Magnetic and structural α-ϵ phase transition in Fe monitored by x-ray emission spectroscopy

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The iron structural and magnetic transition between the magnetic (bcc-α) and the nonmagnetic (hcp-ϵ) phases has been studied monitoring the pressure dependence of the Fe-$K\beta$ fluorescence line excited with monochromatic synchrotron radiation. The relative intensity of the two multiplets shows an S-shaped pressure curve with flex point at the known transition pressure of 130 kbar. The S width of $\approx$30 kbar also coincides with the one determined in structural determinations, and in magnetism studies using Mössbauer techniques. This shows how the x-ray emission method can be used to probe the local magnetic properties of atoms under extreme thermodynamic conditions. [S0163-1829(99)03745-5]

The investigation of the properties of condensed matter under extreme thermodynamic conditions has received a great impulse since the recent development of very high-pressure techniques based on the use of diamond-anvil cells (DAC). Using a DAC, it is now possible to bring samples at pressures in the Mbar range. The DAC-based methods have been very successful also when used in combination to intense and small size synchrotron radiation-based x-ray beams, especially those produced at third generation x-ray sources, which allow to condense very efficiently the x-ray intensity in submillimeter sized sample volumes. Using these x-ray beams, powerful crystallography methods are now routinely applied to study the structure and, more generally, the equation of state (EOS) of the investigated sample. Besides crystallography, thanks to the intensity and collimation of third generation x-ray beams, one starts to see the possibility to develop as well x-ray based spectroscopy methods as x-ray-absorption spectroscopy, extended x-ray-absorption fine structure,[1,2] Mössbauer spectroscopy (MS),[3] and x-ray emission spectroscopy[4] (XES).

Iron, and specifically iron under extreme conditions of high pressure and temperature, is an element of great importance for its geophysical and practical implications.[5–7] At room temperature and with increasing pressure, iron shows a phase transition from a bcc (α) phase to a hcp (ϵ) phase at a pressure of $\approx$130 kbar.[8] This transition is found to take place in a $\approx$30-kbar pressure interval. Besides the structural phase transition, one finds also an important change in the magnetic properties of the iron atom: namely iron which is ferromagnetic in the α phase becomes nonmagnetic in the ϵ phase. The magnetic properties of iron under pressure and their interplay with the structural phase transitions have been the subject of various theoretical studies: the phase diagram of iron under pressure is rather well described within the fluctuation spin theory,[9] showing the strong magnetovolume coupling in iron. In particular, magnetism is shown to be the primary stabilizing factor of the bcc structure at ambient pressure. Further band-structure-calculations-like techniques[10–12] have also stressed the relevance of the magnetovolume instabilities to understand the properties of iron under pressure. It is therefore of prime importance that its different structural and magnetic phases are studied in great detail on an experimental basis. Using the ^{57}Fe Mössbauer resonance, which shows a hyperfine splitting due to the interaction between the nuclear spin and the magnetic moment of the magnetic electrons on the iron nuclear site, it has been possible to establish the nonmagnetic state of the ϵ phase.[3,13–16]

The recent development of high-energy resolution x-ray emission provides an alternative method to MS to probe the local magnetic properties of atoms. The XES spectra show a series of features which reflect the energies of the different electronic configurations of the excited atom.[17] Together with the Coulomb interactions between the electrons occupying different orbital configurations, there are also those of magnetic origin. In particular, we consider an excited atom which has valence electrons with unpaired spins giving rise to a magnetic moment. Here, the exchange interactions between these magnetic electrons and the core electrons in the orbital where the photon emission process has left a core hole are responsible for the appearance of multiplet families in the emission spectrum with a dominant spin character. The energy separation among these families, and therefore the possibility to observe them easily, is related to the strength of these interactions, which are maximum when the hole is in an orbital with the same principal quantum number n of the magnetic electrons. In the case of iron, this situation is obtained for the $K\beta$ fluorescence line, where the final state hole is in the $3p$ orbital and the magnetic electrons are in the $3d$ orbitals.

In this paper we present an x-ray emission investigation of the magnetism in pure Fe under high pressure. The Fe-$K\beta$ line has been measured across the α-ϵ phase transition, taking place around $P=130$ kbar. The disappearance at the phase transition pressure of the satellite peak at the low emission energy side of the Fe-$K\beta$ line indicates the collapse of the magnetization in ϵ-Fe, confirming earlier MS studies. This transition takes place at the same pressure of the structural phase transition, and its width is found to be as sharp as that of both previous structural and magnetic studies. This observation demonstrates that the XES method can be used successfully to monitor the magnetic properties of materials as a function of thermodynamic variables as temperature and

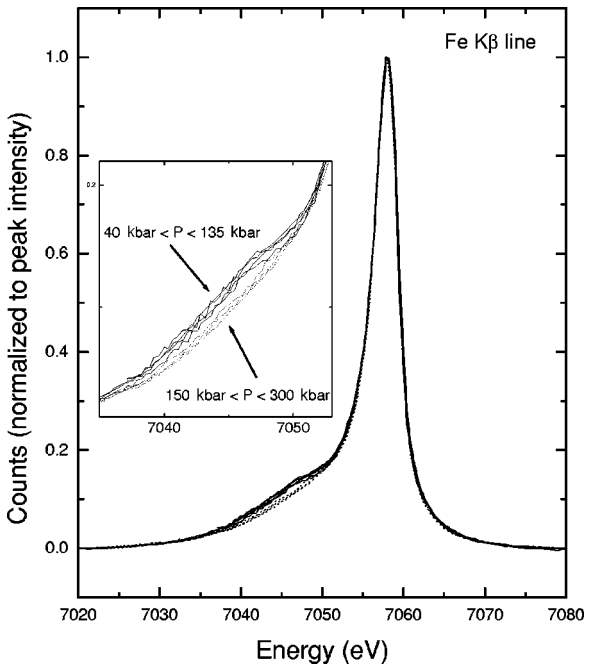

FIG. 1. Fe XES spectra measured at increasing pressures. The spectra were normalized to the intensity of the main peak set to unity, and aligned to 7058 eV. At low pressure, the satellite at 7045.5 eV is characteristic of the magnetic state (solid line) whereas the absence of satellite above 150 kbar denotes the transition to the nonmagnetic state (dotted lines).

pressure. It is, therefore, an alternative/complementary method to MS, particularly attractive on all those atoms without easily accessible Mössbauer isotopes.

The experiment was carried out at the inelastic x-ray scattering undulator beamline ID16 at the European Synchrotron Radiation Facility (ESRF). The detailed setup of the beamline has been described elsewhere.[18] The white beam is monochromatized by a cryogenic He-cooled Si(111) double crystal device, and focused on the sample position by a Rh-coated toroidal mirror to a spot size of 20(vertical) $\times 80$(horizontal) μm^2. This size is comparable and even smaller than the gasket size in the DAC, thus maximizing the incident flux for the excitation of the emission line. The fluorescence signal is detected by a 1-m Rowland circle spectrometer operating in the horizontal scattering plane. The analyzer consists of a (531) single crystal wafer elastically bent and glued onto a spherical substrate of 1-m radius. The analyzer is operated at Bragg angles around the value of 73.12°, corresponding to the Fe-$K\beta$ emission line. The use of these Bragg angles, the horizontal source size, and the natural optical aberrations of the analyzer give a total-energy resolution of ≈ 300 meV, a value smaller than the intrinsic linewidth of the Fe-$K\beta$ line. The Fe-$K\beta$ emission spectra are excited with monochromatic radiation of 11 KeV photon energy. This value is dictated by an optimal choice between available intensity, maximum Fe photon absorption, and minimal photon attenuation by the 2-mm-thick diamonds of the DAC. The detector is a Peltier-cooled silicon pin diode. A high-purity Fe foil was loaded in a membrane-type DAC with N_2 as pressure medium. The sample was inserted in a 100-μm-diameter and 20-μm-thick Re gasket. Pressure on the sample was measured by the conventional ruby fluorescence technique using a He-Ne blue laser. For a complete characterization of the Fe structure, diffraction patterns were also recorded from the sample in the DAC in both low- and high-pressure phases. The diffraction measurements were performed on the high-pressure station ID9 at ESRF using an image plate technique.

Iron x-ray emission spectra are shown in Fig. 1 for pressure ranging from 40 to 300 kbar at room temperature. The spectra were arbitrarily normalized to the main peak intensity, and aligned to the theoretical Fe-$K\beta$ fluorescence energy of 7058 eV. The spectra consist of an intense narrow peak at 7058 eV followed on the energy-loss side by a broad satellite located at ≈ 7045 eV. As shown in the inset of Fig. 1, this spectral feature decreases in intensity with increasing pressure, and tends to disappear when the pressure exceeds 135 kbar, assuming afterwards an almost constant shape up to 300 kbar, the highest measured pressure point. This satellite peak, well established from experimental studies on the $K\beta$ line of other transition metals, as well as on the $L_{2,15}$ lines in rare earths, and by theoretical calculations within the multiple approach,[17,19] is predominantly due to final state configurations where the total spin of the core orbital ($3p$ in transition metals and $4d$ in rare earths) is aligned opposite to the magnetic moment of the valence electrons ($3d$ in transition metals and $4f$ in rare earths). Its presence (absence)

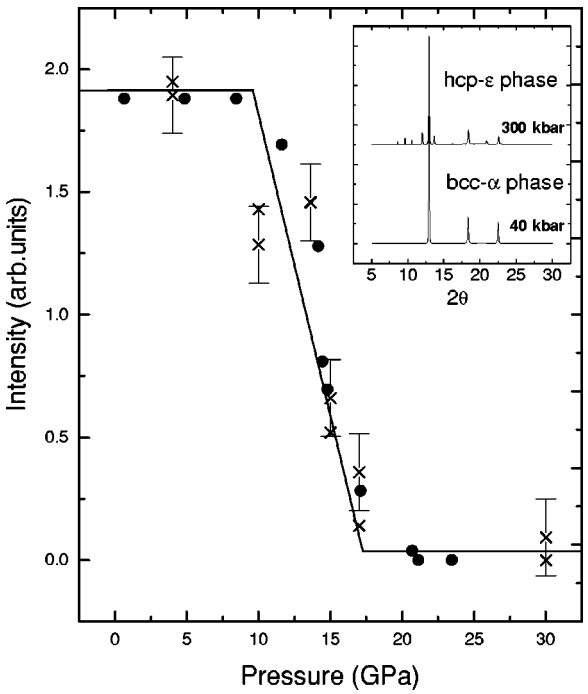

FIG. 2. Integrated intensity of the satellite shown in Fig. 1 (crosses) compared to the α-phase fraction determined by Mössbauer spectroscopy (Ref. 16) (solid circles) upon pressure increase. The latter curve has been scaled to the low-pressure XES satellite intensity. The solid line is a guide to the eyes. The intensity of the XES satellite was calculated from the difference spectra obtained by subtracting the 230-kbar spectrum from each scan (crosses) or by subtracting the spectra after normalization to the integrated intensity (open circles). The plateau at low (high) pressure corresponds to the magnetic (nonmagnetic) phase. The diffraction pattern measured in both phases, shown in the inset, confirm the structural change.

therefore testifies the presence (absence) of a magnetic moment arising from the considered valence orbital. The intensity of this peak, among other contributions, strongly depends on the spatial overlap between the valence orbitals and those of the core electrons where the final-state core hole has been created by the emission process: this explains why this method is extremely sensitive, and, in fact, we believe almost exclusively sensitive, to the magnetic moment induced by the considered valence orbitals of the excited atom. The result reported in Fig. 1 is therefore interpreted as the disappearance of a substantial amount of the magnetic moment due to the Fe $3d$ valence electrons.

The fine analysis of the intensity decrease of the satellite peak is reported in Fig. 2. The satellite structure amplitude is determined as a function of pressure as follows: the amplitudes are obtained calculating the integral of the difference spectrum between the spectrum at pressure P and that at $P = 300$ kbar, after normalization of all the spectra to the peak intensity of the main peak at 7058 eV. An alternative method consists in normalizing all emission spectra to the same integral value, and then calculating the integral of the modulus of the difference spectrum. The two methods give essentially identical results, which are reported in Fig. 2, that is, a plateau of high intensity at low pressure followed by a sharp drop in intensity around $P_o = 135$ kbar and a low intensity plateau at higher pressure. The uncertainty in the absolute pressure determination, due to mechanical relaxation processes and to the pressure gradients in the cell, is about 5 kbar. The plateau at low (high) pressure can be readily associated with the magnetic-α (nonmagnetic-ϵ) phase. The corresponding diffraction patterns shown in the inset of Fig. 2 confirm the structural transition. The value of P_o coincides, within the indetermination, with the one determined in other structural studies for the α-Fe to ϵ-Fe transition pressure. The pressure width of the transition, ΔP, found in the present emission study is ≈ 30 kbar, a value comparable to that found in both structural[2] and magnetic determinations as shown in Fig. 2 where the α-phase fraction determined by Mössbauer spectroscopy has been reported.[16]

In conclusion, this study shows that the Fe-$K\beta$ emission spectra strongly depend on pressure, and the relative intensities of the spectral features indicates the collapse of the $3d$ electron magnetic moment at the α-ϵ phase transition. As already shown by MS, this confirms that the structural and magnetic phase transitions take place simultaneously and in the same pressure range, and therefore that the iron atom in the hcp phase has no longer a magnetic moment. Finally, this study, performed here with monochromatic beam, testifies the power of the present technique to monitor important modifications of the magnetic and electronic structure of condensed matter under extreme conditions. In the specific case of iron, it has been possible to show that the structural and magnetic phase transitions take place simultaneously and in the same pressure range.

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