LABORATORI NAZIONALI DI FRASCATI
SIS – Pubblicazioni

LNF–96/046 (R)
10 Settembre 1996

Seven Harmonic Susceptibilities in Oxygen and Hydrogen Loading of Sintered YBCO by μs Pulsed Electrolysis in an Aqueous Solution at Room Temperature

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Proceedings of "1996 Applied Superconductivity Conference"
Pittsburgh, August 25–30, 1996, MHD–8

Submitted to
IEEE Transaction Magnetics

Abstract **- The complex AC susceptibility of high T_c superconducting materials ($\chi_n = \chi'_n + i\chi''_n$) has been described in terms of the first seven harmonic component of Fourier series. Has been measured the χ'_n and χ''_n (n = 1,7) of sintered $YBa_2Cu_3O_{7-x}$ (YBCO) bulk oxygen and hydrogen loaded samples versus amplitude and frequency of AC magnetic field at fixed temperature. The samples have been loaded by μs current pulses electrolysis in an aqueous solution (0.3N $LiOH+H_2O$) at room temperature. In addition to the simplicity *of the* experimental set-up, this procedure allows to obtain extremely high equivalent hydrogen/oxygen gas pressure on the surface of the electrodes. The YBCO electrode is polarized by short pulse width (0.5-10 μs) and high power (120 W) peaks with a variable repetition rate (0.1-10000 Hz). The pulses are obtained by an home-made pulse generator. The differences in the behavior of the susceptibilities harmonic component between the deficiency and oxygen or hydrogen loaded samples give us the possibility to connect the susceptibilities with variations of the flux pinning in respect to normal losses in the superconducting materials. The loading can be a good probe to have information on the mechanism of the processes that sustain the critical current density Jc in this situation these effects appear strongly dependent on the loading condition. By comparison of this measurements has been observed drastic change in behavior of susceptibility.**

I. INTRODUCTION

Since the discovery of the superconducting oxides, the correlation between the oxygen and the superconducting properties has been extensively studied [1,2,3].

Usually to get appropriate oxygen stoichiometry in HTSC the processes [4] involved high temperature treatments, while the only procedure to oxygen loading at room temperature in these materials is the electrochemical process [5], the advantage, for example, in oxygen loading is to avoid problems in hybrid semiconductors-superconductors devices.

As regards to hydrogen loading there is a general interest for its dynamics in metals [6], in particular superconducting properties have been studied in hydrogen loaded YBCO sample (H-YBCO) using high pressure gas [7,8,9,10] and electrochemical procedure [11]. It has been showed that hydrogen can be decrease[12] or increase [7,11] the critical temperature Tc. However a general worsening of the sample is observed, this deterioration depends loading procedure time of the hydrogen. The hydrogen diffusion strongly depends on its penetration on the sample surface and this is a function of the surface hydrogen pressure. We deal this loading by mean electrochemical procedure [11]. In addition to the simplicity of the experimental set-up, the electrolysis allows to obtain an high equivalent gas pressure on surface of the sample. To avoid the hydrogen or oxygen bubbles on YBCO-chatode or anode which forbids electrochemical process [11] and to have very high gas pressure we not used D.C. electrolysis, but the pulsed electrochemical technique. This innovative method has been carry-out by our staff [11,13,14] to charging different metal, like palladium, palladium alloy, nickel, titanium and YBCO pellets.

In the present letter we used the multi-harmonic magnetic measurements in function of the frequency and amplitude of AC magnetic field (H_{AC}) a fixed temperature. This give the possibility to study not only the pinning effect just aspected [15], but also the different flux dynamics [16,17] present before in the oxygen-deficiency YBCO sample and after the oxygen/hydrogen loading. Infact from their comparison is possible to study the different magnetic relaxation, due the flux and creep dynamics together the irreversible effects (critical state) present in the samples.

In section II we briefly describe the sample preparation, the experimental loading set-up , its procedure and the AC susceptibility measurement apparatus. In section III the set-up of the measurements are reported. In section IV the experimental results are plotted and discussed.

II. EXPERIMENTAL SET-UP

The YBCO samples have been prepared following a modified citrate pyrolisis procedure [18]. The typical sample is a slab of about 0.12 cm^3. Their chemical stability in aqueous environment has been previously checked [11].

Oxidation and hydrogenation has been done in aqueous solution of 0.3N $LiOH$-H_2O using cylinder of nickel as anode during hydrogen loading and as cathode during oxygen loading in YBCO. The samples has been placed in the center of cylinder.

Has been performed the electrochemical loading by the set up described in a previous paper [11]. The "μsec pulsed electrolysis" apparatus consists by an home-made capacitive-discharge pulse generator [11] which supplied

Manuscript received August 26, 1996.
This work was supported in part by ORIM s.r.l., Italy.

high peak power (up to 1.2 KW) with negative polarity, the duration of the flat region of the pulse is 1500 nsec with a high repetition rate (up to 5Khz) and high peak current density on the YBCO surface (3 A/cm^2). Between the output of pulse generator and imput of the electrolytic cell there is a fast-power diode, in this way is possible to avoid the self-discharging phenomena of the electrolytic cell during the off-period of the pulser and to keep a self-polarization of YBCO sample. The electrolytic cell vessel is made of commercial glass.

Has been measured the seven harmonic component of AC magnetic susceptibilities by means a susceptometer done double coil like a pick-up coaxial to an external coil for exciting AC magnetic field coaxial to another external coil for exciting DC magnetic field. The samples has been placed in one of the double coil. The pick-up signal has been measured by an AC Lock-in amplifier (EG&G 5302) able to measure the first seven harmonic of the main frequency setted. Has been measured the AC electric current circulating in the AC external coil in order to know the exciting AC magnetic field. Has been used a temperature controller (Lake Shore DRC 91C) for measuring two platinum thermometer, the first on the sample and the second on sapphire holder and to control the temperature with two heater. The experimental data are acquired by a computer.

III. MEASUREMENTS METHOD

The harmonic coefficients of AC magnetic susceptibility has been measured versus temperature at constant frequency and amplitude of AC magnetic field (A procedure), versus frequency of AC magnetic field at constant temperature and amplitude of field (B procedure), versus amplitude of AC magnetic field at constant temperature and frequency of field (C procedure). All measurements has been made at zero DC magnetic field. In the (A) procedure has been measured the AC susceptibilities in field cooling (FC) with decreasing of temperature step by step (typically 0.25 K) and when stabilized the temperature has been measured all seven harmonic of susceptibilities keeping constant AC magnetic field. In the (B) procedure, after temperature stabilization of system at fixed temperature, has been increased the amplitude of AC magnetic field step by step. Has been measured all seven harmonic component every step keeping constant frequency of AC magnetic field. In the (C) procedure has been operated like in the (B) procedure changing the frequency of AC magnetic field keeping constant the amplitude of field.

The sample for each measure with procedure B,C is warmed above 100K and cooled in ZFC to avoid trapped flux in the sample.

The measurement of the temperature dependence of AC susceptibility is useful to characterizing the superconductor, but for the purpose of the dynamic analysis (critical state and losses) it is convenient to evaluate the harmonic susceptibility in respect to B and C procedure. In this letter we present plots made by these last procedures. However The YBCO sample before the loading has the χ'," temperature onset at T = 92K and temperature offset at T = 82K. This shows a sample oxygen-deficiency. The measurement parameter was H_{AC} = 1G, H_{DC} = 0G and f = 107Hz.

IV. RESULTS AND DISCUSSIONS

Has been compared only qualitative behaviors, because is unknown the system calibration α. In this communication the harmonic components and their modules are presented in arbitrary units and normalized up to higher value.

In figure [1] it is show the dependence of AC field amplitude of the first four odd harmonics AC susceptibility at fixed temperature and frequency (T = 85K, f = 107Hz) of "virgin" YBCO sample.

These are a typical behaviors [15,17] of YBCO sample oxygen poor. In χ_1" plot, the peak corresponding the coupling component is present at H_{AC} = 1.5G. In χ_3" and χ_5" these peaks are present at higher H_{AC}. Third harmonic has peak at H_{AC} = 1.6G and fifth harmonic at H_{AC} = 1.9G. These facts, probably, are due to intragrain structure. In general the plots showed in figure [1] have behaviors like to other measurements or model calculations [15,16]. The oscillation of higher harmonic components, in the critical state, is a function of the ratio between amplitude of applied magnetic field H_{AC} and full penetration magnetic field H_p with period decreasing with number coefficient increasing [19]. The normal losses affects these higher harmonic oscillations. In agreement [16,17], the oscillation of the third harmonic measurements are function of the AC magnetic field frequency [16], this behavior is showed also by calculation model where are considered normal losses.

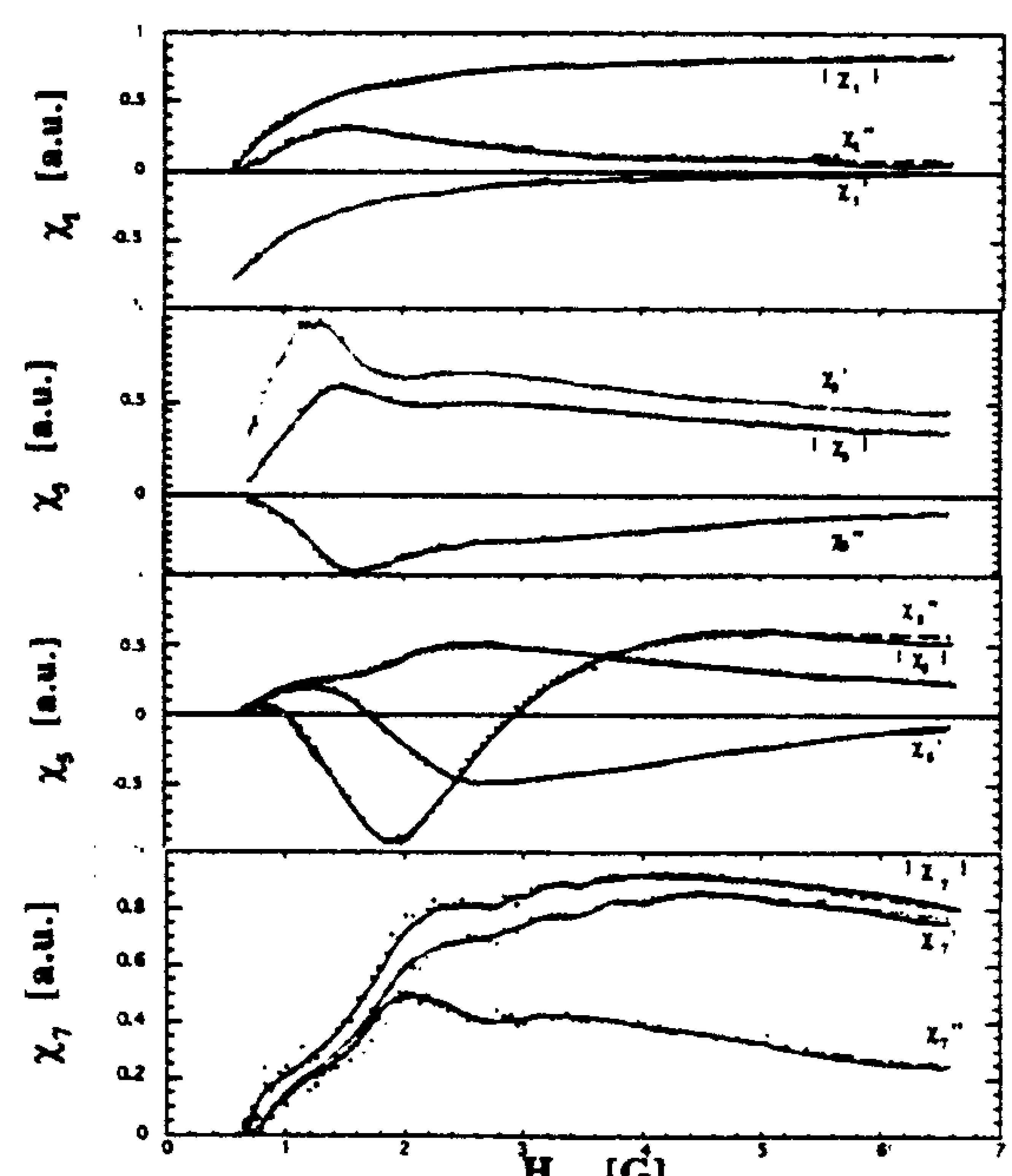

Fig. 1 - Odd-harmonic susceptibilities $\chi'_{1,3,5,7}$ and $\chi''_{1,3,5,7}$ of the "virgin" YBCO sample as a function of AC magnetic field amplitude. The measurements parameter were T = 85K, H_{DC} = 0G, f = 107Hz.

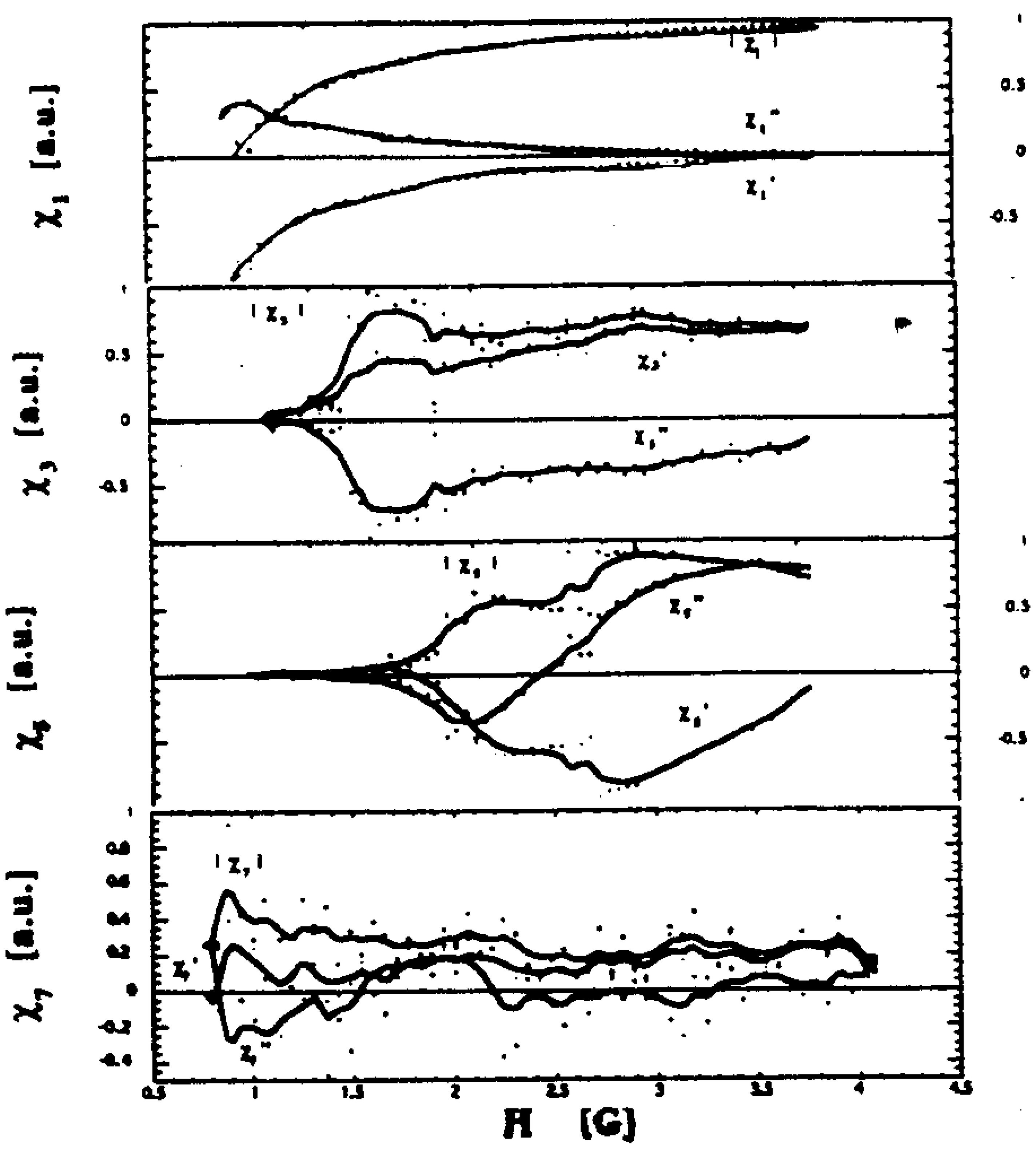

Fig. 2 - Odd-harmonic susceptibilities $\chi'_{1,3,5,7}$ and $\chi''_{1,3,5,7}$ of the "oxidized" YBCO sample as a function of AC magnetic field amplitude. The measurements parameter were $T = 85K$, $H_{DC} = 0G$, $f = 107Hz$.

In figure [2] it is show the dependence of AC field amplitude of the first four odd harmonic AC susceptibility at fixed temperature and frequency ($T = 85K$, $f = 107Hz$) after the oxidation of the YBCO sample.

Evidently the measurements have more scatter data respect the "virgin" sample. The peak of χ_1'' is shifted to lower value of AC magnetic field amplitude, $H_{AC} = 0.7G$.

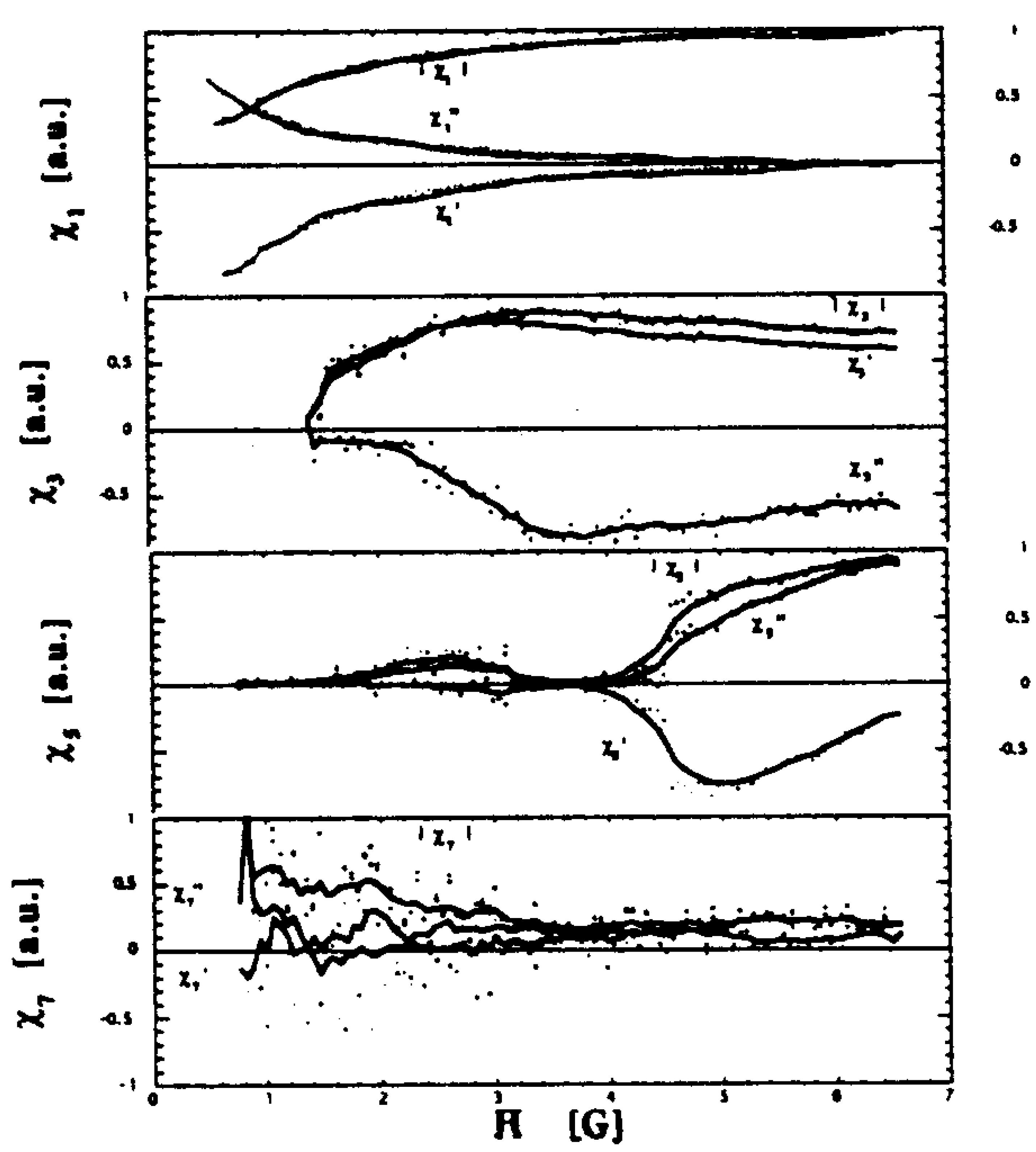

Fig. 3 - Odd-harmonic susceptibilities $\chi'_{1,3,5,7}$ and $\chi''_{1,3,5,7}$ of the "hydrogenated" YBCO sample as a function of AC magnetic field amplitude. The measurements parameter were $T = 85K$, $H_{DC} = 0G$, $f = 107Hz$.

The behaviors of higher harmonic are weakly changed, but the peaks of $\chi''_{3,5}$ have the minimum at the same H_{AC} amplitude value like 'virgin' YBCO, $H_{AC} = 1.6G$ (χ_3'') and $H_{AC} = 1.9G$ (χ_5''). The zero value of fifth harmonic component is present for a lower H_{AC} amplitude after oxidizing ($H_{AC} = 2.4G$) in comparison to 'virgin' YBCO ($H_{AC} = 2.9G$). This decreasing of zero value is in correlation with the shift of χ_1'' peak to lower H_{AC} amplitude. This behavior shows an over-oxidizing that worsening the intergrain superconductive structure (correlation shift) and weakly affect the intragrain structure ($\chi''_{3,5}$ peaks).

In figure [3] it is show the dependence of AC field amplitude of the first four odd harmonics AC susceptibility at fixed temperature and frequency ($T = 85K$, $f = 107Hz$) after the hydrogenation. The peak of χ_1'' disappeared. The peaks of $\chi''_{3,5}$ have the minimum for bigger H_{AC} amplitude value in respect to 'virgin' and oxidized YBCO, $H_{AC} = 3.8G$ (χ_3'') and $H_{AC} = 3.8G$ (χ_5''). The zero value of fifth harmonic component is present for a higher H_{AC} amplitude after hydrogenation ($H_{AC} = 4.1G$) in comparison to 'virgin' YBCO ($H_{AC} = 2.9G$). These behaviors shown that hydrogenation worse the intergrain superconductive structure (χ_1'' peak is missing) but improve the intragrain superconductive structure (higher harmonic peaks and zero of χ_5''). The shape of χ_3'' in function of H_{AC} amplitude is similar to the previous behavior, completely different is the shape of the χ_5'' which do not shows the negative minimum peak.

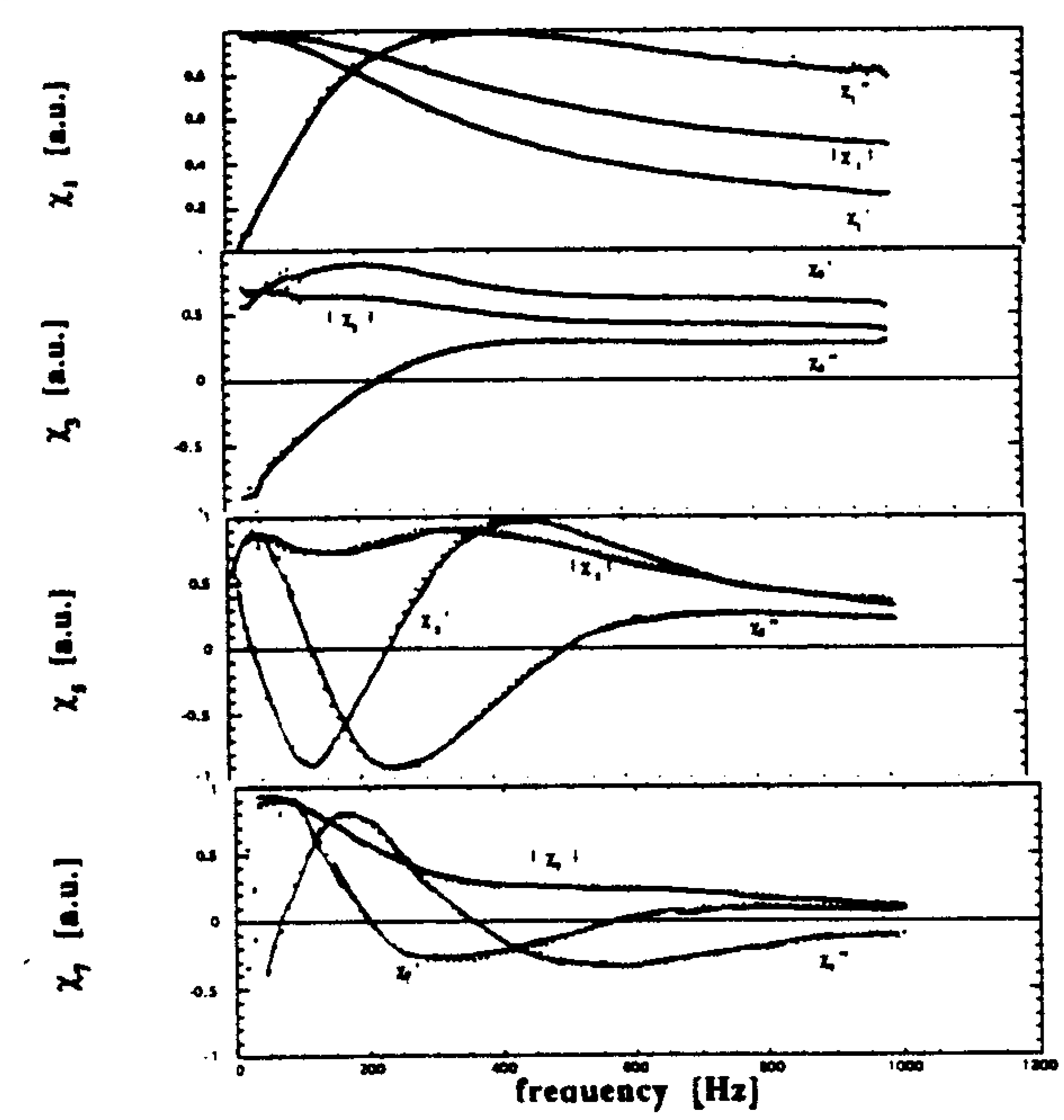

Fig. 4 - Odd-harmonic susceptibilities $\chi'_{1,3,5,7}$ and $\chi''_{1,3,5,7}$ of the "virgin" YBCO sample as a function of AC magnetic field frequency. The measurements parameter were $T = 85K$, $H_{DC} = 0G$, $H_{AC} = 3.5G$.

In figure [4] and figure [5] it is show the dependence of the frequency of AC magnetic field of the first four odd harmonics AC susceptibility at fixed temperature and frequency (T = 85K, Hac = 3.5G), "virgin" and (T = 85K, Hac = 1.5G) after the hydrogenation.

In the framework of the Bean model the normal losses do not have effect on the higher harmonics AC susceptibility, only pinning effect must be observed and the measurements do not depend to the frequency. In recent works [20,16,17] the frequency effect on AC response has been confirmed.

This behavior is showed in figure [4] to "virgin" YBCO sample, where all harmonics component are depending to the frequency. These frequency dependence are evident after hydrogenation too, figure [5].

The module of third harmonic coefficient, $|\chi_3|$, decrease when frequency increase [20] in "virgin" YBCO. While the "hydrogenated" YBCO the $|\chi_3|$ shows a double peaks and decrease with frequency increase. The double peaks probably are due to a multi-phase YBCO.

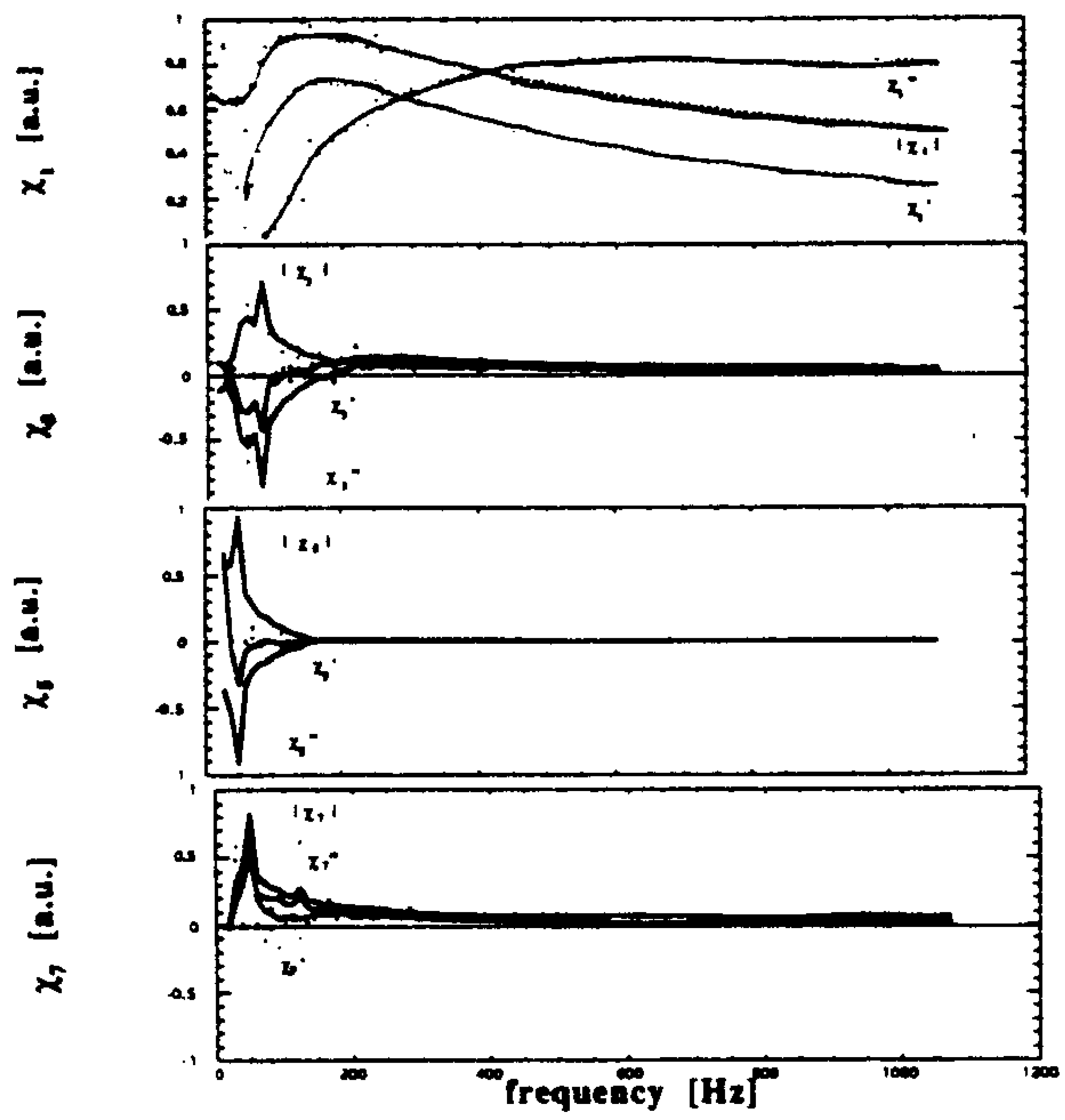

Fig. 5 - Odd-harmonic susceptibilities $\chi'_{1,3,5,7}$ and $\chi''_{1,3,5,7}$ of the "hydrogenated" YBCO sample as a function of AC magnetic field frequency. The measurements parameter were $T = 85K$, $H_{DC} = 0G$, $H_{AC} = 1.5G$.

V.CONCLUSIONS

This letter is a first qualitative approach to evaluate the superconducting and losses properties of the HTSC YBCO samples, before and after an easy room temperature electrolytic oxygen/hydrogen loading.

It is evidently which higher harmonic AC susceptibility components give information on mechanism which sustain or limit the pinning process.

Has been shown that the peaks of the first three harmonic components χ''_n versus H_{AC} amplitude in the 'virgin' YBCO are very close (1.5, 1.6, 1.9 G).

After electrolytic oxidizing the peak of χ_1'' versus H_{AC} amplitude, decrease down to 0.7G (due to over-oxidizing) while the χ_3'' and χ_5'' are unchanged (1.6, 1.9G). This means that the oxidizing acts on the intergrain structure and not on the intragrain structure of sintered YBCO.

After electrolytic hydrogenation the peak of χ_1'' versus H_{AC} amplitude, disappear (less than 0.2G) but the peaks of χ_3'' and χ_5'' are increased both to 3.8G. This means that the hydrogenation worse the intergrain structure but the intragrain structure of sintered YBCO is better.

The prove that hydrogen acts on the intragrain structure is shown by frequency analysis through the appearance of double peaks on the $|\chi_3|$.

In order to have a quantitative higher harmonic AC susceptibility analysis we are working also to solve with numerical method the non-linear diffusion magnetic equation for the induction B(r,t) with sinusoidal boundary condition, where the Fourier coefficients of the magnetization cycle are higher harmonic AC susceptibility. In this simulation we consider together at different critical state models also creep and flow losses.

VI. ACKNOWLEDGMENT

We thanks Dr. Roberto Messi for his helpful.

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