Magnetovolume instabilities in the pressure dependence of the K-edge circular dichroism of Fe₃C Invar particles

E. Duman, M. Acet, and E. F. Wassermann
Experimentalphysik, Universität Duisburg-Essen, D-447044 Duisburg, Germany

J. P. Itié
Physique des Milieux Condensés, CNRS-UMR 7602, Université Paris VI, Bât. 4, place Jussieu, F-75252 Paris CEDEX 05, France

F. Baudelet
Syncrotron Soleil L’Orme des Merisiers, Saint-Aubin-BP 48 F-91192 Gif-sur-Yvette Cedex France

O. Mathon and S. Pascarelli
European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France
(Dated: July 1, 2019)

The p-electrons of carbon in the interstitial compound Fe₃C hybridize with the Fe d-band and enhance the valence electron concentration of the metal increases. Fe has a valence electron concentration of the metal increases. Fe has a valence electron concentration of the metal increases. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases. Fe has a valence electron concentration of the metal increases. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases. 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. Fe has a valence electron concentration of the metal increases.

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 μB for Fe₀.₆₅Ni₀.₃₅) to a small-volume low-moment state of nearly vanishing magnetic moment. These states are separated by a small energy difference of several meV, which is a value within the thermal range of the solid state. Therefore, it is thought that by increasing the temperature, the small-volume low-moment state is progressively occupied at the expense of the large-volume high-moment state 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 Fe₀.₆₅Ni₀.₃₅, Fe₃C is orthorhombic, and the Fe atoms are arranged in a manner such that they have two different environments denoted as FeI and FeII. However, both materials have nearly equivalent electron concentrations and exhibit nearly identical Invar-typical features in the temperature dependence of the thermal expansion and the bulk modulus, although Fe₃C consists of only a single metal atom species. Such data are supporting evidence for the presence of the Invar effect in Fe₃C, 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 Fe₃C 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, ac-susceptibility, x-ray magnetic circular dichroism (XMCD), or x-ray emission spectroscopy, usually with the sample located in a diamond anvil cell (DAC). For the case of Fe₃C, the Mössbauer technique has the drawback that it requires an ⁵⁷Fe enriched sam-
ple 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+$\text{Fe}_3\text{C}$ 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$_3$C cannot be sintered in pure form, since it decomposes under pressure at the required high sintering temperatures. The XMCD technique with Fe$_3$C 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, for which the results can only be interpreted qualitatively at present due to complexities involved in theoretical modeling.

We have investigated the pressure dependence of the XMCD at the K-edge of Fe in Fe$_3$C at room temperature and pressures up to 20 GPa on increasing and decreasing pressure. The measurements were carried out at the 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 ellipticities and both magnetic field directions were taken in order to eliminate systematic errors arising from the flipping of the quarter wave plate and 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 [10]. Fe$_3$C 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 [5]. 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$_3$C 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 data at ambient pressure previously reported [11]. The position of the first dip on the low energy side of both Fe and Fe$_3$C lies at about 7112 eV (position I). The feature at position II in the Fe$_3$C 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$_3$C data at the position denoted as III. Since in Fe$_3$C, 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$_3$C.

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. A clear transition from a high-moment to a low-moment state is observed without any hysteresis in the increasing and decreasing 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$_3$C (high-moment state) can be estimated to drop 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$^3$. Under ambient conditions, $a=0.504$ nm, $b=0.673$ nm, and $c=0.448$ 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$_{0.35}$ [4]. 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 [10] as opposed to 174 GPa [10] for cementite.

By probing the magnetic degree of freedom with Fe K-edge XMCD spectroscopy, we find direct evidence for the presence of a magnetovolume instability in Fe$_3$C. 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. To gain more information on the effect of the magnetism of the individual Fe sites in Fe$_3$C on the magnetovolume instability, it is necessary to provide more elaborate modeling for K-edge XMCD spectroscopy of Fe and Fe$_3$C.

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

* Corresponding Author, Electronic address : macet@ttphysik.uni-duisburg.de, tel.: ++49 (203)379 2023 fax: ++49 (203)379 2098

[1] M. Acet, B. Gehrmann, E. F. Wassermann, H. Bach and W. Pepperhoff, J. Magn. Magn. Mater. 232, 221 (2001).
[2] E. F. Wassermann, in Ferromagnetic Materials, Ed. K. H. J. Buschow and E. P. Wohlfarth (North Holland, Amsterdam, 1990) Vol. 5, S. 238.
[3] V. L. Moruzzi, Phys. Rev. B, 40, 6939, (1990).
[4] W. Pepperhoff and M. Acet, Constitution and Magnetism of Iron and its Alloys, (Springer-Verlag, Berlin-Heidelberg, 2001), p.166.
[5] E. Duman, M. Acet, T. Hülsler, E.F. Wassermann, B. Rellinghaus, J.P. Itié and P. Munsch, J. Appl. Phys., (to be published).
[6] M. M. Abd-Elmeguid and H. Micklitz, Physica B, 161, 17 (1989).
[7] M. Matsushita, S. Endo, K. Miura, and F. Ono, J. Magn. Magn. Mater. 265, 352 (2003).
[8] S. Odin, F. Baudelet, J. P. Iti, A. Polian, S. Pizzini, A. Fontaine, Ch. Giorgetti, E. Dartyge and J. P. Kappler, J. Appl. Phys., 83, 7291 (1998).
[9] J. P. Rueff, A. Shukla, A. Kaprolat, M. Krish, M. Lorenzen, F. Sette and R. Verbeni, Phys. Rev. B, 63, 132409 (2001).
[10] T. Hülsler, unpublished
[11] O. Mathon F. Baudelet, J. P. Iti, S. Pasternak, A. Polian and S. Pascarelli, J. Synchr. Rad., 11, 423, (2004)
[12] L. J. E. Hofer and E. M. Cohn, J. Am. Chem. Soc. 81, 1576 (1959).
[13] I. N. Shabanova and V. A. Trapeznikov, JETP Letters, 18, 339, (1973).
[14] I. N. Shabanova and V. A. Trapeznikov, J. Electron Spec-
[15] J. Häglund, G. Grimvall and T. Jarlborg, Phys. Rev. B, 44, 2914 (1991).

[16] P. Renaud and S. G. Steinemann, Physica B, 161, 75, (1989).