# Magnetism of Invar alloys under pressure examined by inelastic x-ray scattering

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The magnetic properties of the Invar alloy $Fe_{64}Ni_{36}$ have been investigated by x-ray emission spectroscopy as a function of pressure up to 20 GPa. With increasing pressure, the amplitude of the Fe local moment, deduced from the Fe $K\beta$ line satellite intensity, is reduced at two characteristic step values. This pressure dependence is interpreted in terms of transitions from a high-spin state to a low-spin state at $\approx 5$ GPa followed by a transition to a nonmagnetic state above 15 GPa. This behavior provides a microscopic picture of the Fe magnetism in agreement with the $2\gamma$-state model.

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The puzzling properties of Invar alloys have generated a tremendous amount of work[1,2] since their discovery more than a century ago.[3] The Invar effect is the anomalously low and stable thermal expansion of certain metallic alloys over a wide range of temperature. So far, however, no general agreement on the precise physical mechanism has been reached. One of the most commonly accepted models is the so-called $2\gamma$-state model proposed by Weiss.[4] According to this model, iron can occupy two different states: a high volume state and a slightly less favorable low volume state. This low volume state is thermally populated thus compensating the thermal expansion. This almost *ad hoc* model is supported by fixed-spin moment calculations, which show the existence of a high spin (HS) to low spin (LS) transition in Invar alloys as function of temperature.[5] The same effect is also expected under applied pressure at ambient temperature. State-of-the-art band calculations for Invar alloys[6,7] have provided strong clues in this direction by identifying the HS to LS transition with a charge transfer from the majority antibonding (AB) $t_{2g}$ states to the minority nonbonding (NB) $e_g$ states. A charge transfer, similar in nature, albeit opposite, has also been identified experimentally by paramagnetic neutron scattering in anti-Invar.[8]

A recent theoretical reexamination of the magnetic properties of the Fe-Ni alloys within an *ab initio* model was motivated by some experimental inconsistencies, and this gave a new impulse to the understanding of the Invar effect. The model proposed by van Schilfgaarde *et al.*[9] explains the volume expansion anomaly by the noncollinearity of the iron (and to a smaller extent of the nickel) magnetic moments. This effect is accompanied by a slow and continuous decrease of the amplitude of the Fe magnetic moment as a function of pressure. This continuous behavior is in contrast with the steplike transitions predicted by the $2\gamma$ state model.

X-ray emission spectroscopy (XES) is a well suited technique to address these issues. Indeed, XES is now a well established technique providing direct information on the local magnetic properties of atoms, without reference to the long-range magnetic order. It has been already utilized to identify magnetic transitions in Fe-based systems.[10–12] Thus XES differs from other spectroscopic probes of magnetism compatible with high-pressure measurements such as x-ray circular magnetic dichroism (XMCD) or Mössbauer spectroscopy (MS), because of its extreme sensitivity to the magnetic moment associated to a specific class of valence orbitals—in the case of the Fe $K\beta$ emission these are the Fe $3d$ orbitals. This local sensitivity, and the insensitivity to long-range magnetic order—responsible for the XMCD signal, and to a certain extent for the hyperfine splitting in MS—is crucial in the case of the Invar alloys. Changes in the circular magnetic dichroism at the Pt-$L_3$ edge in Fe-Pt Invar as a function of pressure observed by Odin *et al.*,[13] and the disappearance of the hyperfine splitting viewed in the $^{57}Fe$ Mössbauer spectra of $Fe_{72}Pt_{28}$ at high pressure by Abd-Elmeguid and co-workers[14–16] have been interpreted in term of HS/LS transition. In these cases, however, the strong reduction of the Curie temperature with pressure leads to the emergence of a paramagnetic phase which cannot be distinguished using XMCD or MS from a true reduction in amplitude of the magnetic moment on the individual Fe atoms.

In this paper, we report the investigation of the magnetic properties of a Fe-Ni Invar alloy under high pressure using high-resolution x-ray emission spectroscopy. The spin state of Fe in $Fe_{64}Ni_{36}$ was monitored by high-resolution measurements of the Fe $K\beta$ line up to 20 GPa in a diamond-anvil cell (DAC). The low-pressure spectrum is found to be characteristic of high spin iron. With increasing pressure, we observed a two-step reduction of the local moment amplitude. This is interpreted in terms of a high spin to low spin transition followed by a collapse of the magnetic moment at about 15 GPa. These results therefore strongly support the $2\gamma$-state model.

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.[17] The white beam is monochromatized by a cryogenically 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) $\mu m^2$. This size is smaller than the sample 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 Si(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

 

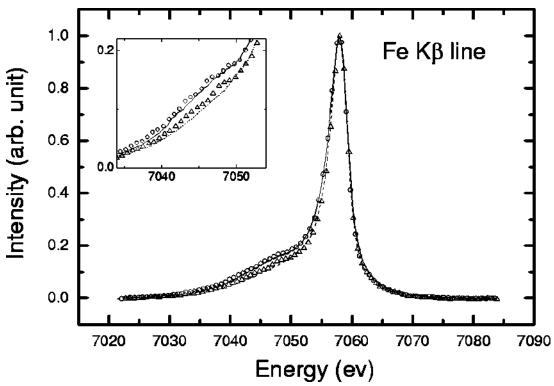


FIG. 1. XES spectra measured at 0 (open circles) and 20 GPa (open triangles) in Fe-Ni Invar. As an element of comparison, XES spectra measured in pure Fe are also shown for both low-pressure $\alpha$-Fe (solid line) and high-pressure $\epsilon$-Fe (dashed line) phases. A blowup of the satellite region is shown in the inset.

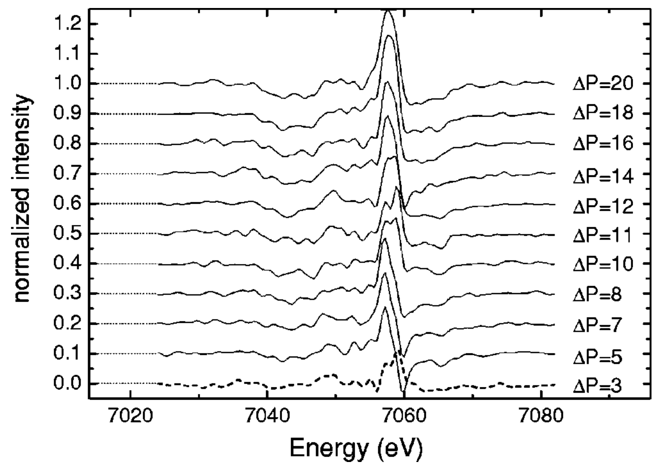


FIG. 2. Difference spectra at the indicated pressures (in GPa). The difference spectra were obtained using the spectrum at $P=0$ GPa as lowest pressure point. The spectra were arbitrarily translated and the zero position is indicated by the dotted line. For the sake of clarity, the spectra have been smoothed by convolution with a Gaussian having a full width at half maximum of twice the experimental resolution.

horizontal source size, and the intrinsic optical aberrations of the analyzer give a total energy resolution of $\approx 300$ meV, a value smaller than the intrinsic linewidth of the Fe $K\beta$ line. The Fe $K\beta$ emission spectrum is 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 2.5-mm-thick diamond of the DAC. The detector is a Peltier-cooled silicon pin diode. In order to follow the intensity of the incident beam, a second detector was installed to monitor the total fluorescence yield coming out of the sample. For normalization purpose, only the Fe and Ni-fluorescence yield were considered by on-line filtering of the signal through a multichannel analyzer.

The sample was a high purity $Fe_{64}Ni_{36}$ 10-$\mu$m-thick foil (Goodfellow Ref. LS194738), and it was loaded in a membrane-type DAC with $N_2$ as pressure medium. The sample thickness was chosen to correspond to one absorption length at 11 KeV. The sample was inserted in a 200-$\mu$m-diameter and 80-$\mu$m-thick hole of a Re gasket. The sample pressure was measured by the conventional ruby fluorescence technique using a He-Ne blue laser.

The Fe $K\beta$ line in $Fe_{64}Ni_{36}$ was measured in the DAC at 300 K as a function of pressure in the 0–20-GPa range. The data presented here were recorded in three series at different times. At equivalent pressure, the spectra in all series were found to superimpose on each other within the error bar, thus proving the reliability and reproducibility of the experimental setup. Pressure was stable within less than $\pm 0.25$ GPa during data acquisition. Figure 1 shows the XES spectra, recorded at pressures of 0 and 20 GPa. The two spectra are normalized to the main peak intensity, and were aligned to the theoretical Fe $K\beta$ fluorescence energy of 7058 eV. The intense narrow peak at 7058 eV is followed on the energy loss side by a broad satellite located at $\approx 7047$ eV. As evident from the inset of Fig. 1, the satellite intensity decreases as the pressure is increased.

The observed spectral changes are interpreted in terms of the main physical process responsible for the appearance of the broad satellite peak. The $K\beta$ line XES spectrum is characterized by a final-state with a core hole ($3p^5$) and an electron excited in the continuum. In transition metals, the possible final-state configurations are strongly affected by the interaction between the five core electrons in the partly filled core level $3p^5$ and the $n$ electrons in the $3d^n$ valence band.[18] Besides the spin-orbit interaction, the $K\beta$ line mainly reflects the multiplet structure due to the exchange interaction between the $3p$ and the $3d$ electrons, which is consequent to the presence of a net magnetic moment in the $3d^n$ ground-state configuration of the $3d$ electrons. This results in a splitting of the final state into two multiplets with opposite spin character, namely the $3p^{5\uparrow}3d^{n\uparrow}$ and the $3p^{5\uparrow}3d^{n\downarrow}$ states. These two main multiplet families can be recognized in the $K\beta$ XES spectrum as the main peak and the low-energy satellite, respectively. Therefore the intensity of this satellite peak can be related directly to the presence, and eventually magnitude, of a magnetic moment in the $3d^n$ ground-state configuration of the $3d$ valence orbitals. In fact, the satellite amplitude, correlated with the strength of the $p$-$d$ exchange interaction, is proportional to the amplitude of the $3d$ local magnetic moment[19] while the energy splitting between the main peak and the satellite and their intensity ratio may be slightly modified by the configuration interaction.[20]

The information on the magnetic moment of the Fe atom can be extracted from the Fe $K\beta$ XES spectra by taking the difference between the spectrum measured at pressure $P$ and the lowest pressure point ($P=0$). This is done after normalizing the area under each spectrum to unity. As an example, the resulting difference spectra of the last of the three series of data are reported in Fig. 2. These spectra are mainly composed of two peaks of opposite sign, which arise from the reduction of the satellite intensity on the low-energy side, and the corresponding broadening and growth of the main peak. As seen in Fig. 2, with increasing pressure $P$, these two structures grow in magnitude. Qualitatively, this directly indicates a reduction of the magnetic moment of the iron atom

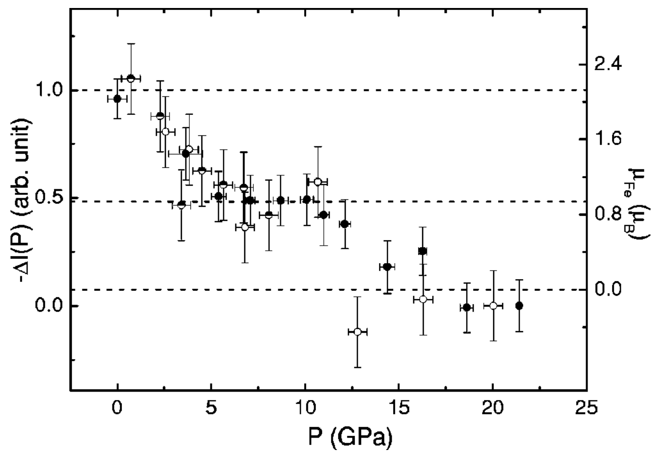


FIG. 3. Pressure dependence of the iron magnetic moment (solid squares) in the Fe-Ni Invar after analysis of the difference spectra. The open, half filled, and solid circles represent the integral of the absolute value of the difference spectra for the consecutive series of measurements. The right scale is deduced from the pure Fe XES data of Fig. 1. The lines are guides to the eye; they represent the average value on the concerned pressure range in order to emphasize the three magnetic states of the Fe atom.

with increasing pressure. A more quantitative analysis to extract the relevant magnetic information is done by determining the integral of the absolute value of these difference spectra, $\Delta I$. The pressure dependence $\Delta I(P)$ is shown in Fig. 3. To facilitate the comparison with the iron magnetic moment, we plot $-\Delta I(P)$. Statistical and pressure error bars are also shown. It can be noticed that the analysis carried out on the different series of data (the absolute values of the integrated difference reported on the Fig. 3 are shown *as calculated* without any scaling) yields a coherent set of points. In the low pressure region below 5 GPa, the curve presents a linear decrease followed by a plateau in the intermediate pressure region which extends up to about 12 GPa. At higher pressures, the intensity drops to zero around 15 GPa and plateaus there up to the highest measured pressure point around 20 GPa. The existence of two plateaus supports the interpretation of two magnetic transitions taking place in the 2–5-GPa and in the 12–15-GPa ranges, respectively. This clearly demonstrates the existence in this Invar alloy of three distinct magnetic states that are successively reached as the pressure is increased.

Further information on the magnetism in Invar can be obtained comparing the Invar XES spectra with those previously measured in pure iron under pressure.[12] As shown in Fig. 1, the pure iron and the Invar spectra at 0 GPa, and those at high pressure are almost identical. This confirms that: (i) the Fe atom in the Invar alloy is in a high-spin state at zero pressure as it is in $\alpha$ iron,[21] and, (ii) at high pressure (20 GPa), the Fe atom in the Invar alloy is in a nonmagnetic state as it is in $\epsilon$ iron, (iii) therefore the plateau in the intermediate pressure region can be associated with the existence of a low spin magnetic state. Moreover, the comparison of Fig. 1 between Invar and pure iron data allows also the following observations: (i) it confirms that the XES emission spectra are very sensitive only to the magnetism of the valence electrons of the core-excited atom, and much less to the local bonding and crystallographic environment,[22] and (ii) from the equivalence between the low- and high-pressure spectra of Invar and pure iron it is possible to scale $\Delta I(P)$ into the iron magnetic moment in absolute units $\mu_{Fe}(P)$, as shown on the right vertical axis of Fig. 3.

In summary, the XES measurements reported in Fig. 3 support a picture of a transition of the iron magnetic state from high spin at low pressure to low spin in the intermediate pressure region. At higher pressure, eventually, the magnetic moment on iron collapses. This interpretation supports the $2\gamma$-state model and is also in qualitative agreement with the XMCD and the Mössbauer measurements carried out on both Fe-Pt Invar and Fe-Ni Invar under pressure although these suffer from eventual contributions due to the change in long-range magnetic order. The HS-LS transition is theoretically recognized as a first-order transition but appears here with a finite width of about 3 GPa. This apparent disagreement stems from the experimental limitations due to pressure drifts and pressure gradients in the DAC as well as from the fact that the measurements were carried out at a finite temperature. The HS-LS transition is further supported by the quantitative value of the iron magnetic moment, estimated to be $2.2\mu_B$ as in pure iron at $P=0$—a value consistent with the saturation magnetization of $1.66\mu_B$ per formula unit measured in $Fe_{65}Ni_{35}$ at low temperature,[23] which leads to a Fe magnetic moment of $2.3\mu_B$ and a Ni magnetic moment of $0.5\mu_B$. The value of the iron magnetic moment in the LS state, as estimated by the intermediate pressure plateau of Fig. 3, is $\approx 0.9\pm 0.3\mu_B$—a value consistent with that of $\approx 0.6\mu_B$, typical for the magnetic moment of iron in the low spin state.

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