Change of the HTSC harmonic susceptibility properties with electrolytic hydrogen loading using different aqueous solution as LiOH and NaOH

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Abstract

The higher harmonics magnetic susceptibilities ($\chi = \chi'_r + i\chi'_i$) of HTSC hydrogen loaded as function of the temperature at 6G of ac magnetic field amplitude at 107Hz of frequency have been measured. The samples have been loaded by electrolysis in an aqueous solution using $\mu$s current pulses at room temperature. The HTSC electrodes have been polarized by short pulse width (1$\mu$s) and high peak current (≥4A) with a low duty-cycle ($10^{-3}$) and a variable repetition rate (1–5KHz). The hydrogen influence on HTSC ($T_c$, ac losses) has been measured and the increasing of the superconducting properties, particularly $T_c$ and $J_c$, have been found. These effects appear strongly dependent to the loading process and to the stoichiometric ratio H/YBCO. It has been demonstrated that the electrolyte (Li, Na) do not affect the YBCO superconducting properties.

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1 - INTRODUCTION

Since the discovery of the superconducting oxides, the correlation between the hydrogen and the superconducting properties has been extensively studied, particularly in hydrogen loaded YBCO samples (H–YBCO) using physical adsorption (gas phase) [1–4] and electrochemical adsorption [5–7]. It has been showed that hydrogen can decrease [8–9] or increase [5–7] the critical temperature TC. It is important to observe that hydrogen electrochemical loading is completely different from the physical loading. Infact, for the first process ionic hydrogen is produced, while for the second one molecular hydrogen is available on surface. Moreover, the electrochemical hydrogen equivalent pressure on the surface is very high respect to the physical hydrogen pressure at STP (Standard Temperature and Pressure).

Using chemical loading procedure, the hydrogen pressure linearly increases with current addition, for this reason, using very high electrolytic current, the hydrogen loading is more efficient. This permits to obtain an high equivalent hydrogen H+ pressure on the sample surface. Therefore, in order to avoid the hydrogen bubbles on YBCO cathode surface, which forbids hydrogen adsorption, pulsed instead of dc electrolysis has been used, whereas the mean electrolytic current is very low in comparison to dc electrolysis. This innovative method has been carry–out by our staff [5–7,10,11].

In the present letter it has been showed the multi–harmonic magnetic measurement in function of the temperature with fixed frequency and amplitude of ac magnetic field (Hac = Ho sin ωt). This gives the possibility to study the pinning effect [12] and the different flux dynamics [13,14] that occurs, in the superconductive state, before and after the hydrogen loading in YBCO sample. In section II it has been described, the experimental loading set–up and the ac susceptibility measurement set–up. In section III the experimental results have been plotted and discussed, section IV has been devoted to conclusion.

2 – EXPERIMENTAL SET–UP AND MEASUREMENTS PROCEDURE

In this work YBCO melted samples have been used. The typical geometry is a slab of volume 24 mm3, surface 0.5 cm2 and all samples have been cut from the same YBCO piece.

Electrochemical loading has been performed in aqueous solution of LiOH–H2O (0.3N) and NaOH–H2O (0.3N) using a nickel cylinder as anode and YBCO as cathode.

The μsec pulsed electrolysis apparatus [Fig.1] consists of an home–made capacitive–discharge pulse generator [11] which supplied high peak power (up to 1.2KW) with negative polarity, short duration of the pulse flat region (up to 5000 nsec), high repetition rate (up to 20KHz) and high peak current density [Fig.2] on the YBCO surface (up to 20 A/cm²). In order to keep the self–polarization of electrolytic cell during the off–period between two consecutive pulses, a fast–power diode (RPG5060) before the YBCO sample has been placed.

Hydrogen adsorption processes, have been performed as follows: The sample 1 (0.16gr weight) in LiOH has been electrolyzed with a peak current density of 8.4A/cm², anode–cathode peak voltage of 50V, repetition rate of 1KHz for an electrolysis total time of 100s. Under these conditions has been obtained the stoichiometric ratio H/YBCO = 0.03.

The sample 2 (0.2gr weight) in NaOH has been electrolyzed with a peak current density of 10A/cm², anode–cathode peak voltage of 50V, repetition rate of 1KHz for an electrolysis
total time of 100s. Also in this case has been obtained the stoichiometric ratio \( \text{H/YBCO} = 0.03 \).

The sample 2 has been further electrolyzed increasing the repetition rate at 5KHz and the electrolysis total time at 200s, obtaining the stoichiometric ratio \( \text{H/YBCO} = 0.3 \).

![Electrolytic experimental set-up.]

![Typical current pulse shape during electrolysis.]

The ac susceptibility analysis has been performed measuring simultaneously the first five harmonic components using a double pick-up coil susceptometer. The pick-up coil signal has been measured by a Lock-In Amplifier (EG&G 5320). It has been used a temperature controller (Lake Shore DRC 91C) for the measurement of two platinum thermometers, the first one on the sample and the second one on the sapphire holder. The experimental data are acquired by computer.

The harmonic coefficients of ac magnetic susceptibility have been measured versus temperature at constant frequency (107Hz) and amplitude of ac magnetic field (6G). All measurements have been performed from 77K to 300K, cooling the samples at zero field (ZFC).

In order to analyze the change of superconductive properties of H–YBCO, the following parameters have been introduced (harmonic index \( i=1,3 \)):

a) Critical temperature \( T_c \) as the \( \chi_i'' \) temperature onset.
b) \( T_{p,i} \) as the temperature where \( \chi_i'' \) is maximum.
c) \( \chi_i''(T_{p,i}) \) as the maximum value of \( \chi_i'' \) versus temperature.
d) \( \delta T_{c,i} = T_{c,i}^{\text{hydro}} - T_{c,i}^{\text{virgin}} \) as the change of \( T_c \) due to hydrogen stoichiometry.
e) \( \delta T_{p,i} = T_{p,i}^{\text{hydro}} - T_{p,i}^{\text{virgin}} \) as the change of \( T_p \) due to hydrogen stoichiometry.
f) \( \Gamma_i = T_{c,i} - T_{p,i} \) as the superconductive sample quality.
Since $\chi_1$ represents the area of hysteresis magnetic cycle, an increasing of $\Gamma$ represents a worsening of superconducting properties because, at the same reduced temperature, $J_c$ is decreased. A rigid translation to higher temperature of $\chi_1,3''(T)$, indicated by a constant $\Gamma$ parameter, means that the same magnetic hysteretic losses occur at higher temperature without a sample worsening.

3 – RESULTS AND DISCUSSION

In order to study the effect of hydrogen on HTSC superconducting properties using electrochemical procedure, it is important to know if the alkaline metals (Li, Na) can affect the HTSC properties or not. For this reason have been used two different electrolytic solutions as reported previously.

Analyzing the imaginary components of the harmonic ac magnetic susceptibilities for the virgin samples, has been deduced:

Sample 1 [Fig.3,4] has:

T$_c$\textsuperscript{virgin} = 91.4 K and $\Gamma_1$\textsuperscript{virgin} = $\Gamma_3$\textsuperscript{virgin} = 1 K;

Sample 2 [Fig.5,6] has:

T$_c$\textsuperscript{virgin} = 90.9 K and $\Gamma_1$\textsuperscript{virgin} = $\Gamma_3$\textsuperscript{virgin} = 1 K;

From the comparison between the imaginary part of the third harmonic component for both samples [Fig.4,6], it is evident a different temperature behavior. The sample 2 shows a temperature oscillation that is not present in the sample 1. Because the oscillation is related to the ratio between full penetration and applied alternating magnetic field, i.e. to the critical current $J_C$, the analyzed samples show a little difference.

In the further analysis, the comparison between virgin and hydrogenated sample, will be done on the sample itself, so that, the superconducting properties variation are without ambiguity due to the effects of hydrogen and electrolyte.

After the initial test on the solution conductivity (0.001–1 M), we started the hydrogenation of the YBCO samples at concentration 0.3N.

In figure 3 has been shown the imaginary part of the first harmonic ($\chi''_1$) as a function of temperature for the sample 1, before and after (H$_{0.03}$Y$_1$Ba$_2$Cu$_3$O$_{7-x}$) electrolysis with LiOH–H$_2$O. The figure shows (1):

\begin{align*}
\text{a) } & \delta T_{c,1} = 91.6 - 91.4 = 0.2 \text{ K} \\
\text{b) } & \delta T_{p,1} = 90.7 - 90.4 = 0.3 \text{ K} \\
\text{c) } & \Gamma_1\textsuperscript{virgin} = 91.4 - 90.4 = 1 \text{ K} \\
\text{d) } & \Gamma_1\textsuperscript{hydro} = 91.6 - 90.7 = 0.9 \text{ K}
\end{align*}

Because $\delta T_{c,1} > 0$ and $\delta T_{p,1} > 0$ with $\Gamma_1\textsuperscript{virgin} = \Gamma_1\textsuperscript{hydro}$ then the hydrogen inside YBCO increases the critical temperature $T_c$ without sample worsening.

Analyzing the third harmonic of sample 1, shown in figure 4, it is possible to deduce the
same parameter values calculated for the first harmonic, in particular $\delta T_{c,3} > 0$

![Graph showing $\chi''_1$ as a function of temperature for 107Hz and $H_0=6$ Gauss, for sample 1.](image)

Fig. 3 – $\chi''_1$ as a function of temperature for 107Hz and $H_0=6$ Gauss, for sample 1.

and $\delta T_{p,3} > 0$ with $\Gamma_3^{\text{virgin}} = \Gamma_3^{\text{hydro}}$. A rigid translation of the $\chi''_1$ and $\chi''_3$ to higher temperature, with a constant amplitude ($\chi''_3(T_{p,3}), \chi''_1(T_{p,1})$) has been shown. This means that an increasing of the non-linear hysteretic properties (due to the critical state) with an increasing of $J_c$ occurs. The increasing of superconducting properties is as little as the changing of stoichiometry ($H/YBCO = 0.03$).

In figure 5 has been shown the imaginary part of the first harmonic ($\chi''_1$) as a function of temperature for the sample 2, before and after the first ($H_{0.03}Y_1Ba_2Cu_3O_{7-x}$) and the second ($H_{0.3}Y_1Ba_2Cu_3O_{7-x}$) electrolysis in NaOH–H$_2$O. The first electrolysis has been performed to analyze the effect of solution in comparison to the sample 1. The second one has been performed to study the hydrogen effects on the superconducting properties. From the first hydrogenation following has been deduced (2):

\begin{align}
\text{a)} \quad \delta T_{c,1} &= 91.1 - 90.9 = 0.2K \\
\text{b)} \quad \delta T_{p,1} &= 90.2 - 89.9 = 0.3K \\
\text{c)} \quad \Gamma_1^{\text{virgin}} &= 90.9 - 89.9 = 1K \\
\text{d)} \quad \Gamma_1^{1^{\text{st}}\text{hydro}} &= 91.1 - 90.2 = 0.9K
\end{align}

(2)

Also in this case because $\delta T_{c,1} > 0$ and $\delta T_{p,1} > 0$ with $\Gamma_1^{\text{virgin}} = \Gamma_1^{1^{\text{st}}\text{hydro}}$, the hydrogen inside YBCO increases the critical temperature $T_c$, without sample worsening.

As well as for the sample 1, also for the sample 2, the analysis of the third harmonic [Fig.6] shows that the first hydrogenation produces an equal rigid translation to higher temperature. The critical current $J_c$ has been increased.

The similar results of LiOH (1) and NaOH (2) show that different alkaline metals (Li, Na) have no influence on the superconducting properties of HTSC and the increasing of $T_c$ and $J_c$ is only due to hydrogen.
A further hydrogenation of the sample 2 shows (3):

a) $\delta T_{c,1} = 91.6 - 90.9 = 0.7K$

b) $\delta T_{p,1} = 90.6 - 89.9 = 0.7K$

c) $\Gamma_{1}^{\text{virgin}} = 90.9 - 89.9 = 1K$

d) $\Gamma_{1}^{2\text{nd\,hydro}} = 91.6 - 90.6 = 1K$

(3)

It is evident a subsequent improvement of superconducting properties. Moreover, analyzing the third harmonic of sample 2 [Fig.6], is still possible to deduce that $\delta T_{c,1} = \delta T_{c,3}$, $\delta T_{p,1} = \delta T_{p,3}$, $\Gamma_{1}^{2\text{nd\,hydro}} = \Gamma_{3}^{2\text{nd\,hydro}}$.

It has been proved that the increasing of hydrogen stoichiometry at H/YBCO=0.3 increases the critical temperature $T_c$ and the critical current density $J_c$. The hydrogen increases the superconducting properties, specially the pinning process. The hydrogenation has no influence on the normal losses. It is important to emphasize that the samples after thermal cycle (300–77–300K) and subsequently hydrogenation in aqueous solutions have been checked.

Fig.4 $\chi''_3$ as a function of temperature for 107Hz and $H_a=6$Gauss, for sample 1.

Fig.5 $\chi''_1$ as a function of temperature for 107Hz and $H_a=6$Gauss, for sample 2.
4 - CONCLUSIONS

In this paper has been shown that, the analysis of the magnetic response of the hydrogen loading HTSC based on the imaginary part of the first and the third harmonics of the susceptibility suggests the following experimental evidence, particularly from the hydrogenation procedure:

1) Absorbed hydrogen with μs pulsed electrolysis technique has a beneficial effect on the superconducting transition temperature $T_c$. Probably it is due to the following facts:
   1.1) Very short loading time ($10^2$s) in aqueous solutions;
   1.2) Low average but high peak electrolytic current to avoid the hydrogen recombination $H+H \rightarrow H_2$ and the samples worsening;
   1.3) Atomic instead of molecular hydrogen loading;
   1.4) Atomic hydrogen maybe prefers the sites near Y atoms, because the formation enthalphy for Y−H is less than O−H and even less than H$_2$O. This avoids the occupation of oxygen vacancy in CuO−planes with subsequently superconductive collapse.

Further comments on the hydrogen adsorption process must be done:

2) Physical adsorption is completely different from the chemical adsorption;
   2.1) In the physical loading the hydrogen is adsorbed from molecular form H$_2$ and the sites close to oxygen or copper are energetically favourable and in any case the superconducting properties are destroyed because H$_2$O formation.
   2.2) In the chemical loading the hydrogen is adsorbed as a ion, because the affinity with yttrium is so strong, sites close to Y are preferred.

3) Electrolytic solutions have no influence on the HTSC superconducting properties, because in two different solutions (LiOH, NaOH), using the same loading procedure identical results have been obtained.

4) Hydrogen is responsible for the increasing of superconducting properties. Addictioning
hydrogen stoichiometry H/YBCO has shown the following evidences:

4.1) Quality of HTSC samples do not change:
\[ \Gamma_1^{\text{virgin}} = \Gamma_3^{\text{virgin}} = \Gamma_1^{\text{hydro}} = \Gamma_3^{\text{hydro}} \]

4.2) Increase of the critical temperature \( T_c \):
\[ \delta T_{c,1} = \delta T_{c,3} > 0 \]

4.3) Increase of the peak temperature \( T_p \):
\[ \delta T_{p,1} = \delta T_{p,3} > 0 \]

Because the increasing of the \( T_p \) is the same for the first and the third harmonics:

5) Hydrogen increases the non-linear hysteretic response due to the pinning processes.

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REFERENCES