Magnetic Instabilities in Fe_3C Cementite Particles Observed with Fe *K*-Edge X-Ray Circular Dichroism under Pressure

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(Received 1 October 2004; published 23 February 2005)

The ferromagnetic interstitial iron compound Fe_3C (cementite) is expected to have Invar properties, whereby a high-moment to low-moment transition should occur when the atomic volume is reduced below a critical value. We, therefore, examine the pressure dependence of the Fe *K*-edge x-ray magnetic circular dichroism in Fe_3C at ambient temperature and pressures up to 20 GPa. We find clear evidence for a high-moment to low-moment transition around 10 GPa.

DOI: 10.1103/PhysRevLett.94.075502 PACS numbers: 62.50.+p, 75.50.Bb, 75.50.Tt, 78.70.Dm

Metalloid atoms such as boron, carbon, or nitrogen take up interstitial lattice positions in 3*d* metals when forming alloys and compounds. The outer *p* states of the metalloid atoms hybridize with the host metal *d* states in such a manner that the effective electron concentration of the metal increases [1]. Fe has a valence electron concentration e/a of eight $(s + d)$ electrons per atom, whereas in Fe_3C (cementite), in which C has two *p* electrons, the electron concentration per metal atom becomes $[8(0.75) + 2(0.25)]/0.75 = 8.67$. This concentration corresponds to a value where large spontaneous magnetostriction associated with magnetovolume instabilities in the alloys of 3*d* systems are found. Such magnetostrictive phenomena are known as the Invar effect, and the archetype material is the face centered cubic $Fe_{0.65}Ni_{0.35}$ Invar alloy with $(e/a) = 8.66$ [2].

A magnetovolume instability is a rapid change of the magnetic moment with respect to a small change in the atomic volume. Under applied pressure at low temperature, a system incorporating such an instability can undergo a transition from a large-volume high-moment state (about $1.7\mu_B$ for $Fe_{0.65}Ni_{0.35}$) to a small-volume low-moment state of nearly vanishing magnetic moment. The physical origin of the high-moment to low-moment transition is related to the features of the density of states characteristic of Invar alloys. In the high-moment state of $Fe_{0.65}Ni_{0.35}$, strongly repulsive antibonding t_{2g} states below the Fermi level are occupied (large atomic separation), whereas in the low-moment state, these states shift to above the Fermi level, and the less repulsive nonbonding e_{2g} states become occupied (smaller atomic separation) [3]. These states are separated by a small energy difference of several meV [4], which is a value within the thermal range of the solid state. Therefore, it is thought that by increasing the temperature, the less repulsive e_{2g} low-moment states are progressively occupied at the expense of the strongly repulsive t_{2g} high-moment states causing a contraction that counteracts the normal lattice expansion. The overall effect is then a nearly vanishing thermal expansion coefficient in a broad temperature range, namely, the Invar effect.

Differing from the structure of $Fe_{0.65}Ni_{0.35}$, Fe_3C is orthorhombic, and the Fe atoms are arranged in a manner such that they have two different environments denoted as FeI and FeII [5]. However, both materials have nearly equivalent electron concentrations and exhibit nearly identical Invar-typical features in the temperature dependence of the thermal expansion [5] and the bulk modulus [6], although Fe_3C consists of only a single metal atom species. Such data are supporting evidence for the presence of the Invar effect in Fe_3C; however, they provide information only on the lattice properties, and do not give evidence for the presence of instabilities in the magnetic degrees of freedom. This evidence is necessary to understand that the spontaneous volume enhancements and the associated lattice anomalies in Fe_3C are related to its magnetism.

The direct method of detecting a presence of a magnetic instability that is coupled to the lattice degrees of freedom is to measure a magnetization related parameter under applied pressure. This may be done using techniques such as Mössbauer spectroscopy [7], ac susceptibility [8], x-ray magnetic circular dichroism (XMCD) [9], or x-ray emission spectroscopy [10], usually with the sample lo-

0031-9007/05/94(7)/075502(4)$23.00

cated in a diamond anvil cell (DAC). For the case of Fe_3C, the Mössbauer technique has the drawback that it requires an ^{57}Fe enriched sample because of the small quantity of sample material that can be brought between the diamond anvils. Unrealistic quantities of ^{57}Fe would be required to prepare a sample by chemical separation from a starting $Fe + Fe_3C$ ingot, or by any dissociation process of $Fe(CO)_5$. The ac-susceptibility technique requires macroscopic size samples in the order of a cubic millimeter, and Fe_3C cannot be sintered in pure form, since it decomposes under pressure at the required high sintering temperatures. The XMCD technique with Fe_3C under pressure in a DAC, on the other hand, does not have any of the drawbacks mentioned above, and can be applied to observe variations in the magnetic degrees of freedom with applied pressure. Nevertheless, due to the strong absorption of the diamonds at low x-ray energies corresponding to the Fe *L* edge, for which quantitative analysis has a chance, one must work at the alternative Fe *K* edge [11,12], for which the results can be interpreted only qualitatively at present due to complexities involved in theoretical modeling [13–17].

We have investigated the pressure dependence of the XMCD at the *K* edge of Fe in Fe_3C at room temperature and pressures up to 20 GPa on increasing and decreasing pressure. The measurements were carried out at the European Synchrotron Radiation Facility (ESRF) on the ID24 beam line installed on an undulator source. Circular polarization was attained using a quarter wave plate. Two sets of measurements at each pressure with both polarization helicities and both magnetic field directions were taken in order to eliminate systematic errors arising from the positioning of the quarter wave plate for the two helicities and changing the direction of the magnetic field. A magnetic field of 0.4 T was applied with an electromagnet. The magnetization in this field reaches about 80% of the saturation value of the sample used in the present experiments [18]. Fe_3C particles of about 50 nm were prepared by the dissociation of $Fe(CO)_5$ in a hot wall reactor in the presence of methane and were separated from the admixture of C and Fe by chemical and physical methods [6]. After separation, their purity, morphology, and structure were checked by electron microscopy and x-ray analysis. No foreign phase or any mixture with Fe was detected.

Figure 1 shows a comparison of the *K*-edge XMCD spectra of Fe and Fe_3C with both data obtained in the diamond anvil cell under a loading pressure of 0.5 GPa. The present data for Fe are similar to the data at ambient pressure previously reported [12]. The position of the first dip on the low energy side of both the Fe and the Fe_3C spectra lie at about 7112 eV (position I). The feature at position II in the Fe_3C spectrum has no counterpart feature in the Fe spectrum. The broad maximum in the Fe spectrum around 7118 eV coincides with the position around the shoulder in the Fe_3C data at the position denoted as III.

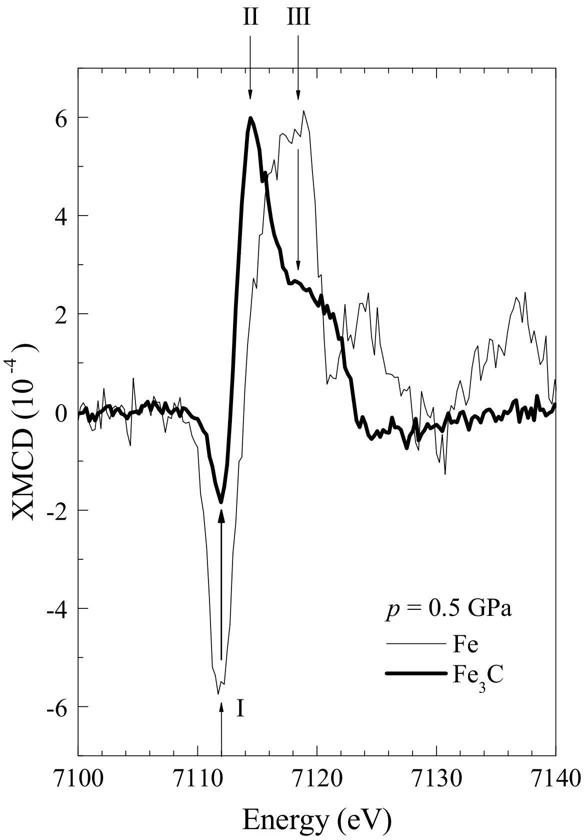

FIG. 1. XMCD of Fe_3C (heavy line) and Fe around the Fe *K* edge.

Since in Fe_3C, Fe occupies two electronically nonequivalent sites, the occurrence of features different from those in the Fe spectrum can be attributed to the different interactions of the excited $4p$ photoelectrons with the spin polarized d bands for the two different Fe sites in Fe_3C.

Figure 2 shows the XMCD spectra from ambient pressure up to about 20 GPa taken on increasing pressure. The data on decreasing pressure are similar and are not shown here. The overall intensity of the spectra diminishes as the pressure increases, and only a remanent feature remains at 19.5 GPa.

The integrated XMCD intensity, obtained after subtracting the background intensity before and after the *K* edge, is plotted in Fig. 3. The integration of the absolute values of the intensity was carried out in the range $7107 \leq E \leq 7125$ eV. A clear transition from a high-moment to a low-moment state is observed without any hysteresis in the increasing and decreasing pressure data. The intensity initially shows no appreciable variation with pressure and then begins to decrease rapidly around 8 GPa. At about 13 GPa, it has dropped down to about 80% of its value at ambient pressure. Assuming a direct proportionality between the integrated XMCD and the average magnetic moment, the moment of $1.8\mu_B$ in the ground state of Fe_3C (high-moment state) [19–22] can be estimated to drop

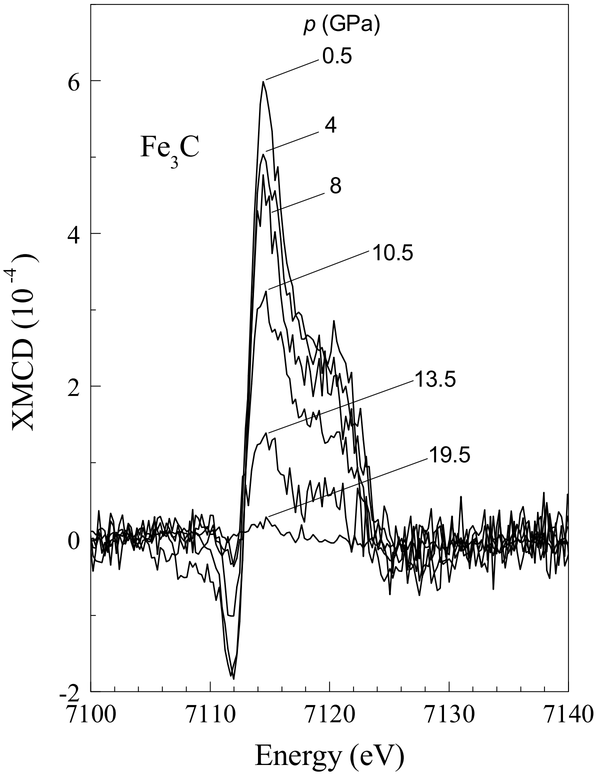

FIG. 2. XMCD of Fe_3C around the Fe K edge at selected pressures.

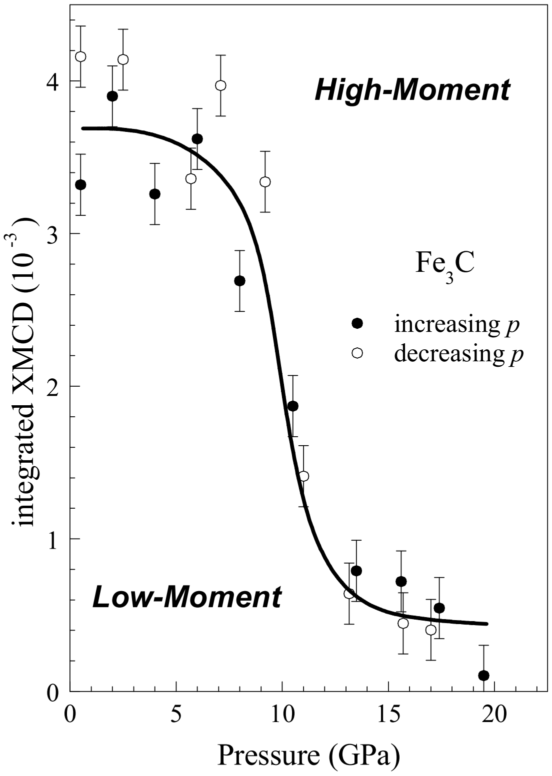

FIG. 3. Integrated XMCD of Fe_3C. The high-moment to low-moment transition takes place at about 10 GPa.

down to about $0.4\mu_B$. At about 12 GPa, the lattice constants acquire the values $a = 0.496$ nm, $b = 0.662$ nm, and $c = 0.440$ nm, and the cell volume is $V = 0.144$ nm^3 [6]. Under ambient conditions, $a = 0.504$ nm, $b = 0.673$ nm, and $c = 0.448$ nm, and the equilibrium cell volume is $V_0 = 0.151$ nm^3. Therefore, a change in atomic volume of about 5% is required to induce the transition. This amount is about the same as for $Fe_{0.65}Ni_{0.35}$ [7]. However, the pressure required to induce the transition is only about 5 GPa for $Fe_{0.65}Ni_{0.35}$ because it is softer with a bulk modulus of 130 GPa [23] as opposed to 174 GPa [6] for cementite.

We note here that the nonhysteretic nature of the high-moment to low-moment transition in Fe_3C displays a contrast situation to that observed in pressure dependent XMCD studies on $Fe_{72}Pt_{28}$ Invar, where a broad hysteresis is found [9]. What exactly the pinning entity is in the electronic structure that leads to a hysteresis for $Fe_{72}Pt_{28}$ and why it is absent for Fe_3C are open issues.

Therefore, pressure dependent XMCD spectroscopy at the Fe K edge proves to be a useful tool to observe volume-driven magnetic instabilities in systems that incorporate Fe. By probing the magnetic degree of freedom with this method, we find direct evidence for the presence of a magnetovolume instability in Fe_3C. These instabilities are expected to be the source of the Invar-typical features observed in the temperature dependence of the thermodynamical parameters for this material. However, how the properties of the instability are related to the local characteristics of the two individual Fe sites (FeI and FeII) remain presently unanswered. To gain more information, it is necessary to provide more elaborate modeling for K-edge XMCD spectroscopy of Fe and Fe_3C. Also, to decide whether the Invar effect in Fe_3C can be explained within the framework of a two state high-moment low-moment model, as for $Fe_{0.64}Ni_{0.36}$ [24], or within a framework that relates the cause to a presence of disordered magnetic moments [25,26], requires further investigation.

This work was supported by the ESRF and the Deutsche Forschungsgemeinschaft (SFB 445).

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