

HYDROGEN IN AMORPHOUS $\text{Fe}_{3-x}\text{Cu}_1\text{B}_6\text{Zr}_x$ ALLOYS¹

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The $\text{Fe}_{3-x}\text{Cu}_1\text{B}_6\text{Zr}_x$ alloys (with $x=7,10,13,16,19$) exhibit changes of magnetic and mechanical properties by hydrogenation. The hydrogenation leads to an increase of the hyperfine magnetic field and linear increase of isomer shift. The hydrogen absorption is lowered by the presence of a metalloïd atom in the system relatively to pure Fe-Zr amorphous system.

The pure two components Fe-ET (ET - early transition metal: Ti, Zr, Hf, Nb, Ta ...) systems exhibit drastic changes of the magnetic and mechanical properties by hydrogenation [1,2]. They store hydrogen relatively well, because of large atomic radius of the ET metal and its affinity for hydrogen. The highest concentration of hydrogen observed in hydrogenated Fe-ET amorphous system is $2x$ (where x is the atomic concentration of the ET metal) [1,2]. On the other hand the Fe - M amorphous system (where M stands for metalloïd: B, P, Sb ...) is known as the poor storage medium of hydrogen. The metalloïd atoms occupy the "interstitial like sites" near the Fe atoms and as a result, from the geometrical point of view, there is less or none free room for the hydrogen atom. The Fe-ET system exhibits the fcc like atomic arrangement [3]. Even in iron rich Fe-ET system the magnetic moment of Fe atoms remains small and the Curie temperature lies below room temperature. The reason for this behaviour is the high sensitivity of exchange integral on the interatomic distance of Fe-Fe atomic pairs. The drastic changes of magnetic properties are therefore observed under hydrogenation where the interatomic separation is influenced by hydrogen. The magnetic properties of bcc-like Fe-M system on the other hand are relatively stable regarding the atomic separation of Fe-Fe pairs. The very interesting system seems to be the mixture between pure Fe-ET and Fe-M systems. The important uptake of hydrogen is expected to be lowered by presence of metalloïd. The volume effect, well known from Fe-ET systems, is also expected to play less significant role. The aim of this work is to report about the influence of hydrogen on the hyperfine parameters of $\text{Fe}_{3-x}\text{Cu}_1\text{B}_6\text{Zr}_x$ amorphous system and to discuss the ability of this system to store hydrogen.

Amorphous $\text{Fe}_{3-x}\text{Cu}_1\text{B}_6\text{Zr}_x$ alloys ($x=7,10,13,16,19$) were prepared by the melt spinning technique. Sample qualities were checked by X-ray diffraction and transmission

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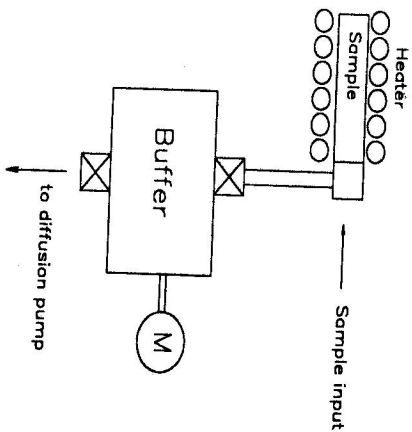


Fig.1: The block diagram of the equipment for measuring the hydrogen content of a charged sample. (Buffer - outgas container of the known volume, M- McLeod manometer).

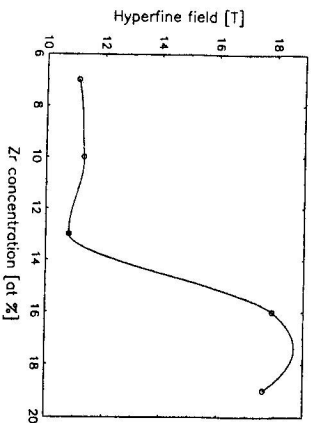


Fig.2 : Dependence of hyperfine magnetic field on Zr concentration of $\text{Fe}_{93-x}\text{Cu}_1\text{B}_6\text{Zr}_x$ amorphous alloys at room temperature.

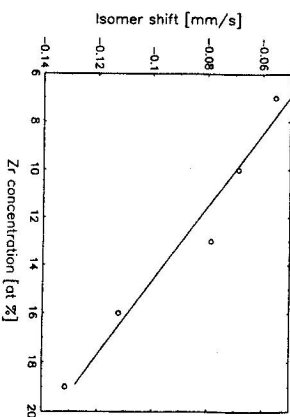


Fig.3: Concentration dependence of mean isomer shift of $\text{Fe}_{93-x}\text{Cu}_1\text{B}_6\text{Zr}_x$ at room temperature.

Mössbauer spectroscopy. The samples with $x=7$ and $x=19$ exhibit a small amount of crystalline α -Fe phase. The ribbons measured 1.6 mm in width and 20 mm in thickness. Mössbauer spectra were obtained using a conventional spectrometer and a $^{57}\text{Co}(\text{Rh})$ source. Mössbauer nitrogen bath cryostat was used for low temperature measurements. All the measurements of hydrogenated samples were done at 125K to limit the escape of hydrogen from the sample. The samples were electrolytically hydrogenated in H_2SO_4 solution containing a few ppm. of CS_2 .

The content of hydrogen in a charged sample was defined from a specific equipment (Fig.1), based on measurement of the pressure of the gas released into the known volume, from the sample heated to about 750K. The hydrogen content was estimated as

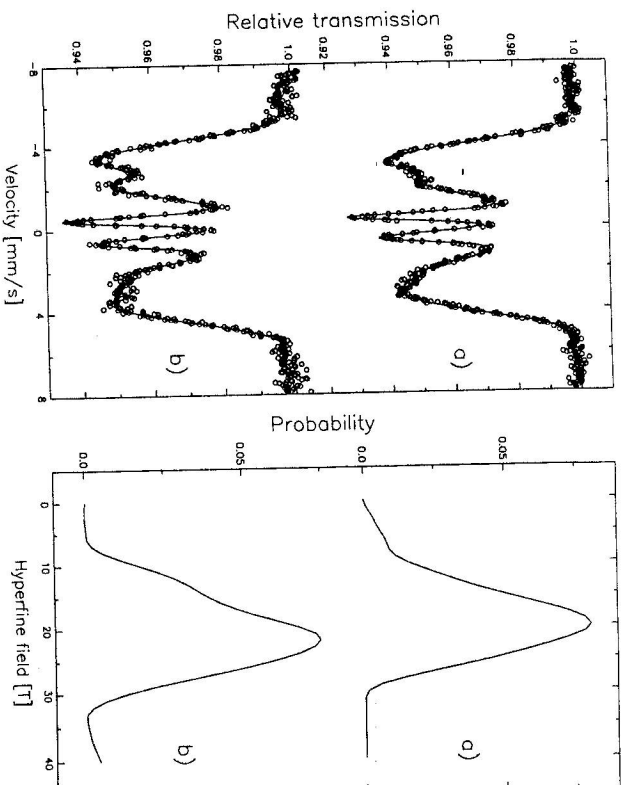


Fig.4 : The Mössbauer spectra and hyperfine field distributions of a) as prepared b) hydrogenated $\text{Fe}_{90}\text{Cu}_1\text{B}_6\text{Zr}_{13}$ taken at 150K

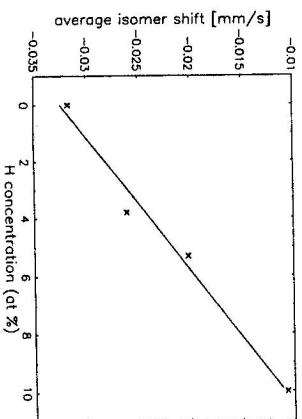


Fig.5: Hydrogen concentration dependence of mean isomer shift of $\text{Fe}_{77}\text{Cu}_1\text{B}_6\text{Zr}_{16}\text{H}_y$ at 150 K.

the difference between released amount of gas from the charged sample and the reference one (as prepared sample). This procedure yields comparable results with results obtained by gas chromatography. The hyperfine distributions were obtained using a model independent LeCaër-Dubois method with linear relation between isomer shift and hyperfine field.

Fig.2. shows the dependence of the mean hyperfine magnetic field on the Zr con-

centration at room temperature. The abrupt increase of the hyperfine magnetic field between 13 and 16 atomic field lies between 16 and 19 at. hyperfine field decreases with increasing Zr concentration, as could be expected from simple dilution of magnetic Fe atoms by Zr atoms. The behaviour of the hyperfine field up to 16 at. is due to changes in the Curie temperature. The Curie temperature reaches its maximum between 16 and 19 at. is similar to the binary iron rich Fe-Zr amorphous system where, due to a short interatomic distances of Fe-Fe atomic pairs, the competition between ferromagnetic and antiferromagnetic exchange takes place at low temperatures.

The concentration dependence of the isomer shift measured at room temperature is shown in Fig. 3. The mean isomer shift decreases to more negative value with increasing Zr concentration. This is probably due to s-electron $Zr \rightarrow Fe$ charge transfer [4]. The substitution of one Zr atom for Fe atom leads to decrease of isomer shift down to 0, 0065 mm/s.

The typical Mössbauer spectra of amorphous $Fe_{3-x}Cu_1B_6Zr_x$ as prepared and hydrogenated sample for $x=13$ are shown at Fig. 4. The better resolved spectrum is obtained after hydrogenation due to the increase of the hyperfine magnetic field. The increase of hyperfine magnetic field is also visible from the hyperfine field distribution.

Fig. 5 shows the dependence of mean isomer shift vs. hydrogen concentration in $Fe_{77}Cu_1B_6Zr_{16}$ amorphous alloys. The hydrogenation leads to an increase of the isomer shift. The concentration dependence of isomer shift is linear similarly to the case of Fe-Zr :

$$IS = 0.0022y - 0.0324$$

where y is the concentration of hydrogen in at.isomer shift in mm/s at 150 K.

The hydrogen prefers the sites in the vicinity of Zr atoms and suppresses the charge transfer of s electrons from Zr to Fe. This explains the isomer shift increase. Moreover the larger interatomic distances in hydrogenated areas are responsible for the effect of the same sign. The maximum hydrogen uptake was, as expected, lowered by the presence of metalloloid atom. The maximum of hydrogen concentration y corresponds to a value in the range $(x - m) < y < 2(x - m)$ where x is the concentration of Zr, m is the B concentration. This is in any case a lower value than $2x$ observed in iron rich Fe-Zr systems.

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