



HAL
open science

Fe magnetic transition under high pressure

O. Mathon, F. Baudalet, J.P. Itié, A. Polian, M. d'Astuto, J.C. Chervin, S. Pascarelli

► **To cite this version:**

O. Mathon, F. Baudalet, J.P. Itié, A. Polian, M. d'Astuto, et al.. Fe magnetic transition under high pressure. 2004. hal-00001588v1

HAL Id: hal-00001588

<https://hal.science/hal-00001588v1>

Preprint submitted on 19 May 2004 (v1), last revised 15 Dec 2004 (v4)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Fe magnetic transition under high pressure

O. Mathon¹, F. Baudelet^{2,3}, J.P. Itié², A. Polian², M. d' Astuto², J.C. Chervin² and S. Pascarelli¹

¹*European Synchrotron Radiation Facility, BP 220 38043 Grenoble Cedex, France*

²*Physique des Milieux Condensés, 4 Place Jussieu, Paris, France*

³*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France*

Abstract:

We have studied the high-pressure iron bcc to hcp phase transition by X-ray Magnetic Circular Dichroism (XMCD) and X-ray Absorption Spectroscopy (XAS). The magnetic and structural transitions simultaneously observed are sharp. Both are of first order in agreement with theoretical prediction. The pressure domain of the transition observed (2.0 ± 0.1 GPa) is narrower than that usually cited in the literature (8 GPa). We have evidence that the magnetic transition slightly precedes the structural one, suggesting that the origin of the instability of the bcc phase in iron with increasing pressure is to be attributed to the effect of pressure on magnetism, rather than to phonon softening.

The iron phase-diagram has attracted considerable interest since a long time. At the beginning the motivation was its central role in the behaviour of alloys and steel [1]. Later its geophysical importance was underlined, because of its predominant abundance in the Earth's core [2] [3]. The phase diagram of iron at extreme pressure and temperature conditions is still far from being established. Under the application of an external pressure, iron undergoes a transition at 13 GPa from the bcc α -phase to the hcp ϵ -phase structure [4], with the loss of its ferromagnetic long range order [5]. In the literature the transition extends over 8 GPa at ambient temperature within which the bcc and hcp phases coexist [6]. In the pure hcp ϵ -phase, superconductivity appears close to the transition between 15 and 30 GPa [7,8].

For these reasons, the evolution with pressure of the magnetic state across this transition is still a subject of active research, traditionally based on Mössbauer measurements [5,9,10,11] and, recently, using inelastic x-ray scattering [12]. The authors of Ref. 12 report on variation of a satellite in the Fe-K β fluorescence line, which shows that the magnetic moment of iron decreases over the same pressure range as the bcc to hcp transition i.e. 8 GPa. These data agree with Mössbauer results [11], which indicate that the main part of the magnetic moment decrease occurs in the same pressure domain. Nevertheless the lack of reproducibility of high pressure conditions does not allow a precise correlation between the structural and the magnetic transition when measured separately.

Considerable ab-initio theoretical studies of this transition have been carried out [2],[8],[13],[14]. The first order nature of the structural and magnetic transitions is well established as well as the non-ferromagnetic state of the hcp phase. During the transition a low spin state [14] is suggested. At higher densities, an incommensurate spin-density-wave-ordered state is predicted in Ref. 15 for a small pressure range starting with the onset of hcp phase, as for superconductivity.

In this paper we report a combined x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) study of the Fe bcc-hcp transition. Our results highlights the close relationship between the structural transition and the decrease of the magnetic moment. The high sensitivity of XMCD allows us to follow the magnetic transition very precisely, and to correlate it to the local structure.

Polarized x-ray absorption spectroscopy contains intrinsic structural, electronic and magnetic probes. These are respectively the extended x-ray absorption fine structure (EXAFS), the x-ray absorption near edge structure (XANES) and X-ray Magnetic Circular Dichroism (XMCD). The first two are able to differentiate clearly the signature of bcc or hcp local symmetry, while the third is very sensitive to polarized magnetic moments variation. Thus, we can obtain information on both the magnetic and structural properties of the system at the same time i.e. on

the same sample in the same pressure conditions. This is very important in the high-pressure domain where reproducibility of high-pressure hydrostatic conditions is difficult to obtain.

XMCD and XAS were recorded at the ESRF on the dispersive XAS beamline ID24. This station is designed to fulfill the requirements of detecting very small XMCD signals (down to $\sim 10^{-3}$) under pressure at the K edges of 3d transition metals [16].

The sample (Goodfellow high purity 4 μm iron foil) was inserted into the Cu-Be Diamond Anvil Cell (DAC) and placed in a 0.4 T magnetic field parallel to the x-ray beam. Silicon oil was used as pressure transmitting medium and the pressure was measured with the ruby fluorescence technique [17]. Real time visualization of the XAS spectra allowed to remove, from the energy range of interest, the parasitic Bragg reflections from the diamond anvils by an appropriate alignment of the cell.

In this experiment, each XMCD spectrum was obtained by accumulating 200 XAS spectra with a change of direction of the applied magnetic field between two successive ones. By comparing the first and the last XAS spectra relative to one XMCD acquisition, it was possible to check the structural stability of the sample during the measurement.

XMCD spectra were recorded in the pressure range up to 22.4 ± 0.1 GPa. Several runs were carried out on freshly loaded samples, to check reproducibility. In each run, spectra were acquired during increase of pressure.

Figure 1 compares the normalized Fe K-edge XAS (left panel) and XMCD (right panel) data of pure Fe foil in ambient conditions (bottom curves), to examples of spectra recorded within the DAC at different pressure values, between 10.0 ± 0.1 GPa and 22.4 ± 0.1 GPa, during a pressure increase ramp

The energy range diffracted by the polychromator is limited to the XANES region and the first oscillations of the EXAFS domain. The XAS data shows very clearly that both the electronic structure and the local structure around Fe are drastically modified above 14 GPa: the pre-peak at 7116 eV becomes more resolved, the white line drifts towards higher energies (from 7132 to 7134 eV) and becomes less intense, and the frequency of the EXAFS oscillations is drastically reduced. The spectrum at 22.4 GPa corresponds to the hcp structure described in ref. [6].

The XMCD curves in panel b correspond to the XAS spectra shown in continuous lines in panel a. The amplitude of the ambient pressure XMCD signal obtained with the sample in the DAC (not shown) is equal to approximately 30% of its value measured outside the DAC due to the small applied magnetic field which cannot overcome the demagnetization factor of the probed iron foil. Figure 1 shows that the amplitude of the XMCD signal starts to decrease at 14 GPa and totally disappears above 15.5 ± 0.1 GPa.

In order to better identify the onset and the evolution with pressure of this phase transition, we have performed the first derivative of all XAS spectra close to the transition region. The amplitude of the derivative signal changes drastically between the bcc phase and the hcp phase at $E = 7137$ eV, $E = 7205$ eV and $E = 7220$ eV. It is at these energy points that we have the highest sensitivity to the bcc/hcp phase fraction.

In Figure 2 we plot (full squares) the evolution of the bcc/hcp phase fraction as a function of pressure, obtained directly from the evolution of the amplitude of the derivative at these specific energy points (note that the phase fraction calculated at the three different energies is identical within the error bar).

The onset of the transition occurs at about 14.0 ± 0.1 GPa and is over at 16.0 ± 0.1 GPa. The EXAFS signature of the different steps of the Fe bcc-hcp transition was already clearly identified by Wang and Ingalls [6] and the bcc to hcp transition was described as a martensitic transition with a slow variation of the relative bcc and hcp phases abundance. In their work, the transition occurred in a larger pressure range than that observed in the present work. This could be attributed to the different conditions of non-hydrostaticity within the cell, and underlines the difficulty of reproducing the same thermodynamic conditions in different experiments.

To quantify the reduction in the amplitude of the XMCD signals with pressure, the background subtracted data was squared and integrated in the energy range 7100 – 7122 eV. The values of the integrals are plotted in Figure 2 (crosses). The pressure error is about ± 0.1 GPa [17]. Figure 2 shows that also the magnetic transition is indeed quite abrupt occurring within a pressure range of 1.5 GPa, with an onset at around 14.0 ± 0.1 GPa. The abrupt drop to zero of the iron magnetic moment when the bcc to hcp phase transition occurs proves the first order nature of the pressure induced magnetic transition, as predicted by Ekman et al.[14]. The black dashed line is a guide for the eye.

The narrower pressure transition domain found in the present work with respect to previous structural and magnetic studies [6, 11,12] could be in part attributed to a lower pressure gradient within the probed region, directly correlated to the smaller sample volume probed by the X-ray beam [18] with respect to previous experiments. The

influence of different experimental conditions to the pressure values of transition onsets and to the pressure range of phase coexistence is well known and frequently addressed in the literature [see for example reference 6]. For this reason, the simultaneous measurement of element specific magnetic properties using XMCD and of element specific local structural and electronic properties using XAS, that overcomes all uncertainty related to different hydrostatic conditions within the pressure cell and different probed volumes, is fundamental to address issues concerning correlation between magnetic, electronic and structural degrees of freedom of a system during phase transitions.

Our data shows that between 14 and 15.5 GPa the XMCD is suddenly reduced to zero, within the error bars, indicating the disappearing of the room temperature ferromagnetic order of iron. A closer look at the transition region in Figure 2 shows that, in the initial part of the transition, the amplitude of the XMCD signal drops very abruptly so that, in the second part of the transition, at a specific pressure point, the amplitude of the XMCD signal is lower than the bcc/hcp phase ratio. This implies that the drop in the magnetic moment occurs at slightly lower pressures with respect to the local structural modifications.

Our observation is in good agreement with the transition pattern given in Ref. 14 where theoretical calculations show that the bcc iron phase instability is not primarily due to phonon softening but to the effect of pressure on the magnetism of iron. In other words, since ferromagnetism has a stabilizing effect in bcc iron, it is only when, under pressure, ferromagnetism disappears that the bcc phase become thermodynamically unstable with respect to the hcp one. This happens long before it becomes dynamically unstable.

As a consequence of the different evolutions of the magnetic moment and of the local structure, towards the last part of the transition the delay between the magnetic and structural path is larger, yielding a magnetic pressure transition domain slightly narrower than the structural one (1.5 ± 0.1 GPa instead of 2.0 ± 0.1 GPa). In this part of the transition, the abundance of bcc is very small and its lattice constant behaves anomalously because it is observed to increase with pressure [6]. This is contradictory with a null magnetic moment and it is questionable to consider the remaining part of the iron, which is not yet hcp, as still in a bcc structure. In reference [14], the authors predict a high-spin to low-spin transition with an intermediate magnetic moment of about $1\mu_B$. In an intermediate phase with a coordination number of 10+2 a stabilization of intermediate magnetic states is possible.

The observed absence of macroscopic magnetization above 15.5 GPa is in good agreement with the recent prediction of anti-ferromagnetic fluctuations for a small pressure range starting with the onset of hcp phase [15], which is suggested as a possible origin of the superconductivity.

We have measured XAS and XMCD of iron metal under pressure along the bcc to hcp phase transition. The simultaneous measurement of element specific magnetic properties using XMCD and of element specific local structural and electronic properties using XAS has an enormous potential in correlating the magnetic, electronic and structural degrees of freedom during phase transitions. For Fe at high pressure, we find that the local structure and the magnetic transition occur within 2.0 ± 0.1 GPa and are much sharper than usually described in literature. This proves unambiguously the first order nature of the iron bcc to hcp transition. Moreover, we have evidence that the magnetic transition precedes the structural one.

References

- [1] H. Hasegawa and D.G. Pettifor Phys. Rev. Lett. **50**, 130 (1983).
- [2] L. Stixrude, R.E. Cohen and D.J. Singh, Phys. Rev. **B 50**, 6442 (1994).
- [3] R. Jeanloz, Ann. Rev. Earth Planet ; Sci **18**, 357 (1990)
- [4] D. Bancroft, E. L. Peterson, and S. Minshall, J. Appl. Phys. **27**, 291 (1956).
- [5] M. Nicol and G. Jura, Science **141**, 1035 (1963)
- [6] F.M. Wang and R. Ingalls Phys. Rev. **B 57**, 5647 (1998).
- [7] K. Shimizu, T. Kimura, S. Furomoto, K. Takeda, K. Kontani, Y. Onuki, K. Amaya, Nature **412**(6844) 316 (2001).
- [8] S.K. Bose, O.V. Dolgov, J.Kortus, O.Jepsen, and O.K. Andersen Phys. Rev. B **67**, 214518 (2003)
- [9] G. Cort, R. D. Taylor, and J. O. Willis, J. Appl. Phys. **53**,2064 (1982).
- [10] R.D. Taylor, G. Cort, and J. O. Willis, J. Appl. Phys. **53**, 8199 (1982)
- [11] R.D. Taylor, M.P. Pasternak, and R. Jeanloz, J. Appl. Phys. **69**, 6126 (1991).

- [12] J.P. Rueff et al. Phys. Rev. **B 60**, 14510, (1999).
- [13] T. Asada and K. Terakura, Phys. Rev. B 46, 13599 (1992).
- [14] M. Ekman, B. Sadigh, K. Einarsdotter and P. Blaha, Phys. Rev. **B 58**, 5296 (1998).
- [15] V.Thakor, J.B. Stauton, J. Poulter, S. Ostanin, B. Ginatempo and Ezio Bruno Phys. Rev. B 67, 180405 (R) (2003).
- [16] O. Mathon et al in preparation. (preprint?)
- [17] J.C. Chervin, B. Canny and M. Mancinelli, High Pressure Research **21**, 305 (2001) .
- [18] S. Pascarelli, O. Mathon and G. Aquilanti, J. of Alloys and Compounds **362**, 33 (2004)

Captions

Figure 1. Fe K-edge XAS (left panel) and XMCD (right panel) as a function of pressure between the ambient pressure bcc phase and the high pressure hcp phase. Continuous lines correspond to examples of data measured simultaneously. The small glitches in the XAS at 7158 and 7171 eV in the high pressure data are artifacts due to small defects of the polychromator crystal.

Figure 2: Evolution of the amplitude of the derivative of the XAS (full squares) compared to the reduction of the amplitude of the XMCD signals (crosses). The dashed line is a guide for the eye that highlights the sharpness of the structural and magnetic transition. The inset is a zoom on the transition region

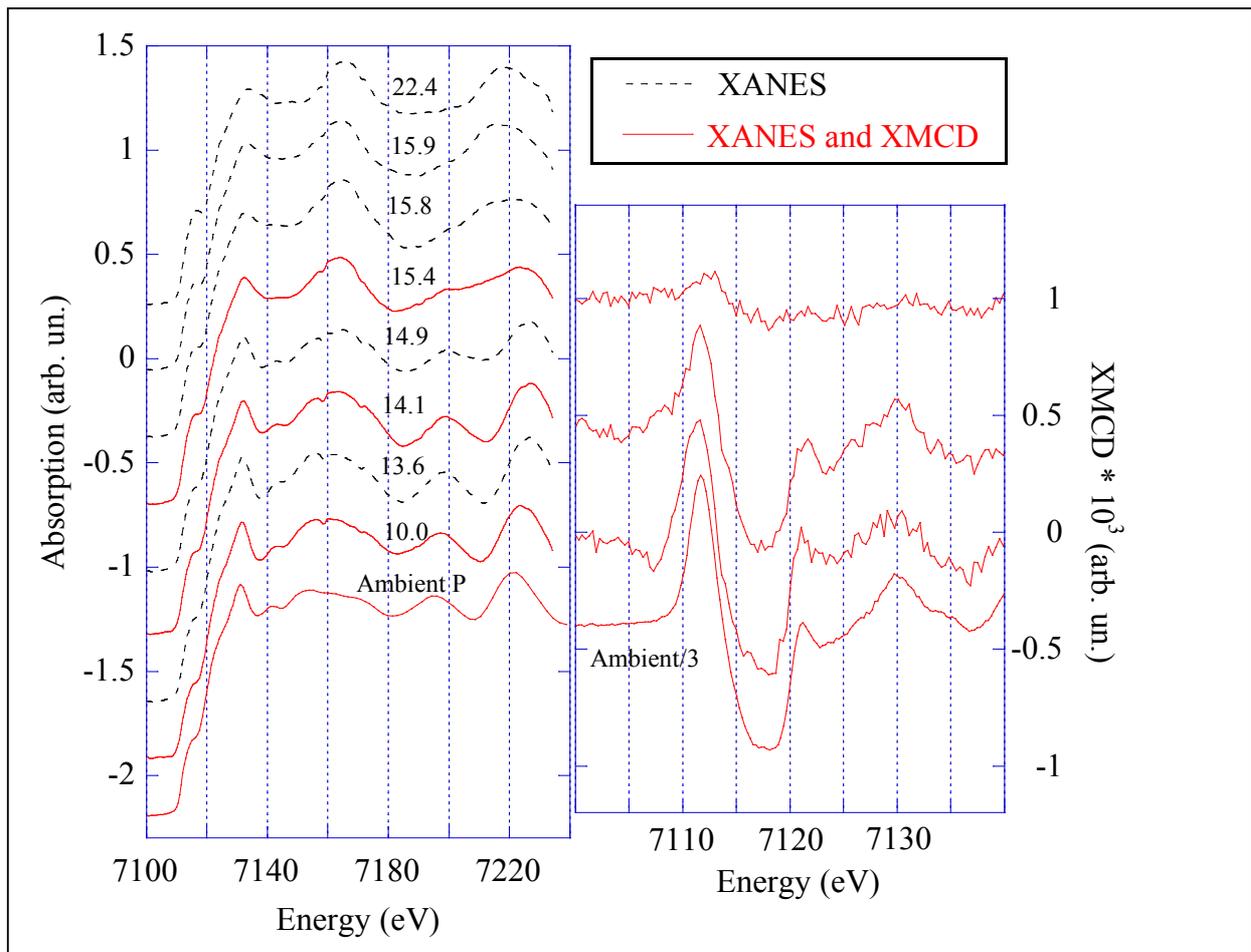


Figure 1

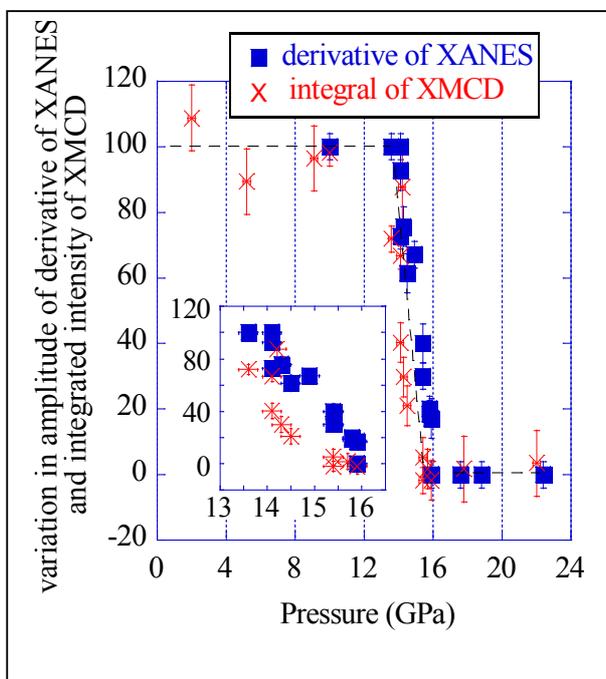


Figure 2