X-ray magnetic circular dichroism in FeZrB amorphous alloys: the influence of the tensile stress

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We present X-ray Magnetic Circular Dichroism experiments (XMCD) on the Fe K edge of FeZrB metallic glasses performed under tensile stress. In these compounds the application of tensile stresses produces a large increase of the Curie Temperature. The XMCD signal presents the features expected for a weak ferromagnet but a gradual enhancement of the ferromagnetism is observed as boron and zirconium concentrations increase. The main effect of the tensile stress is to increase the density of states at the Fermi level as deduced from the increment of the amplitude of the XMCD signal with the stress.

1. Introduction

FeZr amorphous alloys have been extensively studied during the last two decades due to their complex magnetic behaviour, including re-entrant spin glass transition at low temperatures and Invar character below room temperature, (Kaul *et al.*, 1992 & Ryan *et al.*, 1987). It is worth to mention that some magnetic parameters depend strongly on the Zr content. In the case of Curie temperature, T_c, its value increases more than 150 K when Zr content changes from 8 to 20 *at*. %, reaching a value of 270 K for the $Fe_{80}Zr_{20}$ alloy (Fukamichi, 1989). On the other hand, the temperature at which re-entrant spin glass transition takes place shows the opposite tendency, and no evidence of this kind of transition is observed for Zr contents over 11 *at*. %. Also, these compunds exhibit a number of magnetovolume effects such as large high-field susceptibility, large spontaneous and force magnetostrictions, or a large value for the pressure coefficient of the Curie temperature, $\frac{\Delta Tc}{\Delta p}$. All these effects, together with the observed thermal expansion anomaly, are connected with the Invar character showed by these alloys (Fukamichi, 1983). In this way, it is worth to mention that the $\frac{\Delta Tc}{\Delta p}$ coefficient reaches a value of $-60\frac{K}{GPa}$ in the case of $Fe_{90}Zr_{10}$ amorphous alloy, which is higher than in Fe-Ni Invar alloys (Fukamichi, 1989). The effect of introducing B on the FeZr alloys is to increase the Curie temperature and the Fe magnetic moment (Barandiarán, 1994). The FeZrB alloys with low boron content (up to 6 *at*.%) also display a large influence of a simple tensile stress on the Curie temperature, ($\frac{\Delta Tc}{\Delta p} \approx -20\frac{K}{GPa}$ for $Fe_{88}Zr_8B_4$ alloy, Barandiarán *et al.*, 1996). In a Wohlfarth model of itinerant weak ferromagnetism for Invar alloys (Wohlfarth, 1977), it is expected a linear relationship of $\frac{\Delta Tc}{\Delta p}$ with $\frac{1}{T_c}$, crossing through zero near the origin. However, the dependence of the Curie temperature with the stress (or the pressure, *p*) in FeZrB alloys is not well described with this model. The large slope found for $\frac{\Delta Tc}{\Delta p}$ vs $\frac{1}{T_c}$ (Barandiarán *et al.*, 1996) was explained as a transition from a weak ferromagnetism in pure FeZr to a less weak ferromagnetic behavior in FeZrB alloys through a large electronic transfer of the B to the *3d* band of Fe. On the other hand, the effect of the stress was found to reinforce the exchange interaction and it was suggested that an increase in the density of states at the Fermi level was at the origin of the effect. The main aim of the present work is to test the above hypothesis. For this purpose we have used X-ray Magnetic Circular Dichroism (XMCD) at the Fe K-edge. XMCD is the difference between the absorption spectra obtained for right and left circularly polarized X-rays. The exact mechanism giving rise to XMCD at the K edge are not clear near the edge region. Multiple-scattering theory (Brouder *et al.*, 1996) allows to reproduce experimental XMCD in the EXAFS region of the XMCD spectra but fails to reproduce all the details of the edge region, where spin-orbit interactions with the neighbors give strong contributions. The qualitative analysis of the data presented in this paper is based on the experimental observation that a different shape of the K-edge XMCD is obtained for weak ferromagnets (two peaks) and strong ferromagnets (one peak). In a weak ferromagnet as Fe, the majority and the minority bands have unoccupied majority and minority states while in a strong ferromagnet like Co only the minority band has unoccupied states. Qualitatively, the positive peak of the XMCD signal, specific of weak ferromagnetism, can be related, via p-d hybridizations, with the density of unoccupied spin-up *d* states at the Fermi level, while the negative peak observed at higher energies is related to the spin-down density of unoccupied *d* states. Previous experiments have shown the validity of this qualitative approach. Therefore, XMCD at the Fe K-edge is a direct probe of the ferromatic nature of the Fe atoms. The evolution of the ferromagnetic character can be obtained from the ratio of positive and negative intensities of the XMCD signal.

The two fundamental problems that we analyze in this work are in close relation with the above feature:

1. The influence of B over the ferromagnetic character of pure FeZr alloys. For this purpose, we have analysed four compositions with an increasing Boron concentration: $Fe_{90}Zr_8B_2$, $Fe_{88}Zr_8B_4$, $Fe_{87}Zr_6Cu_1B_6$, $Fe_{80}Zr_{10}B_{10}$. In the following, we will call them B2, B4, B6 and B10 respectively.
2. The effect of the applied tensile stress over the ferromagnetic nature of FeZrB alloys. For this purpose, we have recorded the XMCD spectra under different tensile stresses on B2, B4 and B6 compositions.

2. Experimental techniques

FeZrB(Cu) amorphous ribbons have been prepared by melt-spinning method under controlled atmosphere. Typical dimensions were: a cross section of 2*mm* wide x 20μm thick and 10 cm long. The amorphous structure of the samples was checked by x-ray diffraction and Mössbauer spectroscopy. The Fe K-edge XMCD signals of B2, B4, B6 and B10 amorphous samples were obtained in the energy-dispersive beamline (ID24) at the ESRF facility in Grenoble. The spin-dependent absorption coefficient was obtained as the difference of the absorption spectra measured for antiparallel, μ^- , and parallel, μ^+, orientation of the photon helicity and the magnetic field applied perpendicular to the ribbon plane of the sample. The absence of mechanical movement and the parallel acquisition using a CCD camera insures the high stability necessary to measure signals as small as 10^{-3}. The linear polarisation delivered by the plane undulator was transformed into circular polarisation (P_C>95%) using a diamond crystal as quarter wave plate.

In the tensile stress dependent experiments the stress was applied along the ribbon axis of the sample, perpendicular to the X-ray beam and the magnetic field directions, during the absorption experiment. For this purpose, a sample holder was prepared with a spring system that allows to apply a tensile stress as high as 1GP to the ribbons.

The deformation on the sample was measured *in situ* with a strain gage. We could get maximum strains of the order of 1% with perfect elastic recovery. The XMCD experiments were performed close to the Curie temperature of the samples, in order to avoid the magnetoelastic effect. The experiment was performed at room temperature and in a field of 1 T for the samples B4 and B6 (T_c(B4)=283K and T_c(B6)=300K). For the B2 sample, ($T_c \approx$ 230K), the experiment was performed at 200K using a displex cryostat and the field was only 0.5 T.

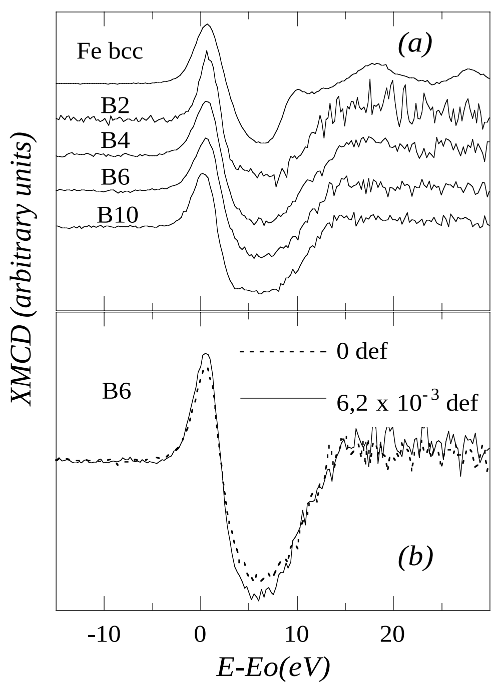

Figure 1
(a) X-ray Magnetic Circular Dichroism spectra normalized to the peak to peak amplitude recorded without stress of B2, B4, B6 and B10. The spectrum of Fe bcc is shown for comparison. (b) X-ray Magnetic Circular Dichroism spectra for B6 sample with and without stress

3. Results and Discussion

The Fe K-edge XMCD spectra have been normalized to the edge jump of the corresponding absorption spectra and the origin of the energy scale has been taken at the inflection point of the absorption edge of the Fe foil (the first peak displayed by the derivative of the absorption jump, at 7108 eV). The background was fitted to a locally weighted least square function in the preedge region and well above the dichroic signal ($> 20eV$) in order to assure the spectra to be flat below and above the edge.

The XMCD spectra of all the samples present a two peak structure characteristic of a weak ferromagnet, quite similar to the bcc Fe, as can be observed in Figure 1(a). The main effect of applying a tensile stress is that the amplitude of the dichroism signal increases, as it is revealed in Figure 1(b). The XMCD spectra have been quantitatively characterized by the following parameters: the maximum amplitudes of the positive and negative peaks ($A1^*, A2^*$), the peak to peak amplitude ($p - p = A1^*$-$A2^*$), the integrated intensities (A1, A2) and the ratio of the integrated intensities ($\frac{A2}{A1}$). The results found are presented in table 1.

Table 1
The maximum amplitude ($A1$, $A2^*$), the integrated intensities (A1, A2) and the ratio $\frac{A2}{A1}$ for the XMCD spectra corresponding to B2, B4, B6 and B10 without and with stress (ϵ) measured in 10^{-3} deformation . The data of the Fe foil are presented for comparison

	ϵ	$A1^*(x10^3)$	$A2^*(x10^3)$	$A1$	$A2$	$\frac{A2}{A1}$
Fe bcc	0	0.97	-0.76	2.17	-3.50	1.6
	0	0.41	-0.39	0.91	-2.9	3.1
B2	3.0	0.40	-0.35	0.96	-2.64	2.8
	5.0	0.36	-0.37	0.79	-3.00	3.8
	0	0.22	-0.27	0.58	-2.04	3.5
	2.5	0.24	-0.31	0.65	-2.2	3.45
B4	3.0	0.24	-0.31	0.64	-2.30	3.6
	3.5	0.26	-0.31	0.71	-2.25	3.2
	4.5	0.27	-0.31	0.74	-2.30	3.1
	0	0.32	-0.40	0.85	-2.96	3.5
	2.1	0.33	-0.43	0.84	-3.02	3.6
	3.0	0.34	-0.45	0.91	-3.14	3.5
B6	4.0	0.35	-0.45	0.91	-3.14	3.5
	5.5	0.35	-0.47	0.89	-3.35	3.7
	6.2	0.36	-0.47	0.97	-3.32	3.5
B10	0	0.44	-0.55	1.10	-4.36	4.0

Although Figure 1 indicates that the change of the ferromagnetic character with B concentration is small, a detailed inspection of the results presented in table 1 suggests that it is not negligible. There exists a slight but gradual increase of the ratio $\frac{A2}{A1}$ with increasing the B content, from 3.1 in B2 to 4.0 in B10. This overall increases indicates that there is a small but sensitive charge transfer between Fe and B, though not high enough to destroy the weak ferromagnetic character. It is outstanding that this behaviour as a function of the Boron concentration has also been found in pure Fe-B amorphous alloys (Fdez-Gubieda *et al.*, 2000). The transition from a weak to a less weak ferromagnetism of the Fe in the FeZr alloys with increasing the B content, was already pointed out in order to explain the different behavior of the Curie Temperature with the tensile stress, which was found to be strongly dependent with the B concentration on the sample. It was proposed that by increasing the B content the Fe becomes less weak ferromagnetic and that is the reason why in the B10 sample the Curie temperature is independent of the stress (Barandiarán *et al.*, 1996).

In table 1, we also present the results related to the evolution of the XMCD spectra with the tensile stress, measured in 10^{-3} deformation. In this case, we did not observe any systematic variation of the ratio $\frac{A2}{A1}$ as a function of the stress (within an error around ± 0.25), but a dependence of the peak to peak signal, *p-p*, with the tensile stress is well observed and is shown in figure 2(a).

To discuss these results, we have to consider whether the applied magnetic field is high enough to overcome the effective anisotropy field, $\mu_0 H^K$, coming from shape and magnetoelastic anisotropy. We have estimated that the anisotropy field, $\mu_0 H^K$, is smaller than 0.45 T for the B4 and the B6 samples at room temperature and for a tensile stress as high as 1 GPa.

For the B2 sample, the anisotropy field should be higher than 0.5 T, at 200K. For this sample the amplitude of the dichoism signal decreases with the tensile stress (see figure 2(*a*)). This behaviour is well explained as a magnetoelastic effect. Increasing the stress, we increase the magnetic anisotropy in the ribbon plane and the magnetic field of 0.5 T applied perpendicular to ribbon plane is unable to balance the increasing anisotropy field.

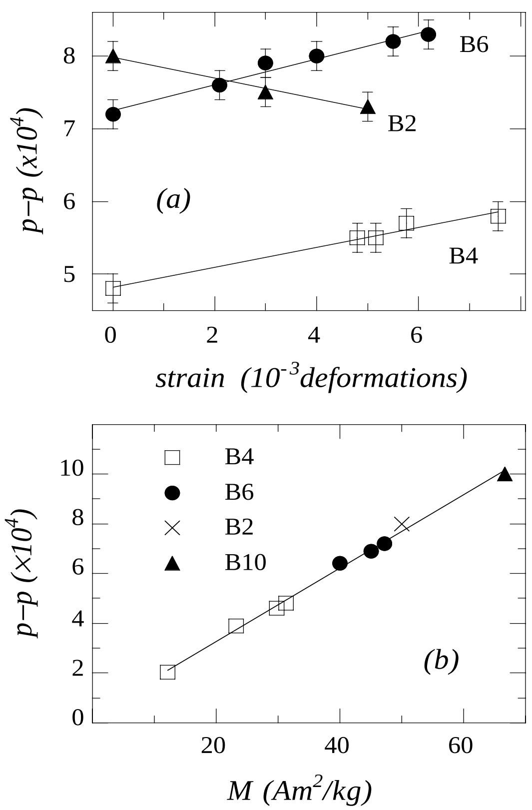

Figure 2
(*a*) Peak to peak amplitude (p-p) as a function of the deformation for the compositions B2, B4 and B6. (*b*) Peak to peak amplitude (p-p) as a function of magnetization measured with the same magnetic field applied perpendicular to the ribbon plane for the four compositions.

On the other hand, for the B4 and B6 samples, the applied magnetic field of 1 T is higher than the effective anisotropy field, so we can be confident that the change found on the dichoism signal with the tensile stress is an intrinsic effect and it is not due to a magnetoelastic effect. For both compositions, the amplitude of the XMCD signal increases linearly as the applied stress does (figure 2(*a*)), the slope for the B4 sample (0.014) being slightly lower than for B6 sample (0.017).

The increment of the dichroism signal with the tensile stress, found for B6 and B4 compositions, should be at the origin of the large influence of the tensile stress on the Curie temperature. In fact, since the K-edge XMCD originates from the *p-d* hybridization, the tensile stress may affect on the hibridized states and eventually should induce changes in the density of states. We suggest that the increase of the peak to peak, *p-p*, XMCD signal with the stress is due to an increase of the density of states at the Fermi level.

In figure 2 (*b*), we also present the *p-p* XMCD signal versus the magnetization of the samples, measured with SQUID magnetometer. Regardless the composition, the *p-p* value presents linear relationship with the magnetization. The slope of the linear function is about $0.15x10^{-4}\ (\frac{Am^2}{kg})^{-1}$ and it crosses through zero near the origin ($0.3x10^{-4}$). This result establishes the relation between the *p-p* amplitude of a K-edge dichroism signal with the magnetization of the sample.

In conclusion, the increment of boron concentration in the FeZrB(Cu) amorphous alloys leads to a transition from a weak to a less weak ferromagnetism of the Fe. The main effect of applying a tensile stress is to increase the amplitude of the XMCD signal, pointing out an increment of the density of states at the Fermi level. This result, previously suggested from magnetic measurements and Mössbauer spectroscopy, is confirmed via XMCD experiments.

3.1. Acknowledgements

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4. References

Barandiarán, J.M., Gorria, P., Gómez Sal, J.C., Fernández Barquín, L. & Kaul, S.N. (1994) *IEEE Trans. Magn.* **30** 4776-4778

Barandiarán, J.M., Gorria, P., Orue, I., Fdez-Gubieda, M. L., Plazaola, F. & Hernando, A. (1996) *Phys. Rev. B* **54** 3026-3029

Fdez-Gubieda, M. L., García-Arribas, A., Barandiarán, J.M., López Antón, R., Orue, I., Gorria, P., Pizzini, S. & Fontaine, A. (2000) *Phys. Rev. B* **62** 5746-5750

Brouder, Ch., Alouani, M. & Bennman, K. H., (1996) *Phys. Rev. B* **54** 7334-7339

Fukamichi, K., (1983) *Amorphous metallic alloys*, edited by F. E. Luborsky **27** 317-340. Butterworth & Co, UK.

Fukamichi, K., Goto, T., Komatsu, H., & Wakabayashi (1989). *Physics on Magnetic Materials*, edited by Gorzkowski, W., Lachowicz, H.K., Szymczak, H. p.354-381. World Scientific, Singapore.

Kaul, S. N., Siruguri, V. & Chandra, G. (1992) *Phys. Rev. B* **45** 12343-12356

Pizzini, S., Fontaine, A., Dartyge, E., Giorgetti, C., Baudelet, F., Kappler, J.P., Boher, P. & Giron, F. (1994) *Phys. Rev. B* **50** 3779-3785

Pizzini, S., Bonfim, M., Baudelet, F., Tolentino, H., San Miguel, A., Mackay, K., Malgrange, Hagelstein, M. & Fontaine, A. (1998) *J. Synchrotron Radiat.* **5** 1298-1305

Ryan, D.H., Coey, J.M.D., Batalla, E., Altounian, Z. & Strom-Olsen, J.O. (1987) *Phys. Rev. B* **35** 8630-8638

Wohlfarth, E.P., (1977) *Physica* **91B** 305-310

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