not show any evidence of Fe³⁺ ions (Dekkers 1988; Oddou et al. 1992; Fillion et al. 1992). In a model containing only 7 Fe²⁺ and 8 S^{ε-2}, ε would be 0.25, so that the 3p layer of the sulphur ions would contain 0.25 holes.

Magnetic properties

In the case of disordered vacancies ($x < 0.125$ in Fe_{1-x}S), pyrrhotite is antiferromagnetic. On the contrary, due to the ordering of the vacancies, 4C pyrrhotite is ferrimagnetic with a Curie temperature of 578 K. A simple way to describe the magnetic structure in the 4C pyrrhotite is to consider that inside a (**a**, **b**) plane, the Fe atoms are ferromagnetically coupled whereas the coupling between the planes is antiferromagnetic. The ferrimagnetic structure stems from the ordering of the vacancies out of two planes.

A simple model for a formula unit would be the following. 5 Fe²⁺, 2 Fe³⁺ and 8 S²⁻ ions would insure the net charge equilibrium. In a simple ionic model where the magnetic moment at saturation for Fe²⁺ is 4 μ_B (i.e. ground state $S = 2$) and Fe³⁺ is 5 μ_B (i.e. $S = 5/2$), it is possible to find a distribution of the various irons so that one obtains the measured magnetic moment at saturation per formula unit. The experimental magnetisation at saturation is 2 μ_B according to Chikazumi (Chikazumi 1997). By setting 4 Fe²⁺ ions on the full planes and the rest of cations (1 Fe²⁺ and 2 Fe³⁺) on the lacunary planes, one finds a net magnetisation of 2 μ_B per formula unit: $4 \times 4 \mu_B - 1 \times 4 \mu_B - 2 \times 5 \mu_B = 2 \mu_B/\text{Fe}_7\text{S}_8$. Although this model is simple and in agreement with macroscopic magnetisation measurements, it is in contradiction with most previous spectroscopic measurements.

On the other hand, a model containing only Fe²⁺ ions and where the vacancies are located out of two

(**a**, **b**) planes would lead to a net magnetisation of 4 μ_B/Fe₇S₈. In such a scheme, it is then necessary to suppose the existence of spin canting either inside the planes or between the planes. This would produce some magnetic disorder responsible for the observed reduction of the magnetic moment at saturation. This model is qualitatively in agreement with spectroscopic measurements as well as with neutron diffraction experiments (Powell et al. 2004).

Aim of the XMCD study and principle of the method

The aim of this study was to acquire proofs of the existence or absence of Fe³⁺ in Fe₇S₈ and to obtain information on the magnetic couplings between the ions in this structure.

Several techniques exist to measure the magnetic properties of materials. Most of them are sensitive to the total magnetization of the measured system and cannot discern between the contributions of different atoms in an alloy or mineral, or between their orbital and spin moments. XMCD is the difference, for a magnetic material, between the absorption of left and right circularly polarized X-rays. In X-ray absorption, the atom absorbs a photon, giving rise to the transition between a core level and an empty state above the Fermi level. The absorption edges have energies which are characteristic for each element and, due to the dipole selection rules, final states with different symmetries can be probed by choosing the initial state. XMCD can thus give information on the magnetic properties coming from a chosen electronic state of a selected atom. Several works have demonstrated the efficiency of XMCD in the field of magnetic minerals (Pearce et al. 2006; Pattrick 2002).

The study has been carried out on synthetic and natural samples. The synthetic samples were obtained by crystallization in gaseous phase in quartz cells. The natural samples are coming from the ore of Trepca, Kosovo. Both natural and synthetic samples were analysed by X-ray diffraction and distinction between monoclinic and hexagonal pyrrhotite was done following the work of Kontny et al. (2000). Both samples present diffraction patterns corresponding to monoclinic pyrrhotite.

XMCD at iron L_{2,3} edges

Absorption and dichroic spectra have been recorded at Fe L_{2,3} edges. The recorded data have been fitted in

the Crystal Field Theory framework in order to determine the oxidation state and geometrical environment of iron.

Experimental details

The experiments have been carried out on the SU23 beamline (LURE, Orsay, France). The photon beam was delivered by an asymmetric wiggler (Saintavit 1992). The monochromator consisted of a grating with 1,800 lines/mm. The polarization rate on the sample, at the Fe $L_{2,3}$ edges, was about 45% (Brice-Profeta 2005). I_0 (intensity on a grid before the sample) and I (intensity on the sample) were collected in the total electron yield mode. The energy calibration was given by the Fe L_3 edge of hematite that reaches its maximum at 716.4 eV. It was not an absolute calibration but the energy stability of the experimental set-up was better than 5 meV. Such tremendous requirements were mandatory to make possible the measurements of tiny XMCD signals.

XMCD is defined as the difference between the X-ray absorption cross-sections measured with left-handed circularly polarized photons and right-handed circularly polarized photons, the sample magnetisation being parallel to the photon wavevector. In the electric dipole approximation, changing the polarization from left to right or reversing the magnetic field are equivalent actions (Brouder and Kappler 1996). For technical reasons, the XMCD spectra recorded here have been obtained by inverting the direction of the magnetic field, keeping the same given circular polarization.

The magnetic field was delivered by an electromagnet that could alternate the field between +1 and −1 T at each point of the spectrum. This prevents from spurious derivative contributions due to energy shifts often observed between the signals measured with positive or negative fields. The field was set parallel to the X-ray beam. The sample was a natural polycrystal. It was stuck on a copper sample holder and set in a 10^{-9} mbar vacuum. A particular care has been taken to eliminate the oxidized surface of the sample by scraping the surface with a file, inside the vacuum chamber.

Data analysis: multiplet calculations and sum rules

The absorption and dichroic spectra are shown on Fig. 1. At the L_3 edge, the absorption spectrum presents a slight pre-edge feature (A at 713.6 eV), a main feature at 715.2 eV (B) and a contribution at 716.4 eV (C). At the L_2 edge, the spectrum presents one contribution: D at 728.3 eV. The dichroic spectrum pre-

sents three features at the L_3 edge: α at 713.2 eV, β at 715.3 eV and γ around 717.9 eV. It presents one feature at the L_2 edge: δ at 728.5 eV. After correction of the polarization rate, the intensity of the dichroic signal is 4% of the isotropic signal. The XMCD signal has been multiplied by 50 for clarity. As stated above, the experimental procedure allowed us to discard any spurious derivative contribution to the XMCD signal. We are then very confident concerning all the measured features even for the small negative peak at 713.2 eV that is less than 0.3% of the isotropic spectrum.

On the isotropic signal, feature C decreases when the surface of the sample is removed. It is due to the oxidation of the surface. Since the sample is polycrystalline, it is impossible to eliminate all the oxidized part that can lie on the grain boundaries. Thus, the contribution persists on the isotropic signal. Nevertheless, the dichroic signal does not evolve during the elimination of the oxidized surface. This means that the surrounding oxide is not magnetic and that this spurious contribution will not affect the work on the XMCD spectrum. In the following calculations, we did not take into account this C contribution.

On the dichroic signal, the presence of feature α shows that in Fe_7S_8 the iron ions participate in a partially ionic bond with sulphur. Nevertheless, the presence of the large γ contribution is the sign of hybridization in the bonds between Fe and S (Arrio 1996). Thus the shape of the dichroic signal confirms the intermediate behaviour of iron sulphides, between ionic and covalent compounds.

One notices on Fig. 1 that the ratio between the intensities of L_2 and L_3 edges is much smaller than 1/2, which would be the expected statistical ratio. From the sum rule for the branching ratio, this small value indicates that Fe^{2+} is in the high spin configuration as expected for a ferrimagnetic mineral (Thole and van der Laan 1988; Charnock et al. 1996).

Multiplet calculations are based on the Ligand Field Theory. We used the TT-Multiplets code written by Thole (Thole et al. 1992) and maintained by de Groot (<http://www.anorg.chem.uu.nl/people/staff/FrankdeGroot/index.htm>). This method fits the spectra taking into account the spin–orbit coupling, the symmetry of the site and the crystal field. It also considers the chemical bonds between the absorbing ion and the ligands by applying a reducing factor on the Slater integrals. Eventually, it takes into account the experimental broadenings due to the life-time of the core hole (Lorentzian broadening) and to the instrumental resolution (Gaussian broadening).

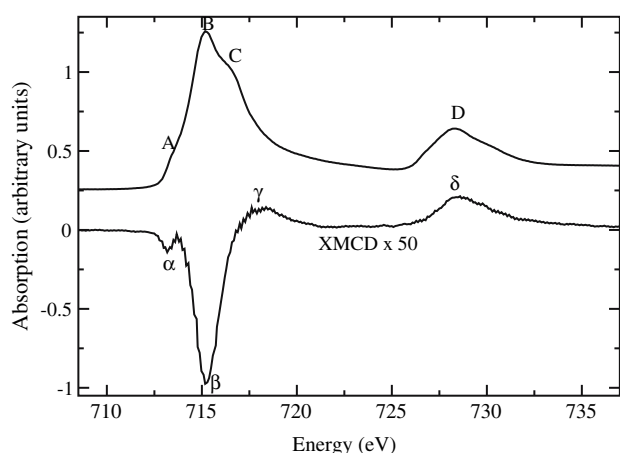


Fig. 1 Experimental isotropic and dichroic signals at Fe $L_{2,3}$ edges in a ± 1 T magnetic field and 300 K on a natural sample. The dichroic signal is multiplied by 50

We used the octahedral symmetry (O_3-O_h branching of the Butler's group subdivisions (Butler 1981)). Different proportions of Fe^{2+} ($3d^6$) and Fe^{3+} ($3d^5$) have been tested. The best fit was obtained without Fe^{3+} .

In order to take into account the hybridization of the chemical bonds, we introduced configuration interactions (CI) between the cation and the ligands. We mixed the two following configurations as shown in Fig. 2: $3d^6$ and $3d^7\bar{L}$, where \bar{L} stands for a ligand with a hole.

The best simulation was obtained for the following parameters. The spin–orbit coupling constants are essentially the atomic ones (Cowan 1981). The various Slater integrals have been multiplied by 80% to take into account covalence. The Fe–S hybridization is further accounted for by CI. The Fe ground state is found to host 6.3 electrons indicating the S to Fe charge transfer and the concomitant creation of $2p$

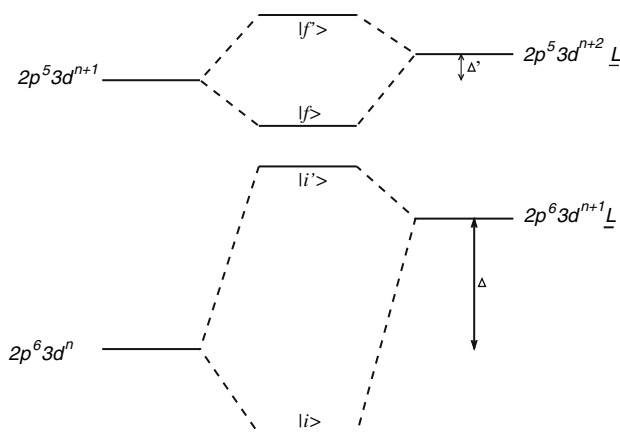


Fig. 2 Scheme of the configuration interactions

holes on the sulphur ligands (the CI parameters are $V_{eg} = 3\text{ eV}$, $V_{t2g} = -1.5\text{ eV}$, $\Delta = 3\text{ eV}$ and $\Delta' = 4\text{ eV}$, see Fig. 2 for the definitions of these parameters). In order to limit the number of parameters and since no linear dichroic measurements were recorded, we performed calculations for Fe in an octahedral environment. The crystal field is then introduced through the 10Dq parameter acting on the excited state (the one with the core-hole). Such a parameter is not necessarily equal to the one measured in UV–Vis spectroscopy. The best fit was obtained for $10Dq = 0.5\text{ eV}$. This is smaller to the one for iron hexa-coordinated to oxygen as expected from the spectrochemical series (Burns 1993).

Calculated isotropic and dichroic Fe $L_{2,3}$ edges are shown on Fig. 3. The isotropic spectrum is reasonably well reproduced. The agreement with dichroic spectrum is also fair except for the contribution of the hybridization (γ) that is under-evaluated. One should notice that the small feature at 713.2 eV is well reproduced in energy position as well as in relative intensity.

From the agreement between experiment and calculation and from the branching ratio sum rule, it can be stated without ambiguity that Fe is in a high spin state. The calculated spin magnetic moment per Fe is $M_S \approx 3.86 \pm 0.1\ \mu_B$.

In order to determine the spin and orbital magnetic moments, we apply the sum rules to the experimental XMCD signal. Thanks to the wide separation between the L_3 and L_2 edges, it is possible to use the spin sum rule here. We also neglect the T_z operator (according to the multiplet calculation, its mean value is 0.06). The relation is then:

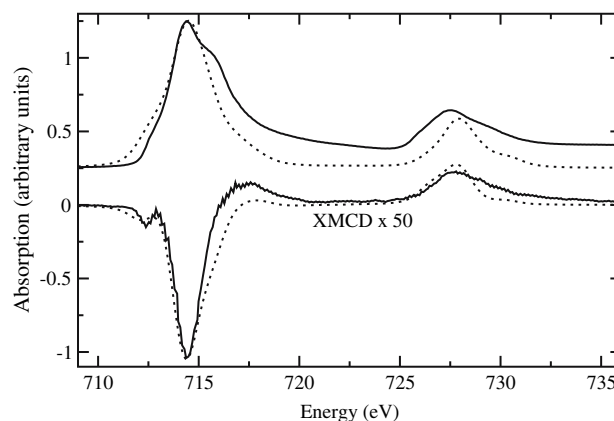


Fig. 3 Comparison between experimental (full line) and simulated (dotted line) signals at Fe $L_{2,3}$ edges. The dichroic signal is multiplied by 50

$$\frac{L_z}{S_z} = \frac{4(I_{\text{dic}2} + I_{\text{dic}3})}{3(I_{\text{dic}3} - 2I_{\text{dic}2})}$$

where $I_{\text{dic}2}$ stands for the integral of the dichroic signal at the L_2 edge and $I_{\text{dic}3}$ the integral of the dichroic signal at the L_3 edge. We find $L_z/S_z = 0.3$, that is $M_L/M_S \approx 0.15 \pm 0.02$. The ratio L_z/S_z is rather large and corresponds to a gyromagnetic factor $g = 2.3$. This very strongly excludes any possibility of a magnetic signal coming from Fe^{3+} for which the orbital contribution to the magnetic moment would be almost zero since it is a ^6S ion.

For a fully polarized Fe^{2+} , $M_S \approx 3.86 \pm 0.1 \mu_B/\text{Fe}$ and the orbital magnetic moment is $M_L \approx 0.58 \pm 0.09 \mu_B/\text{Fe}$. The non zero value experimentally obtained for M_L is coherent with the fact that in sulphides, crystal field is small and hybridization is strong. This leads to high polarization of the orbit.

XMCD at iron K edge

Experimental details

The experiments have been carried out on the ID12 beamline (ESRF, Grenoble, France). The circularly polarized photon beam was delivered by an Apple II undulator (Goulon 1988). The monochromator was a Si(111) two-crystal monochromator. The circular polarization rate at Fe K edge was 92%. The incident beam intensity was measured via the detection of the photons scattered on a 4 mm titanium foil. The sample was a pellet obtained from a synthetic powder (vapour phase crystallisation). It was placed in the center of a superconducting coil that delivered a magnetic field up to 5 T. The intensity on the sample was measured by a photodiode placed in front of the sample and drilled in its center so that the incident beam could go through the diode. The energy calibration was absolute to better than 100 meV and the energy stability was better than 5 meV.

Data analysis

Isotropic and dichroic signals at Fe K edge are presented on Fig. 4. The isotropic spectrum has been normalized to 1 at 7170 eV. The dichroic spectrum is the result of 100 spectra accumulation. The helicity of the photons was inverted between each spectrum and the magnetic field (± 2 T) was inverted every 10 spectra. Great care was taken in the extraction of the XMCD spectra. The dichroic signal is constituted

of one negative contribution at 7113.0 eV and one positive contribution at 7121.5 eV. The intensity of the two dichroic features is around 0.02% of the isotropic signal after correction for the polarization rate. We checked that these two features are inverted when the magnetic field is inverted and that their intensity is independent of the various measurement series.

The dichroic signal appears both on the pre-edge feature (7113.0 eV) and on the main rising edge (7121.5 eV). In X-ray absorption, the pre-edge feature at the iron K edge is due to electric quadrupole transitions from 1s core level towards the 3d orbitals mixed with electric dipole transitions from 1s core level towards p levels hybridized with 3d orbitals. The coordination sphere of Fe in pyrrhotite is a rather distorted sulphur octahedron: the averaged Fe–S distance is 2.45 Å with distances ranging between 2.33 Å and 2.64 Å. In non centrosymmetric sites, as it is the case for pyrrhotite, hybridization between Fe p and 3d levels is possible though the averaged octahedral symmetry around Fe tends to decrease this hybridization.

The positive peak on the XMCD signal (7121.5 eV) can be interpreted in the electric dipole approximation although the absence of spin–orbit coupling on the core-hole makes the analysis quite complicated (Brouder et al. 1996).

XMCD at sulphur K edge

Experimental details

The experiments have been carried out on the ID12 beamline (ESRF, Grenoble, France). The whole

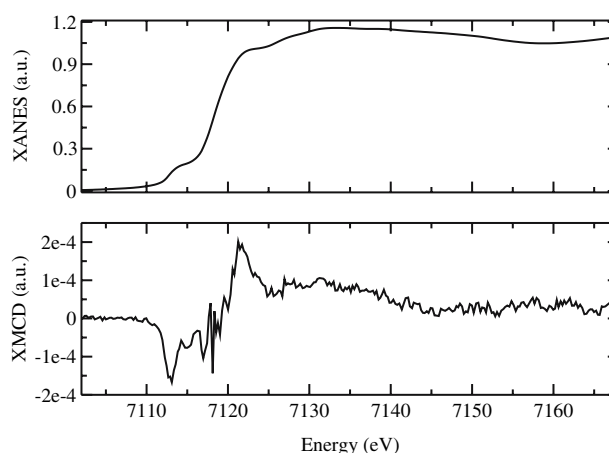


Fig. 4 Isotropic (*upper panel*) and dichroic (*lower panel*) signals at Fe K edge in a magnetic field of ± 2 T and 300 K on a synthetic sample

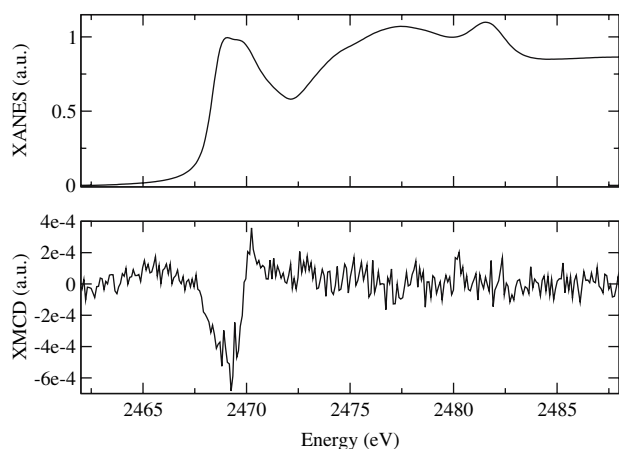


Fig. 5 Isotropic and dichroic signals at S K edge in a magnetic field of ± 2 T and 300 K on a synthetic sample

experimental details are the same as for the Fe K edge measurements except that at the S K edge we used the ElectroMagnet – Permanentmagnet Hybrid Undulator (EMPHU). This undulator can reverse rapidly the polarization of the light. It is thus possible to reverse the light polarization for each point of the spectra. Doing so, one gets rid of eventual energy shifts that might appear between two spectra registered with a constant helicity. Indeed, energy shifts as small as 1 meV at 2 470 eV would have destroyed the XMCD signal.

The circular polarization rate at S K edge was about 20%.

Data analysis

The dichroic spectra shown in Fig. 5 are the result of the acquisition of 16 pairs of spectra, each pair being obtained by 3 inversions of the beam polarization. The magnetic field is inverted between -2 and $+2$ T after each pair.

The intensity of the obtained signal is 6×10^{-4} of the isotropic signal. In order to be sure that this small signal is a dichroic effect, we recorded the evolution of the XMCD intensity at its maximum, i.e. 2 469.2 eV. The result is presented on Fig. 6 and shows the inversion of the dichroic signal when the field is inverted.

The isotropic signal is in line with previous published spectra except for a spurious feature at 2,483 eV, which is characteristic of sulphates. This is probably due to surface oxidation of the sample.

After correction of the circular polarization rate, the intensity of the dichroic signal represents 0.3% of the isotropic signal. This tends to show that the sulphur ions are strongly implied in the magnetic properties of

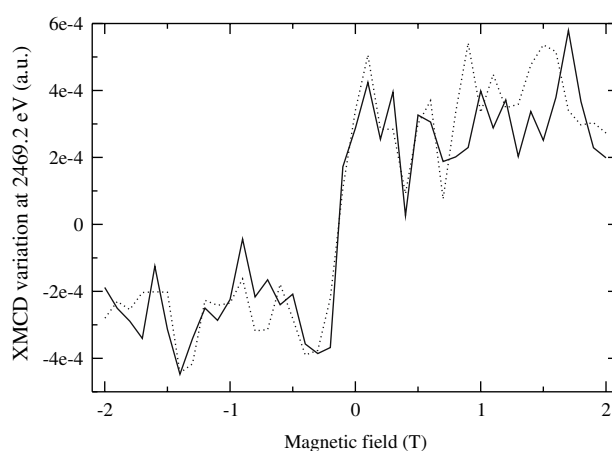


Fig. 6 Variation of the intensity of the S K edge XMCD signal at its maximum (2469.2 eV) between -2 and $+2$ T (full line) and between $+2$ and -2 T (dotted line)

pyrrhotite. Due to the short distance between Fe and S (2.5 vs. 2.9 Å between two Fe atoms), it is highly probable that sulphur participate in a super exchange coupling with irons.

Discussion

The XMCD signals at the Fe $L_{2,3}$ edge present a main sharp negative contribution and broad positive contribution at the L_2 edge. This is indicative of the fact that there is probably only one Fe valence state present in pyrrhotite. The multiplet structures at the $L_{2,3}$ edges have been partially smeared out compared to Fe^{3+} $L_{2,3}$ edges in oxides (Brice-Profeta 2005; Kuiper et al. 1993). This is due to an expected reduction of the crystal field strength and to an increase of covalence that are caused by the Fe–S chemical bond (Burns 1993).

The simulation of the XMCD signals at the Fe $L_{2,3}$ edges, using the Ligand Field Theory framework, shows that pyrrhotite contains only Fe^{2+} . No addition from any Fe^{3+} contribution is necessary. Since the slight oxide contribution at the surface was found to have no effect on the shape of the XMCD signal, we are quite confident concerning the theoretical analysis. Our modelisation of the Fe–S hybridization leads to a S to Fe charge transfer involving 0.3 electron. The conclusion concerning the absence of Fe^{3+} is in agreement with previous Mössbauer spectroscopy experiments (Dekkers 1988; Oddou et al. 1992; Fillion et al. 1992). This is also consistent with the conclusions of a polarized neutron diffraction study by Powell who found only one iron valence state (Powell et al. 2004).

The use of the sum rules on these XMCD signals revealed a rather large orbital magnetic moment ($0.6\mu_B$). Thus, pyrrhotite magnetisation results from a strong structural anisotropy (plane stacking with ordered vacancies) and from a strong orbital magnetic moment ($0.6\mu_B$ vs. $4\mu_B$ for the spin magnetic moment only). The strong orbital moment allows to understand previous high pressure measurements obtained by Mössbauer spectroscopy (Vaughan and Tossel 1973) where magnetisation was found to disappear fastly when the pressure increases. The large orbital contribution to the magnetic moment would be quite sensitive to the variation of the bond length induced by the pressure.

At the Fe K edge, the pre-edge feature on the isotropic spectrum stems from the small p - d hybridization that is permitted by the distortion of the octahedral site. The Fe pre-edge feature has a counterpart on the isotropic sulphur K edge: it is the large peak centered at 2469.2 eV. To better understand the electronic structure of the first empty levels, we performed a spin-polarized Tight-Binding Linear Muffin-Tin Orbital (TB-LMTO) calculation for a hypothetical ferromagnetic troilite (FeS) (Andersen and Jepsen 1984). The local densities of states for up spin and down spin obtained on Fe and S are reported on Figs. 7 and 8. From this two figures, one can attribute the pre-edge features at the Fe K-edge (7113.0 eV) and at the S K-edge (2469.2 eV) to the densities of empty states just above the zero energy (Pong 1994; Li 1995). As can be seen from the LMTO calculation, the DOS in this region are very strongly magnetically polarized. This magnetic polarization of the first empty states can indeed be followed by the XMCD measurements at the Fe and S K edges since both Fe and S pre-edge features give XMCD signals. This clearly shows that sulphur is

strongly engaged in the magnetic structure of pyrrhotite through hybridization of the Fe–S bond.

The DOS calculation can only give indications on the XMCD in the pre-edge region where the transitions come mainly from $1s$ level towards $4p$ levels hybridized with iron $3d$ states. By a comparison between XMCD signals from iron in tetrahedral and octahedral sites, it is obvious that $1s$ to $3d$ electric quadrupole transitions are negligible (Antonov et al. 2003). In the pre-edge region of Fe K edge, one notices a negative peak at 7,113 eV followed by a plateau around 7,115–7,116 eV. This is in line with the difference between spin-up and spin-down empty DOS in the first 5 eV above the zero energy (Fig. 7). In the case of the sulphur K edge, the large negative peak at 2,468 eV followed by a smaller positive one at 2470.5 eV is again well mimicked in the difference between the empty DOS for up and down spin. One should notice that the relation between the difference of empty DOS and the XMCD is reversed in the case of sulphur K edge compared to the case of iron K edge. This is due to the different action of the spin–orbit coupling on the sulphur $3p$ level and on the iron $4p$ level. In the case of sulphur, the $3p$ level is more than half filled and spin and orbit kinetic momentum are ferromagnetically coupled as expected from the third Hund's rule. On the contrary, the iron $4p$ level is almost empty and the spin and orbit kinetic momentum are antiferromagnetically coupled.

The XMCD at Fe K edge presents also a positive peak at 7121.5 eV at the same energy as the maximum of the main rising edge of Fe. Following previous XMCD measurements in Fe compounds where Fe is chemically bond (i.e. no intermetallic compounds) such a positive XMCD feature can be attributed to a magnetic polarization of the Fe $4p$ level parallel to the external magnetic induction (Champion 2001). This is indeed what is expected from our previous findings. Further analysis of XMCD at K edges would require advanced theoretical models, that are much beyond the scope of the present paper.

From XMCD measurements and analysis at Fe $L_{2,3}$ and K edges and at S K edge, it is possible to propose a magnetic structure for pyrrhotite. All the iron ions would be Fe^{2+} species. The small intensity of the Fe $L_{2,3}$ XMCD signal indicates that antiferromagnetic contributions are dominant and the observed net magnetisation results from the non cancellation of the various Fe magnetic moments. The XMCD signals at Fe and S pre-edges clearly indicate the major role that is played by sulphur and its strong magnetic polarization. The Fe–S hybridization can also be tracked by the electronic structure of Fe that is best fitted with a

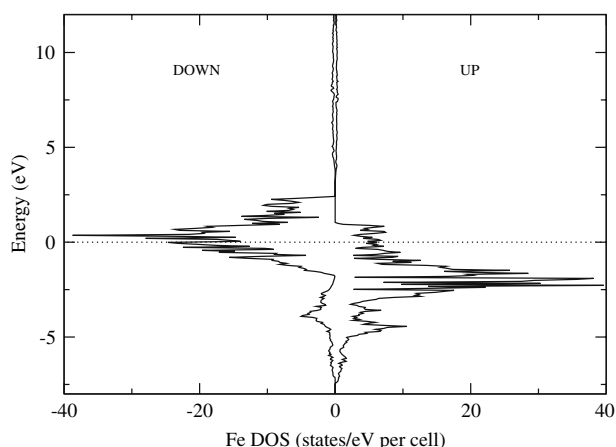


Fig. 7 Density of states of the Fe orbitals

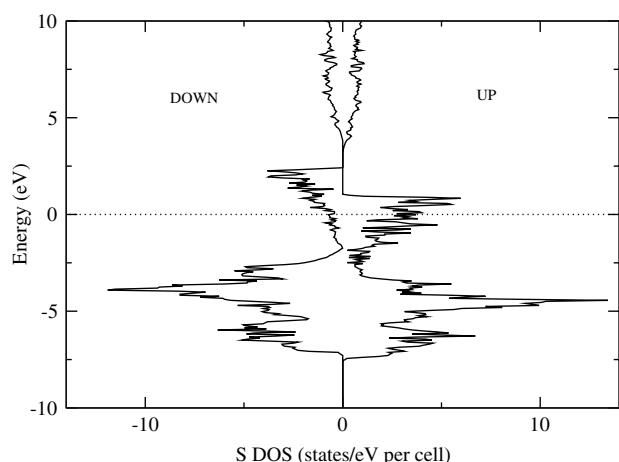


Fig. 8 Density of states of the S orbitals

Configuration Interaction involving Fe–S charge transfer in order to reproduce the γ feature on the Fe XMCD signal (see Fig. 3).

Conclusion

XMCD at Fe $L_{2,3}$ edges gives a direct proof for the absence of Fe^{3+} in Fe_7S_8 . All the iron ions are in the Fe^{2+} ground state, strongly hybridized with sulphur ligands. The iron magnetic moment is mainly built from the spin magnetic moment with a quite large orbital magnetic contribution that amounts to more than 15% of the whole magnetisation.

Isotropic and XMCD signals at Fe and S K edges confirm the strong Fe–S hybridization and show the magnetic polarization of these hybridized states. This suggests the important role played by sulphur in the magnetic structure of pyrrhotite. Spin polarized DOS calculations supported our interpretation for the pyrrhotite electronic structure. XMCD at the K edges contains much more information than could be extracted and theoretical developments and simulations are still needed in this field.

Acknowledgments We acknowledge the Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (Orsay, France) and the European Synchrotron Radiation Facility (Grenoble, France) for provision of synchrotron radiation facilities and we would like to thank José Goulon, Nicolas Jaouen, Andrei Rogalev and Fabrice Wilhelm for assistance in using beamline ID12. We are grateful to Sandrine Brice-Profeta for

her useful advice in the multiplet calculations. We thank Jean-Claude Boulliard for supplying the natural Fe_7S_8 sample.

References

- Andersen OK, Jepsen O (1984) *Phys Rev Lett* 53:2571
- Antonov VN, Harmon BN, Yaresko AN (2003) *Phys Rev B* 67:024417
- Arrio M-A et al (1996) *J Am Chem Soc* 118:6422
- Bertaut EF (1953) *Acta Crystallogr* 6:557
- Brice-Profeta S et al (2005) *J Magnetism Magn Mater* 288:354
- Brouder C, Kappler J-P (1996) *Lecture Notes, Mittelwihl. Magnetism Synchrotron Radiat*, p19
- Brouder C, Alouani M, Bennemann KH (1996) *Phys Rev B* 54:7334
- Burns R (1993) *Mineralogical applications of crystal field theory*, 2nd edn. Cambridge University Press, Cambridge
- Butler PH (1981) *Point group symmetry applications: methods and tables*. Plenum Press, New York
- Champion G et al (2001) *J Am Chem Soc* 123(50):12544
- Charnock J, Henderson C, Mosselmans J, Patrick R (1996) *Phys Chem Minerals* 23:403
- Chikazumi S (1997) *Physics of ferromagnetism*. Oxford Science Publications, Oxford
- Cowan RD (1981) *The theory of atomic structure and spectra*. University of California Press, Berkeley
- Dekkers MJ (1988) *Phys Earth Planet Inter* 52:376
- Dunlop DJ, Özdemir O (1997) *Rock magnetism—fundamentals and frontiers*, vol 3. Cambridge University Press, Cambridge
- Fillion G, Mattei JL, Rochette P, Wolfers P (1992) *J Magnetism Magn Mater* 104–107:1985
- Goulon J et al (1988) *J Synchrotron Radiat* 5:232
- Keller-Besrest F, Collin G (1982) *Acta Crystallogr B* 38:296
- Kontny A, Wall HD, Sharp TG, Posfai M (2000) *Am Mineral* 85:1416
- Kuiper P, Searle BG, Rudolf P, Tjeng LH, Chen CT (1993) *Phys Rev Lett* 70:1549
- Li D et al (1995) *Can Mineral* 33:949
- Li F, Franzen HF (1996) *J Solid State Chem* 124:264
- Oddou JL, Jeandey C, Mattei JL, Fillion G (1992) *J Magnetism Magn Mater* 104–107:1987
- Patrick RAD et al (2002) *Eur J Mineral* 14:1095
- Pearce CI, Henderson CMB, Patrick RA, van der Laan G, Vaughan DJ (2006) *Am Mineral* 91:880
- Pong WF et al (1994) *Phys Rev B* 50:7371
- Powell AV, Vaqueiro P, Knight KS, Chapon LC, Sánchez RD (2004) *Phys Rev B* 70:014415
- Quidelleur X, Valet J-P, Thouveny N (1992) *Earth Planet Sci Lett* 111:23
- Saintavit P et al (1992) *J Appl Phys* 72:1985
- Thole T, van der Laan G (1988) *Phys Rev B* 38:3158
- Thole BT, Carra P, Sette F, van der Laan G (1992) *Phys Rev Lett* 68:1943
- Vaughan DJ, Craig JR (1978) *Mineral chemistry of metal sulfides*. Earth Science Series, Cambridge University Press, Cambridge
- Vaughan DJ, Tossel JA (1973) *Science* 179:375