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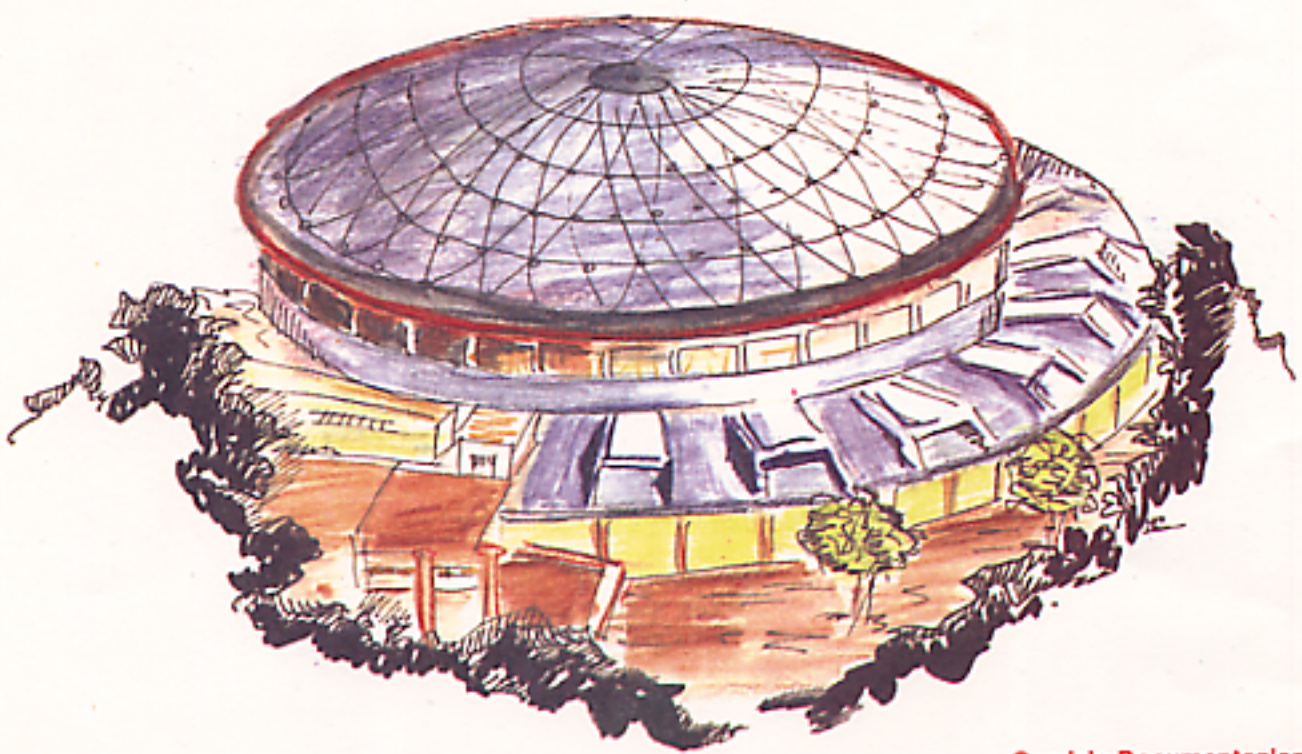

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FIRST RESULTS ABOUT HYDROGEN LOADING BY MEANS OF PULSED ELECTROLYSIS OF $Y_1Ba_2Cu_3O_7$ PELLETS

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ABSTRACT.

$Y_1Ba_2Cu_3O_7$(YBCO) sintered pellets have been loaded at room temperature with hydrogen by means of electrolysis in an aqueous solution (LiOH 0.3 N) with μs current pulses. The superconducting features of loaded samples have been measured as a function of the temperature by the ac magnetic susceptibility. In some conditions the YBCO pellets exhibited an enhancement of the transition temperature up to 95.4 K without a significant weakening of the superconducting grain coupling. These effects appear strongly dependent on the loading conditions.

1. — INTRODUCTION

Our general aim is to understand the effects of hydrogen and deuterium on superconducting features of metals and of $Y_1Ba_2Cu_3O_7$(YBCO) sintered pellets. The variations of the critical temperature (T_c) of YBCO loaded with hydrogen using high pressure gas have been studied by some Authors [1-4], giving different relations between the transition temperature and the hydrogen content.

In a recent paper [5] we described the enhancement of the critical temperature up to 100 K of YBCO by means of a loading procedure using deuterium gas with a pressure between 38 and 53 bar and a complex thermal cycle. These processes sometimes lead to the deterioration and, in the worst cases, to the destruction of the sample. Anyway the deterioration is strongly dependent on the pellet quality.

Since the hydrogen diffusion strongly depends on its penetration on the pellet surface, which increases with the pressure, our purpose is to study the hydrogen loading at room temperature at very high pressures. However, by the gas loading procedures, it is very hard to reach very high pressures (> 1000 atm) and it requires different thermal cycles [3] in order to activate the charging process. For these reasons it is necessary a more efficient and safe charging experimental set-up, which should avoid the drawbacks of the gas loading.

The only procedure that we know for this purpose is the electrolysis. The room temperature electrochemical loading of cathodically polarized metal with hydrogen is a procedure widely used [6]. In addition to the simplicity of the experimental set-up, the electrolysis allows to obtain extremely high hydrogen and/or deuterium equivalent pressure on the surface of the cathode. Indeed, by a Nerst-type expression [7, 8], the hydrogen equivalent pressure increases exponentially with the effective cathodic overpotential η_2', which is the potential difference between the cathode and the platinized-platinum reference electrode, measured after that the electrolysis has been switched off (typically after 30 μs), so that it is only a fraction of the whole overpotential. For these reasons, in order to be sure to reach large (> 1000 atm) effective pressures, as high as possible overpotentials are necessary.

As regards the dc electrolysis large values of currents are not available, not only due to the intrinsic current saturation limit, but mainly because the evolution of the hydrogen bubbles on the cathode forbids the electrochemical process. For these reasons in this paper, in order to reach large overpotential values and very high equivalent pressure, the pulsed electrochemical technique has been explored. This method has been set by our staff for the charging of different metals, as palladium, to high D/Pd ratio (up to 1.2 [9]) at room temperature. This method is not reported in literature for YBCO. In the pulsed electrolysis the hydrogen bubbles are not a serious problems and the existence of intrinsic current limits in dynamical conditions is not yet clear. Using high current (overpotential) peaks, higher loadings should be available since the electrochemical cell works always far away from the saturation conditions.

The YBCO pellet is the cathode of an aqueous solution containing the electrolyte and is polarized by short (1-5 μs) and high power peaks with a low duty-cycle at room temperature.

In section II we briefly describe the ac susceptibility apparatus used for the measurements of superconducting features and the sample preparation; moreover, some details of the electrochemical cell are given. In section III the loading procedures and the results are reported and discussed.

2. — EXPERIMENTAL SET-UP

In order to measure the superconducting properties of the pellets, we performed ac magnetic susceptibility measurements using a two-coils susceptometer. The external coil generates the sinusoidal magnetic field, the inner one is the pick-up. The real (χ') and the imaginary part (χ'') of the susceptibility are proportional to the in-phase and the out-of-phase voltage signals induced in the pick-up coil: they are detected by the lock-in amplifier (EG&G 5208). The χ' increases with the shielding effect of the sample, while the χ'' is proportional to

the area of the hysteretic magnetization curve; both are determined by the temperature dependent critical current density $J_c(T)$. In our measurements the amplitude of the ac magnetic field H_0 is equal to 0.2 or 1 G at the frequency of 107 or 1070 Hz. A room temperature magnetic shield is used to reduce the ambient magnetic field to 0.2 G. We apply the ac magnetic field at room temperature, later on the samples are cooled down to T=77 K (Field Cooling, FC). After at least one hour at 77 K, the measurements are performed with a warming-up rate of 0.3 K/min up to room temperature.

We have chosen 3 main parameters to characterize the samples: the onset temperature of the superconducting transition T_{on}, the temperature T_p corresponding to the maximum of χ'' as a function of temperature and the FWHM (Full Width Half Maximum) of the peak of $\chi''(T)$.

The T_{on} is defined as the temperature corresponding to the beginning of the deviation of χ' and χ'' from the normal state behaviour and its variation is related to the change of the superconducting properties of YBCO generated by the presence of hydrogen inside the grains.

The temperature T_p, following the Bean model and neglecting the demagnetization factor, corresponds to the full penetration conditions of the magnetic field: $J_c(T_p) = H_0/r$, where r is the radius of the pellet. In this way, for a given transition temperature, an increasing or a decreasing of T_p respectively correspond to an increasing or a decreasing of $J_c(T)$, at each temperature. In a granular system $J_c(T)$ is determined by the Josephson coupling between grains, so that a decreasing of $J_c(T)$ is the direct evidence of the increasing of non-superconducting phases in the grain boundaries and vice versa.

The value of $(T_c-T_p)/T_c$ or the FWHM is a measurement of the intergranular coupling also if T_c changes: greater is the superconducting coupling among the grains, lower is the FWHM value [10].

The YBCO pellets have been prepared following a modified citrate pyrolysis procedure and only two subsequent thermal treatments (calcination and sinterization) in ozone-enriched atmosphere [11]. The typical sample dimensions (within 5%) have a diameter and a height respectively equal to 20 mm and 5 mm. These samples do not show spurious phases in the limit of the X-ray diffraction sensitivity. All the samples, fabricated in the same batch and measured before loading, showed a quite good superconducting grain coupling (T_p=89.3÷90.7 K and FWHM ≈ 1 K at 1 G and 107 Hz). Moreover their chemical stability in aqueous environments is enough for our purposes: the superconducting features are not significantly affected by a 20 hours immersion in distilled water.

In Fig. 1a the experimental apparatus used to perform the μs pulsed electrolysis is reported. The pulses, with negative polarity, are obtained by means of an home-made capacitive-discharge pulse generator. The power pulse generator (PPG) supplies high peak power (up to 1.2 KW) with a high repetition rate (up to 10 KHz) and high peak current density on the YBCO surface (3 A/cm^2). Between the output of the PPG and the input of the electrolytic cell there is a fast-power diode D1 (40HFL80S05). In this way we can avoid the self-discharging phenomena of the electrolytical cell during the off-period of the pulser (typically 99%) and we obtain, at the same time, a self-polarization of the YBCO sample. In Fig. 1b we describe a simplified scheme of the PPG.

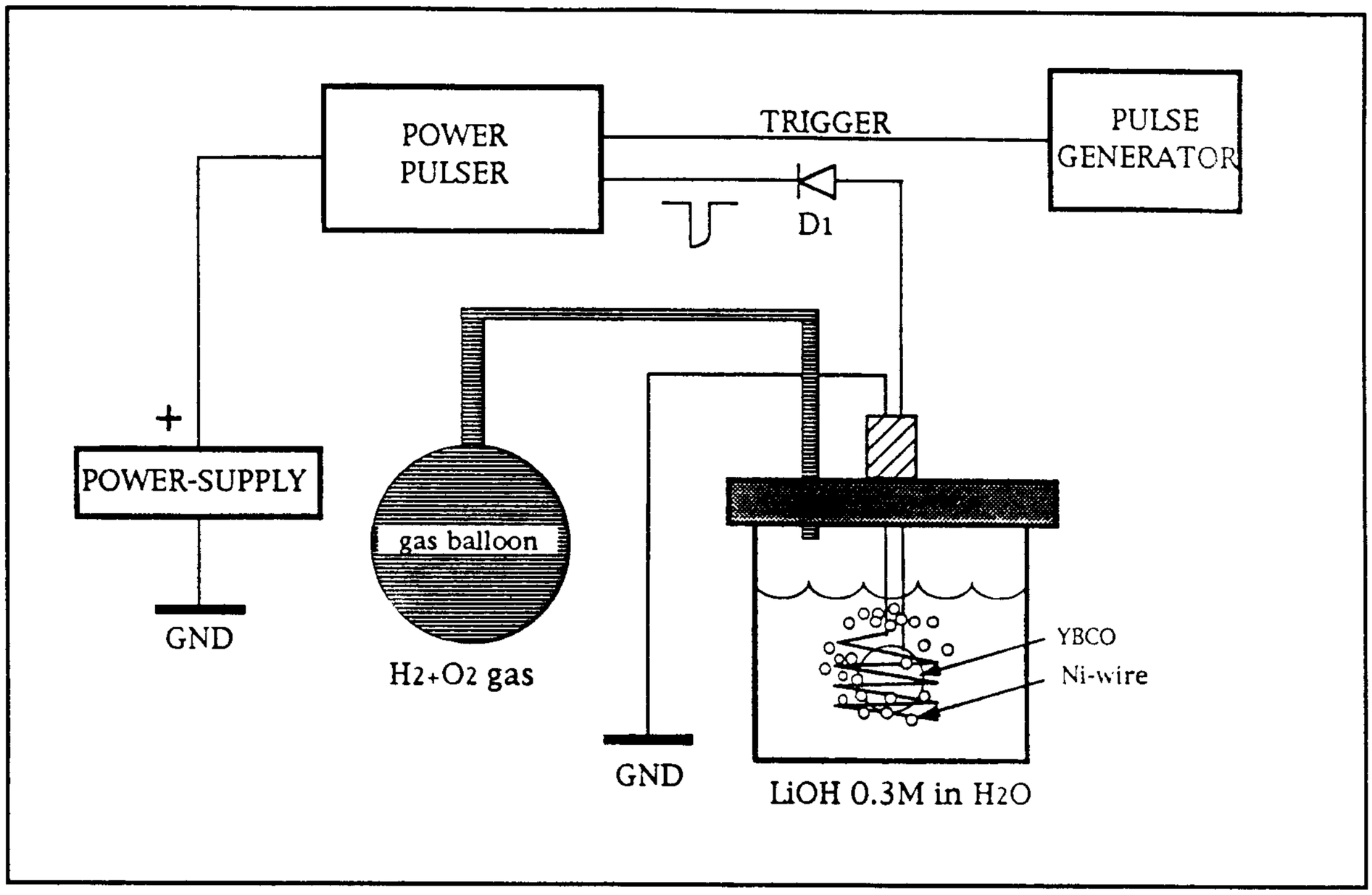

FIG. 1a - Experimental set-up for hydrogen loading by means μs pulsed electrolysis.

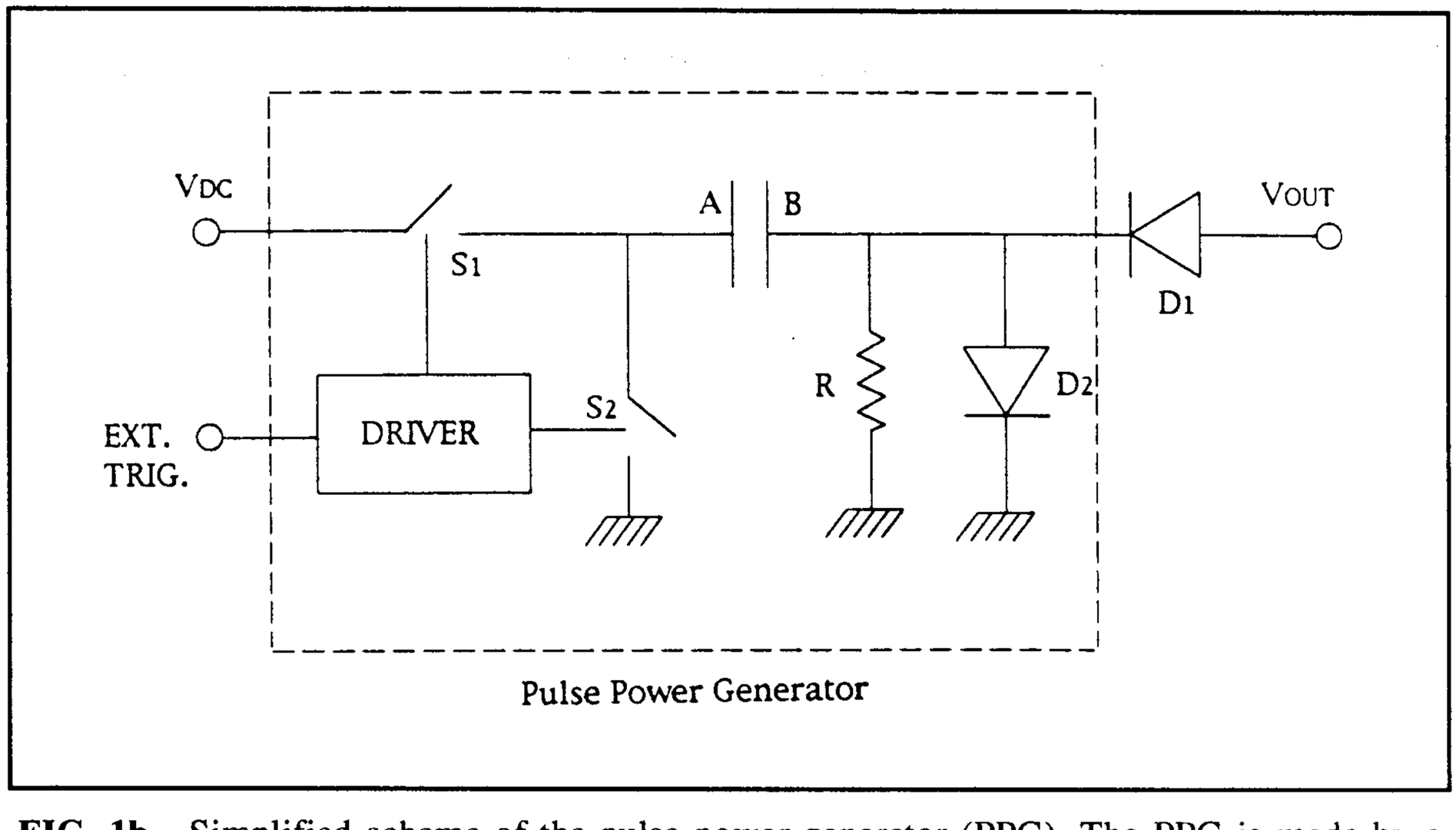

FIG. 1b - Simplified scheme of the pulse power generator (PPG). The PPG is made by a driver, controlled by an external trigger, which drives the 2 switches, S1 and S2, in counter-phase. The switches allows the discharging of the capacitor through the electrolytitical cell for a duration, supplying to the cell a pseudo-trapezoidal voltage signal. The pulses are fast (rise time < 200 ns, fall time < 300 ns) with an high repetition rate (up to 10 KHz). The high frequency is allowed by the 2 switches, which are active circuits, and by the fast recovery diode D2 (1N4937A), which allows a fast restoring of the charge.

3. — LOADING PROCEDURE AND EXPERIMENTAL RESULTS

We prepared an aqueous solution of LiOH (0.3 M). The YBCO pellet is the cathode, around which we have wrapped a nickel-passivated wire, which is in good electrical contact with the sample and leads the current to it. The cathode is faced to the anode, made by a grounded nickel-passivated network.

In the pulsed electrolysis method the absorption rate into the bulk of the sample is to be optimized as a function of the width and height of the pulses. For this purpose we loaded several samples at room temperature, changing some parameters, but keeping constant the repetition rate of the pulses (5 KHz).

The first pellet (α) was charged imposing the pulse height equal to 12 V (5.5 A of peak current) and the width equal to 5 μs; the loading lasted 20 hours. In Fig. 2 and 3 are respectively shown the real and imaginary part of magnetic susceptibility measured at 1 G and 107 Hz, before (α1) and after (α2) the charging. In Fig. 2 we did not see any significant variation of the T_{on}, but only a larger transition width with a lower value of the modulus of χ' at 77 K of α2 in respect to α1. In Fig. 3 we observed a FWHM enlargement equal to 1.4 K in respect to the same measurement before the loading and a value of χ'' at 77 K different from zero. From the above results, we can infer that in this case the hydrogen weakened the coupling without modifying the superconducting properties of the grain. In fact [12] the hydrogen loading usually causes the precipitation of non-superconducting hydrides, which decouple the grains. Further on the precipitation should probably prevent the diffusion of the hydrogen into the grains, so that the variations of the superconducting properties [2] of the material are not allowed and the T_{on} does not change.

A second pellet (β) was subjected to the charging for 2 hours with an higher pulse height (35 V, 15.2 A), but with a shorter width (1.3 μs). In this way we nearly halved the area of the pulse. In Fig. 4 and 5 the ac susceptibility measurements at 1 G and 107 Hz before (β1) and after (β2) the loading are compared. In respect to the previous sample, we can observe an enhancement of the T_{on} of about 5 K (95.2 K) without a significant enlargement of the FWHM. In this case the loading did not substantially decrease the intergranular coupling, while it enhanced the transition temperatures. A possible explanation is that the higher pulse height determines an higher equivalent hydrogen pressure which allows the hydrogen to penetrate into the grains. Moreover in these conditions the precipitation of the hydrides at the grain boundaries seems not to give significant effects. During this charging the sample lost a little material, this fact could be related to the decreasing of the value of the modulus of χ' at 77 K.

After these positive results we decided to verify them with a further test, keeping constant the electrical parameters used for the electrolysis of the β sample. We loaded a new pellet (γ sample) for 120'. Subsequently the sample was cooled down to 77 K and the ac susceptibility was measured at 0.2 G and 1070 Hz during the warming up to 300 K. Afterwards the sample has been loaded for 30' and the magnetic susceptibility has been measured warming again the sample. After the first charging, the temperature dependence of the imaginary parts, plotted in the curves γ2 of Fig. 6, shows a T_{on} enhancement from 91.7 K to 92.5 K without a meaningful variation of FWHM with respect to the curve γ1 measured before the loading. On the contrary,

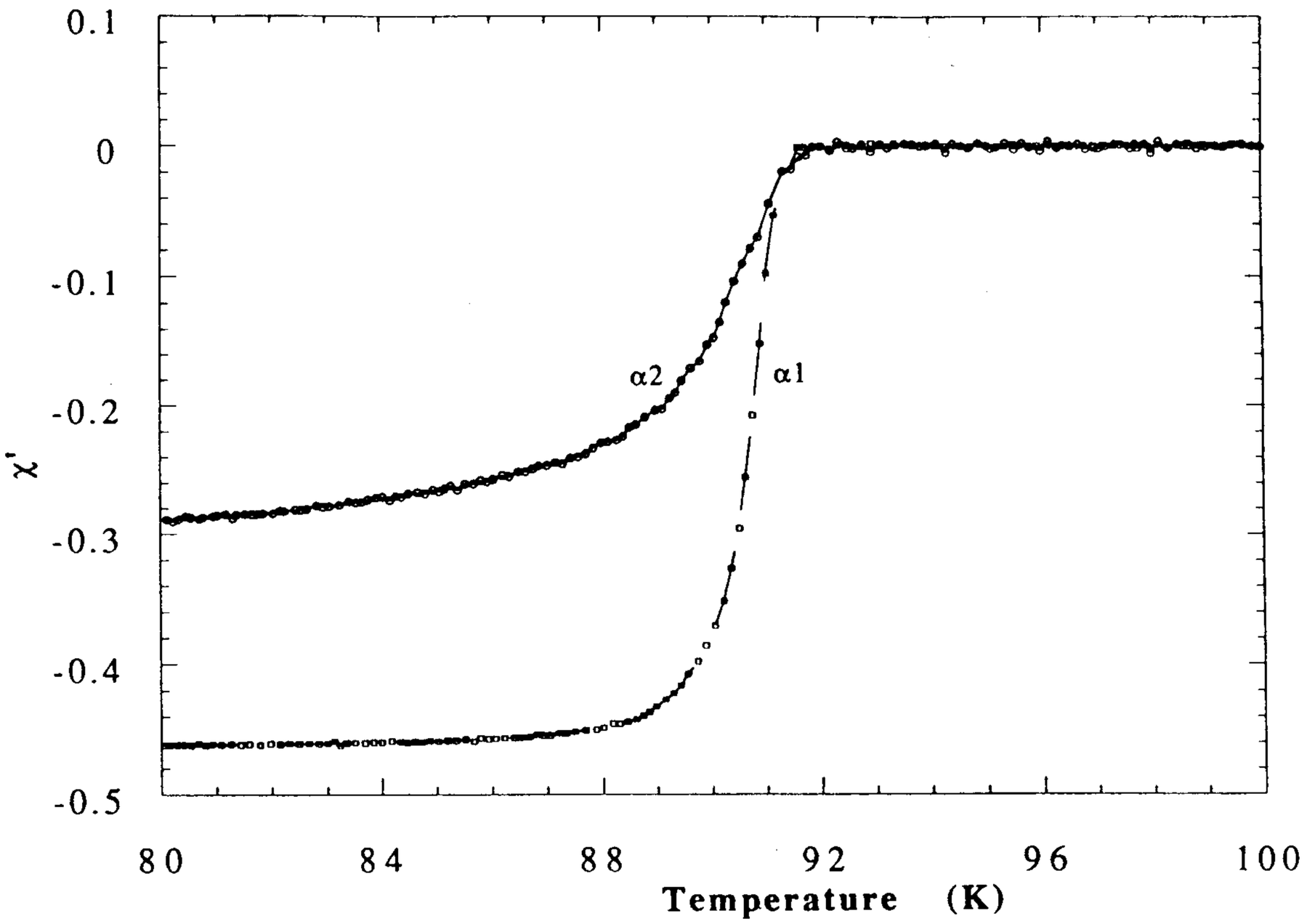

FIG. 2 - Real part of the magnetic susceptibility (χ') for the α sample. α1 YBCO pellet before H_2 loading; α2 YBCO sample after H_2 loading.

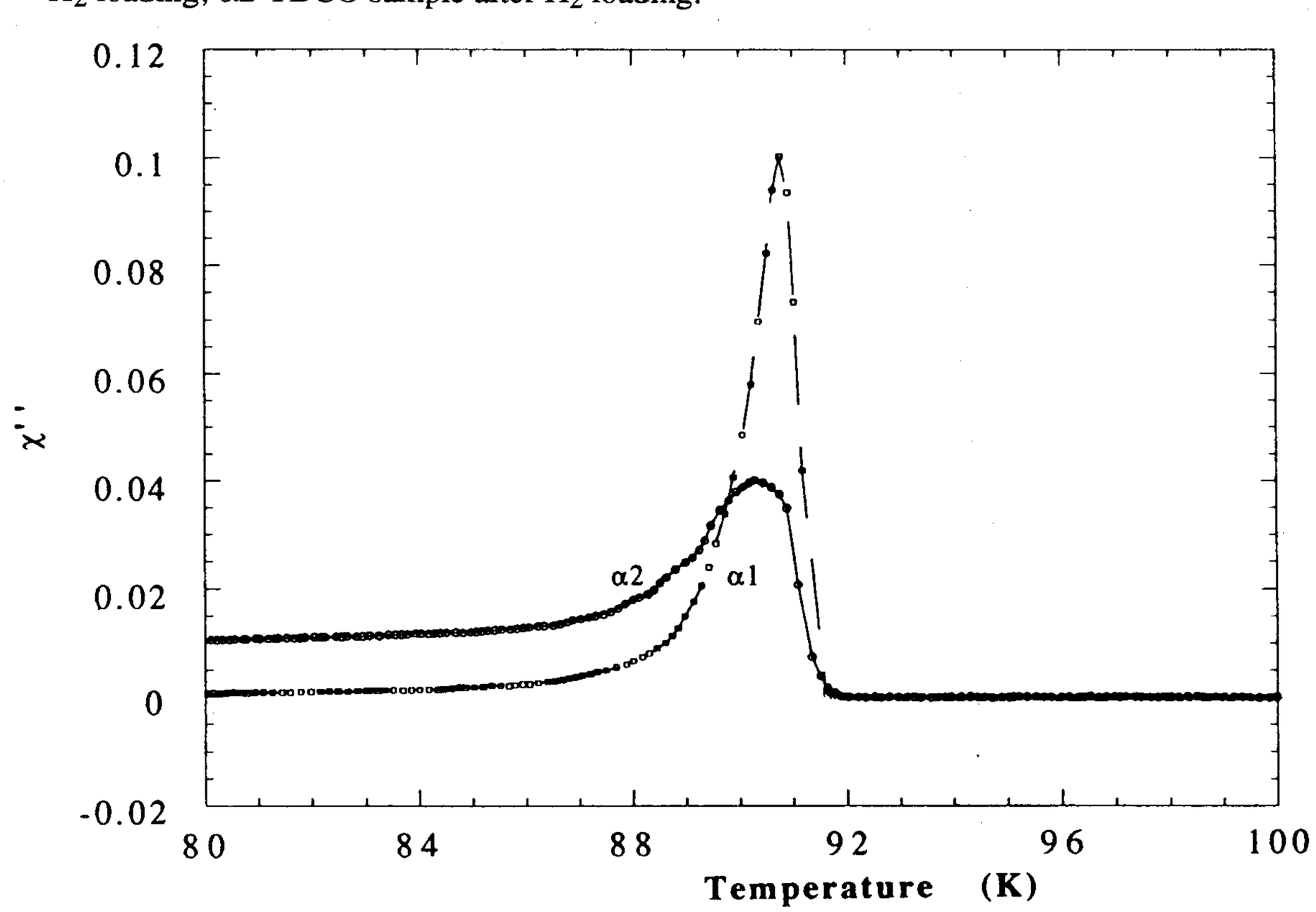

FIG. 3 - Imaginary part of the magnetic susceptibility (χ') for the α sample. α1 YBCO pellet before H_2 loading; α2 YBCO sample after H_2 loading.

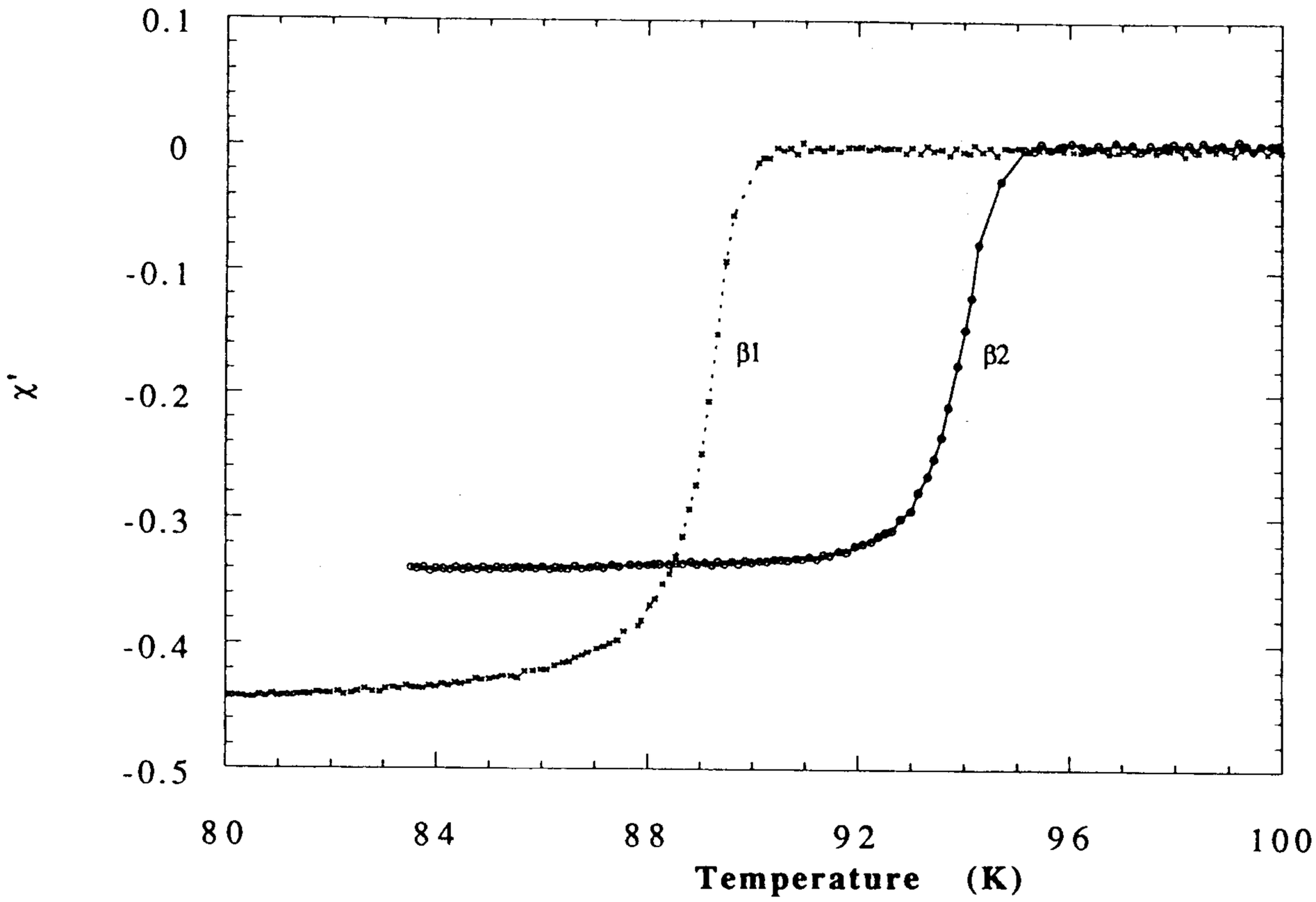

FIG. 4 - Real part of the magnetic susceptibility (χ') for the β sample. β1 YBCO pellet before H_2 loading; β2 YBCO sample after H_2 loading.

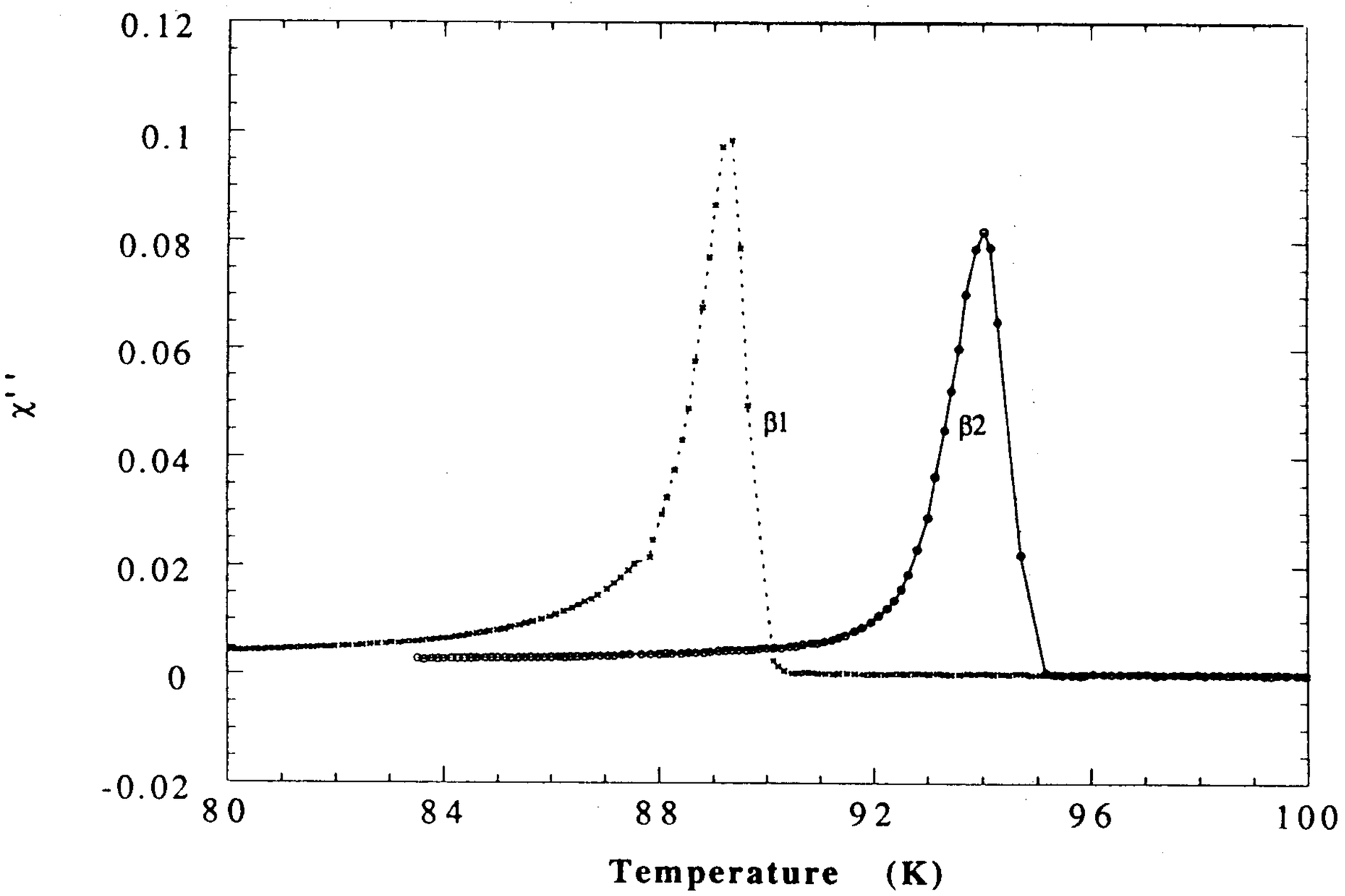

FIG. 5 - Imaginary part of the magnetic susceptibility (χ') for the β sample. β1 YBCO pellet before H_2 loading; β2 YBCO sample after H_2 loading.

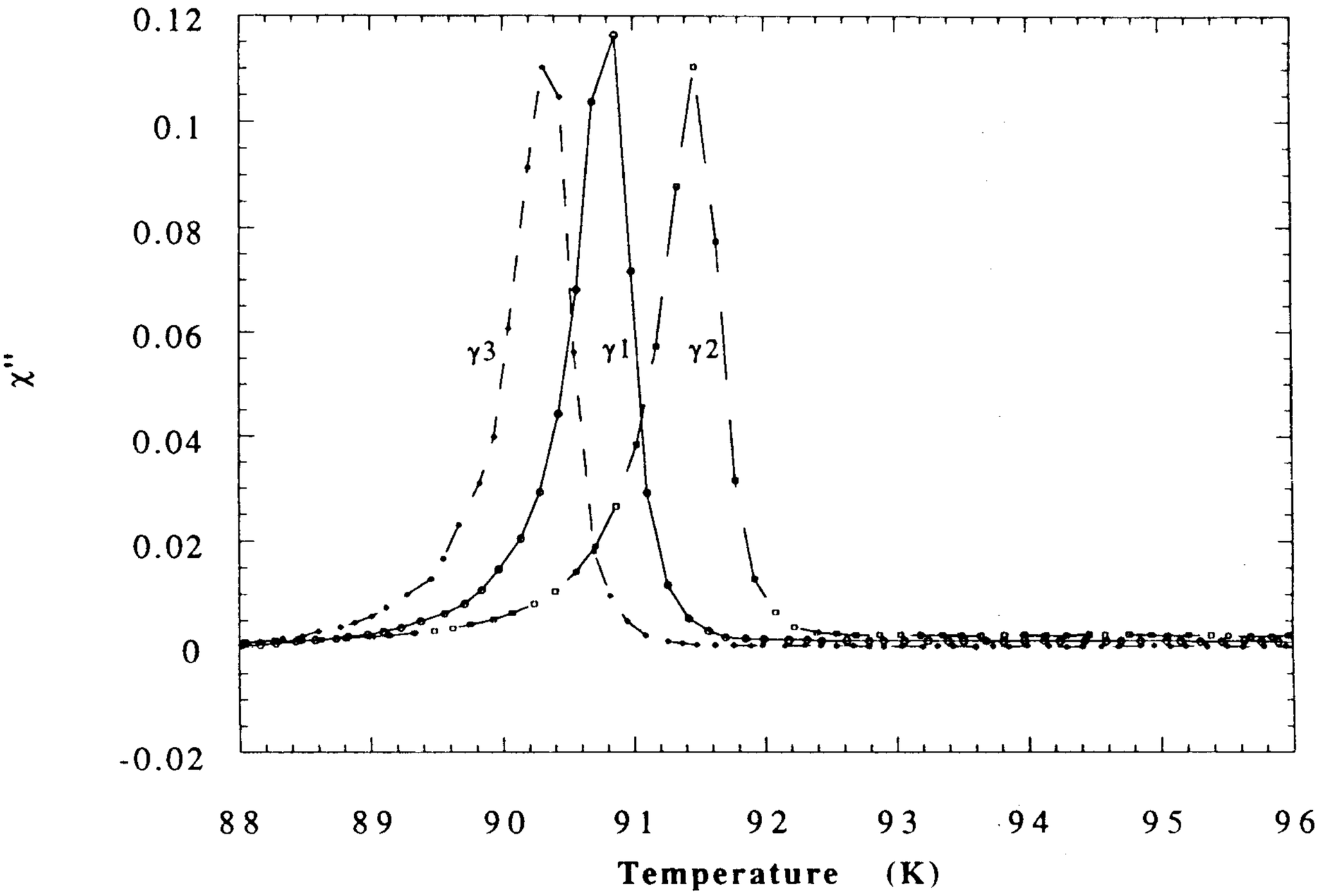

FIG. 6 - Imaginary part of the magnetic susceptibility (χ') for the γ sample. γ1 YBCO pellet before H_2 loading; γ2 YBCO sample after the first H_2 loading (120'); γ3 after the second H_2 loading (30').

as shown in the plot of χ'' (curve γ3 of Fig. 6) obtained after the second loading, the T_{on} decreased about 0.4 K in respect to the curve γ1, while the FWHM is not changed.

Because of the non-monotonic variation of the T_{on}, generated by two subsequent loadings, we decided to repeat this experiment in order to verify such a behaviour on the same sample, without changing any experimental condition. Between the first and the second couple of loadings 7 days elapsed with the sample kept at room temperature in a closed environment. The susceptibility measurements are shown in Fig. 7. After the first loading (curve γ4), T_{on} increased from 91.5 K to 95 K (3.5 K), while we observed an enlargement of FWHM. Later on the second loading (γ5) T_{on} diminished of about 3.4 K, while FWHM showed values closed to the ones of γ3.

From the first two chargings (Fig. 6) we can deduce that:

a) since the FWHM does not increase, the hydrogen loading does not decrease the intergranular coupling between the grains, so that the quantity of spurious phases at the grain boundaries are not increased;

b) the hydrogen penetrates into the grains and changes the critical temperature T_{on}.

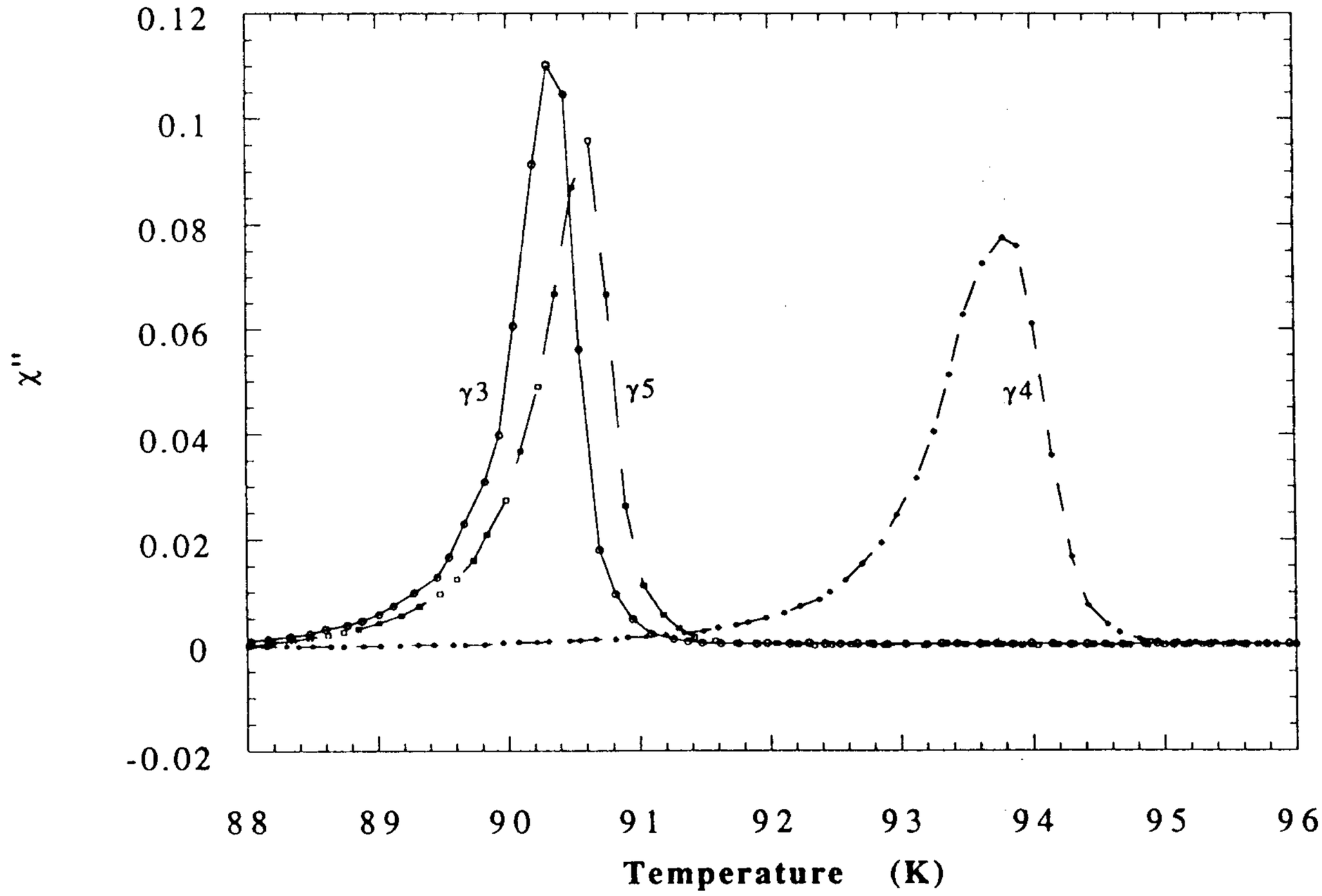

FIG. 7 - Imaginary part of the magnetic susceptibility (χ'') for the γ sample. γ3 YBCO pellet after the second H_2 loading; γ4 YBCO sample after the third H_2 loading (120'); γ5 after the forth H_2 loading (30').

Moreover in the first charging of the second couple (Fig. 7) there is a greater enhancement of the T_{on} in respect to the first chargings and a broadening of FWHM due to a decreasing of the intergranular coupling. In this way it is possible to deduce that the pellet has a memory of the first couple of loadings, as the second one has been performed in the same experimental conditions, while different results are obtained.

As the last charging (and/or the thermal cycle) has restored the FWHM of the curve γ5 to about the value of the curve γ3 before the loading, the enlargement observed on γ4 is reversible. For this reason, the effect can not be generated by hydrides precipitation, since in this case the enlargement of FWHM would have been permanent. The worsening could be due to an "overloading" of the pellet surface.

In conclusion we think that the pulsed electrochemical method can be used to load quickly YBCO samples with hydrogen by means of an easy and safe experimental apparatus, if compared with our previous experience about gas loading. In a reproducible way, with this procedure, we are able to increase the transition temperature of sintered pellets without weakening the superconducting coupling between grains. It clearly appears that these effects are dependent on the hydrogen equivalent pressure.

Anyway the effects of the hydrogen loading by pulsed electrolysis seems to be rather complex. In order to explain the non-monotonic behaviour of the transition temperature with the number of loadings, three possibilities exist:

1 – the hydrogen may go out from the material during the thermal cycles, so that we are not sure that subsequent loadings increase the hydrogen content;
2 – a maximum of the transition temperature vs. the hydrogen content may exist;
3 – the loadings and/or the thermal cycles up to room temperature may arrange the hydrogen in different sites into the crystal structure, with different effects on the transition temperature.

In order to distinguish among the different possibilities, it should be necessary not only a measurement of the mean hydrogen content in the whole pellet, but its effective location. Indeed it may be present both concentration gradients in the grains or in grain boundaries, and different sites in the crystal structure of YBCO. This tangled situation could explain the contradictions among results reported by different authors [1, 2, 4, 13-15] as far as the dependences of both T_c and of lattice parameters on hydrogen content is concerned. Up to now detailed measurements of the hydrogen content in our loaded pellets are not available. Moreover the most of mean hydrogen content measuring techniques cannot be easily used in our case. A systematic X-ray diffraction analysis and the evaluation of the mean hydrogen content by an electrochemical method and by the outgoing gases are in progress.

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