

## MÖSSBAUER SPECTROSCOPIC CHARACTERIZATION OF SAMPLES FOR COLD FUSION EXPERIMENT

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### Introduction

In this contribution we show a case in which we have applied the Mössbauer spectroscopy for characterization of samples which were expected to show anomalous nuclear effects upon to their deuterization.

The Mössbauer spectroscopy can provide information about the surrounding of a Mössbauer atom in deuterized samples by measuring the electrical monopole and quadrupole as well as magnetic dipole interactions. The introduction of deuterium (or hydrogen) into the vicinity of a resonance atom will influence the physical parameters which govern the Mössbauer spectrum, thus changes will be expected in the hyperfine interactions e.g. in isomer shift, quadrupole splitting, magnetic splitting (Fig. 1) and in other parameters. Consequently, the localization of deuterium can be sensitively studied.

The main question is : how can these investigations help us to understand more about the conditions of cold nuclear fusion?

In our previous works [1,2] Mössbauer spectroscopy (as well as neutron and gamma-spectroscopy) was used to study the possibility of cold

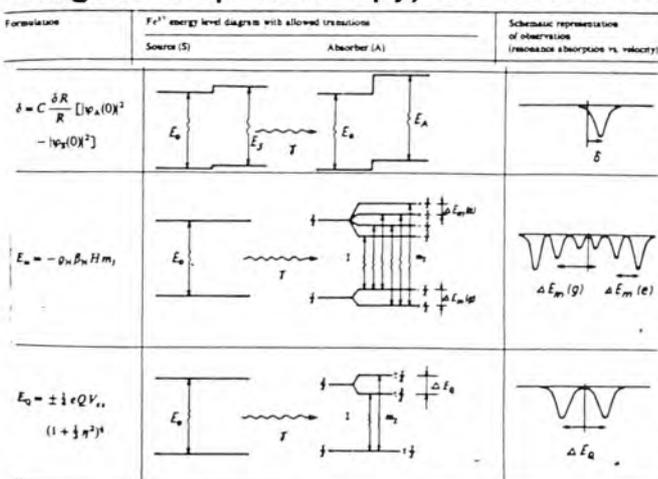


Fig. 1. Mössbauer isomer shift  $\delta$ , magnetic splitting  $E_m$ , quadrupole splitting  $E_Q$

nuclear fusion in Fe-Zr amorphous alloys deuterized electrolytically both in air and in nitrogen atmosphere.

Mössbauer spectroscopy can be especially advantageously applied to the study of the effect of electrolytical hydrogenation of Fe-Zr amorphous alloys because the considerable changes appearing in the spectra (due to the change in the deuterium concentration or due to small heat effects) allow us to detect any structural change caused by deuterization [3].

We have performed experiments on high temperature superconductors because Celani et al. [4] have shown anomalous nuclear effects due to deuterization in such a materials. Our earlier studies on high  $T_C$  superconductors [e.g. 5-7] showed that the different crystallographic sites can be sensitively investigated by Mössbauer spectroscopy.

## Experimental

$\text{EuBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$  high temperature superconductor samples were sintered from  $\text{Eu}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{BaCO}_3$  and  $^{57}\text{Fe}_2\text{O}_3$  at  $875^\circ\text{C}$  for 120 min and heated at  $430^\circ\text{C}$  for 960 min in oxygen atmosphere.

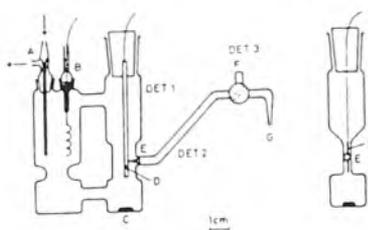


Fig. 2. Cell for deuterization

Hydrogenation and deuterization of samples were performed either by applying gas pressure (30 bar) in a bomb for 12 hours or by cathodic polarization of samples. The electrolysis was carried out in a cell (Fig. 2) using 0.1n NaOH or NaOD electrolyte for 60 min at 30 mA current and  $-1.7$  mV potential relative to calomel electrode in nitrogen atmosphere. Effusing of hydrogen of gas loaded samples was performed in nitrogen atmosphere at  $200^\circ\text{C}$ .

$^{151}\text{Eu}$  and  $^{57}\text{Fe}$  Mössbauer spectra of nonhydrogenated and hydrogenated or deuterized samples were recorded in transmission geometry at 295 K and at 85 K by a conventional constant acceleration Mössbauer spectrometer. Isomer shifts are given relative to alpha-iron and  $\text{EuF}_3$ . The spectra were evaluated by conventional least-square fitting of lines.

Positron annihilation lifetime spectra of nonhydrogenated and gas loaded samples were measured at 295 K and at 55 K.

## Results and discussion

Fig. 3. shows the structure of most intensively investigated high temperature superconductor of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ . It has a threefold stacked orthorhombic perovskite structure having two different Cu sites: the Cu(1) (chain site) and the Cu(2) (plain site) between the Y and Ba-O layers.

Typical  $^{151}\text{Eu}$  and  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{EuBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$  sample are illustrated in Fig. 4. The broad singlet of Eu spectrum corresponds to a  $\text{Eu}^{3+}$  being in the rare earth site. The Fe spectrum can be decomposed into 3 doublets D1, D2 and D3. The Mössbauer parameters are shown in Table 1.

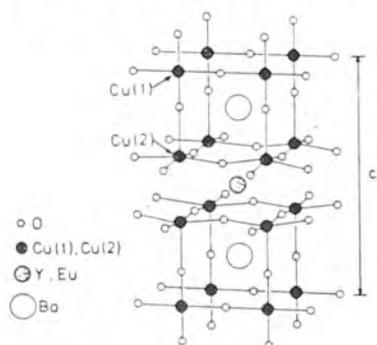


Fig. 3. Structure of 1-2-3 high  $T_c$  superconductor

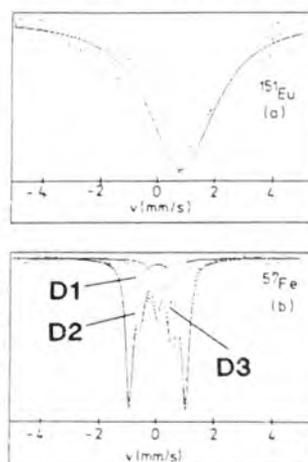


Fig. 4.  $^{151}\text{Eu}$  (a) and  $^{57}\text{Fe}$  (b) Mössbauer spectra of  $\text{EuBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$

Table 1.

MÖSSBAUER PARAMETERS OF  $\text{EuBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$  SUPERCONDUCTOR

$^{57}\text{Fe}$ spectrum (T=85K)	IS (mm/s)	QS(mm/s)
D1	0.07+0.01	1.99+0.02
D2	-0.02+0.01	1.35+0.02
D3	0.39+0.01	0.64+0.02

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$^{151}\text{Eu}$ spectrum (T=295K)	IS(mm/s)	W (mm/s)
	0.95+0.02	2.63+0.03

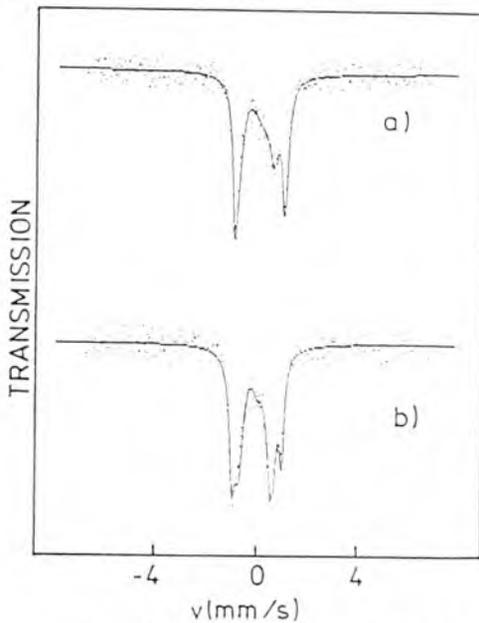


Fig. 5.  $^{57}\text{Fe}$  Mössbauer spectra of non-hydrogenated (a) and gas-hydrogenated (b) sample

D1 doublet is associated with Fe in four coordinated Cu(1) site while D2 doublet is attributed to Fe in five coordinated Cu(1) site [6]. D3 doublet corresponds to Fe in Cu(2) site [6].

Fig. 5 and 6 shows the  $^{57}\text{Fe}$  spectra of gas-hydrogenated and nonhydrogenated samples having lower and higher oxygen content. It can well be seen in Fig. 5-7 that the relative intensity of D2 doublet (representing iron atoms at Cu(1) site) in  $^{57}\text{Fe}$  spectra increases due to gas deuterization.

The spectra of electrolytically hydrogenated (Fig. 8) and deuterized (Fig. 9) reflect how the relative intensity of the D3 doublet (representing iron atoms at Cu(2) site) in the  $^{57}\text{Fe}$  spectra increases due to cathodic polarization.

No considerable changes appear in the  $^{151}\text{Eu}$  spectra upon gas hydrogenation or deuterization as illustrated in Fig. 10 where Eu spectra of non-hydrogenated and gas deuterized sample are shown.

However, the isomer shift and the linewidth decrease in the  $^{151}\text{Eu}$  spectra due to cathodic polarization, as shown in Fig. 11.

A lifetime positron annihilation spectrum of non-hydrogenated sample is shown in Fig. 12. No changes were observed in the spectrum after gas-hydrogenation or gas-deuterization.

The changes of the relative intensity of D2 can be associated with hydrogen or deuterium localized in the vicinity of Cu(1) site. The changes of the relative intensity of D3 doublet can be associated with hydrogen or deuterium in the vicinity of Cu(2) site. In the case of the cathodic polarization this change can partly be attributed to the appearing of some new Fe(3+) compound due to the decomposition of the sample.

The change of the hyperfine parameters (isomer shift, quadrupole splitting) of Eu spectra can be connected with the effect of hydrogen or deuterium in the neighbourhood of Eu.

The positron annihilation spectroscopy results are consistent with the site preference of hydrogen and deuterium around the Cu(1) site in the gas loaded samples because this technique is more sensitive to the neighbourhood of Cu(2) site.

It could have some consequences that negative charged ion sites are supposed to be occupied by hydrogen or deuterium.

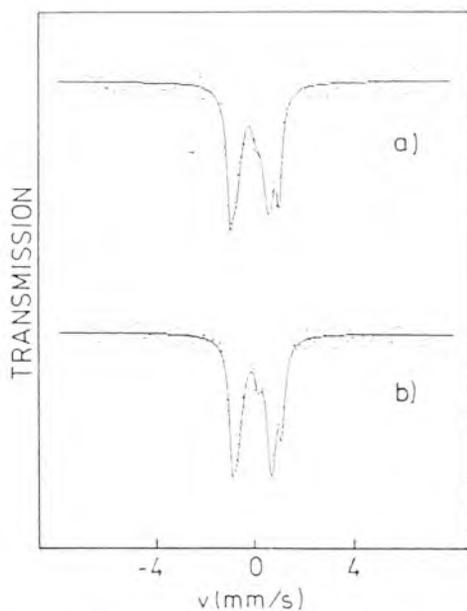


Fig. 6.  $^{57}\text{Fe}$  Mössbauer spectra of non-hydrogenated (a) and gas-hydrogenated (b) sample

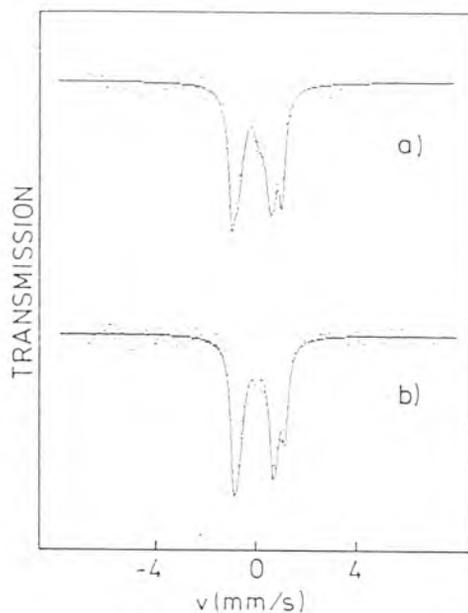


Fig. 7.  $^{57}\text{Fe}$  Mössbauer spectra of non-hydrogenated (a) and gas-deuterized (b) sample

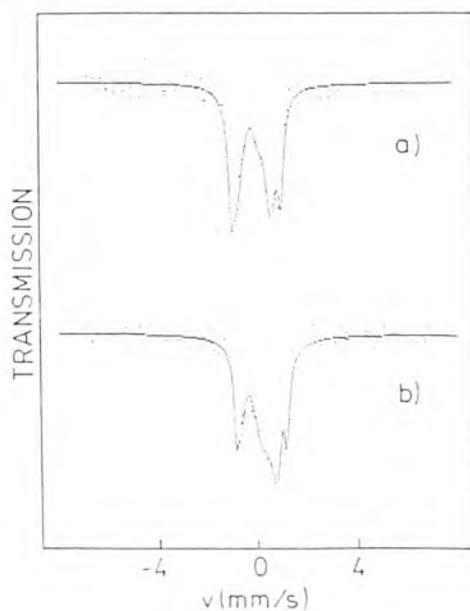


Fig. 8.  $^{57}\text{Fe}$  Mössbauer spectra of non-hydrogenated (a) and electrolytically hydrogenated (b) sample

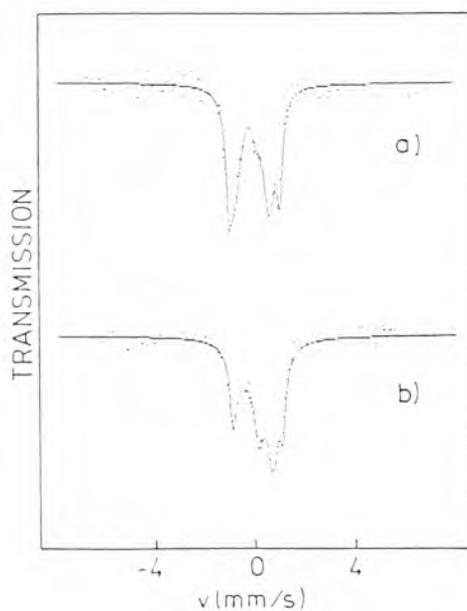


Fig. 9.  $^{57}\text{Fe}$  Mössbauer spectra of non-hydrogenated (a) and electrolytically deuterized (b) sample

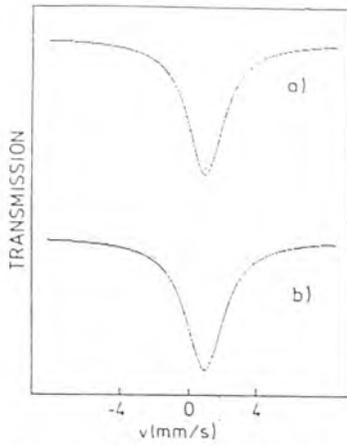


Fig. 10.  $^{151}\text{Eu}$  Mössbauer spectra of non-hydrogenated (a) and gas-deuterized (b) sample

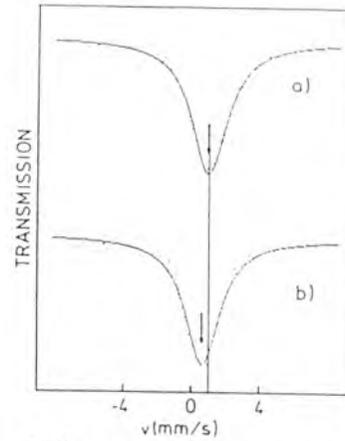


Fig. 11.  $^{151}\text{Eu}$  Mössbauer spectra of non-hydrogenated (a) and electrolytically deuterized (b) sample

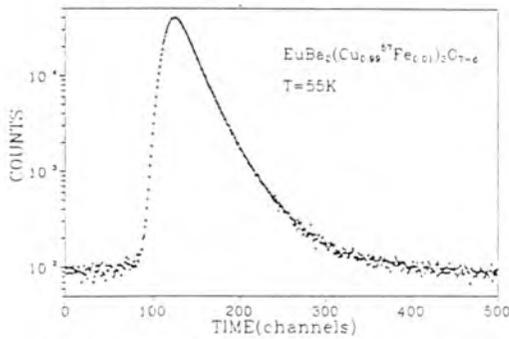


Fig. 12. Positron annihilation spectrum of a non-hydrogenated sample

The following conclusions can be drawn from the results:

(1) The hydrogen or deuterium is localized mainly around the Cu(1) site in these high temperature superconductors hydrogenated or deuterized by gas loading. (2) No differences can be detected between the localization of hydrogen and deuterium by gas loading. (3) The electrolytic hydrogenation and deuterization of these superconductors are accompanied by partial decomposition of the material. Part of the hydrogen and deuterium tends to be localized around the Cu(2) sites.

## References

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