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Further enhancement of the critical temperature up to 105 K of hydrogen loaded YBCO melted samples by μs pulsed electrolysis

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Abstract

We report results about enhancement of the transition temperatures of $Y_1Ba_2Cu_3O_{7-\delta}$ melted samples hydrogen loaded (H-YBCO) with high power μs pulsed electrolysis. The fundamental ac magnetic susceptibility has been measured as a function of the temperature for different frequency values of the exciting magnetic field. The H-YBCO sample exhibited a magnetic onset temperature (T_{on}) as high as 105 K. The susceptibility behavior below the T_{on} shows significant change of shape. Results, previously reported, on a sintered YBCO pellets have been reproduced using melted YBCO samples.

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Keywords: Superconductivity; Hydrogen; Pulsed electrolysis; Susceptibilities; T_c enhancement

1. Introduction

The effects of hydrogen and its isotopes on superconducting properties of metals [1,2] and on superconducting materials [3–8] have been widely analyzed in the past time.

As reported in our previous papers [4,5,8], an increase of the critical temperature of YBCO sintered pellets has been obtained using different loading procedures (gas pressure loading and pulsed electrolysis loading).

A general worsening of the superconducting grain coupling has been observed in sintered H-YBCO [9] and this effect could hide the eventuality of an enhancement of the critical temperature.

However, the hydrogen, inside the YBCO, can dispose in three possible interstitial sites [10]:

(A) between the sites of the Cu(1)–O chain (along the *b*-axis);

(B) in an oxygen vacancy (along the *a*-axis) site;

(C) in some interstitial sites into the yttrium plane; in this case the hydrogen is surrounded by two atoms Cu(2) and four yttrium atoms.

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The interstitial sites of case (C) probably are occupied by a high concentration of hydrogen.

In this paper, susceptibility magnetic measurements of melted YBCO and H-YBCO samples are reported. Moreover, a hydrogen loading procedure is described.

2. Experimental setup and procedure

The ac magnetic susceptibility (herein indicated as $\chi = \chi' + i\chi''$) has been measured using a two-coil coaxial susceptometer. The external coil generates an ac magnetic field and the inner one is used as a pick-up coil. In spite of the higher sensitivity of a bridge configuration, the simpler two-coil system avoids the frequency dependent balance. In order to detect the real part χ' and the imaginary part χ'', we acquire the in-phase and the out-of-phase voltage signals at the pick-up coil by a lock-in amplifier (EG & G 5302). Measurements have been performed with a 7 G ac amplitude magnetic field at 107 or at 1070 Hz. The local earth magnetic field was shielded by a μ-metal screen. The temperature was measured by two platinum thermometers (PT100). One of them was in good thermal contact with the samples (YBCO) located on the sapphire sample-holder device, the other one was just in contact with the sample-holder device. In this way it is easy to check the thermalization of the sample. The temperature measurement was performed by a high-resolution temperature controller (DR91C, Lake Shore Cryotronics) which is moreover used to regulate the sample temperature (from 78 to 300 K operating range).

The thermal cycle procedure used can be summarized as:

(a) Start up from room temperature. The samples are cooled down to $T = 79$ K with a decreasing rate of 5 K/min without ac applied magnetic field (defined as zero field cooling (ZFC));

(b) Thermalization of at least one hour at 79 K;

(c) Begin of measurements with a warming-up rate of 0.3 K/min, up to room temperature. The measurement is performed each second and the data is recorded as an average of many points while the temperature is not varied more than 0.1 K.

The parameters used in this paper are the following:

The onset temperature T_{on} is defined as the temperature corresponding to the beginning of the deviation of χ' and χ'' from the normal magnetic state; its variation is related to the change of the superconducting properties of YBCO (reference state). With respect to this state, the H-YBCO can show an effect which is just generated by the presence of hydrogen inside the grains.

The off-set temperature T_{off} is defined as the temperature corresponding to the end of the deviation of χ' and χ'' from the superconducting transition shape.

The χ'' peak temperature T_{peak} is defined as the temperature corresponding to the maximum value of it.

In the hydrogen loading procedure, the YBCO sample is used as cathode in an electrochemical solution of LiOH (0.1 M). The anode was a nickel passivated grounded cylinder. The electrolytic parameters have been optimized in order to have a high hydrogen loading as follows:

(1) voltage peak pulse was settled at 60 V (corresponding to a peak electrolytic current of 1 A);

(2) duration time of the pulse was settled at 500 ns;

(3) repetition rate of the pulse was settled at 1 kHz;

(4) electrolysis time was about 200 s.

The electric charge passing through the electrode was about 100 mC. In this condition we have about 10 μmol of hydrogen inside YBCO and the loading ratio is $H/YBCO \simeq 0.01$.

3. Experimental results

We performed the hydrogen loading by using melted YBCO high density samples. The samples are slabs quite similar (within $\pm 5\%$) in shape (length 5 mm, height 2 mm, width 4 mm).

The superconducting properties of these samples

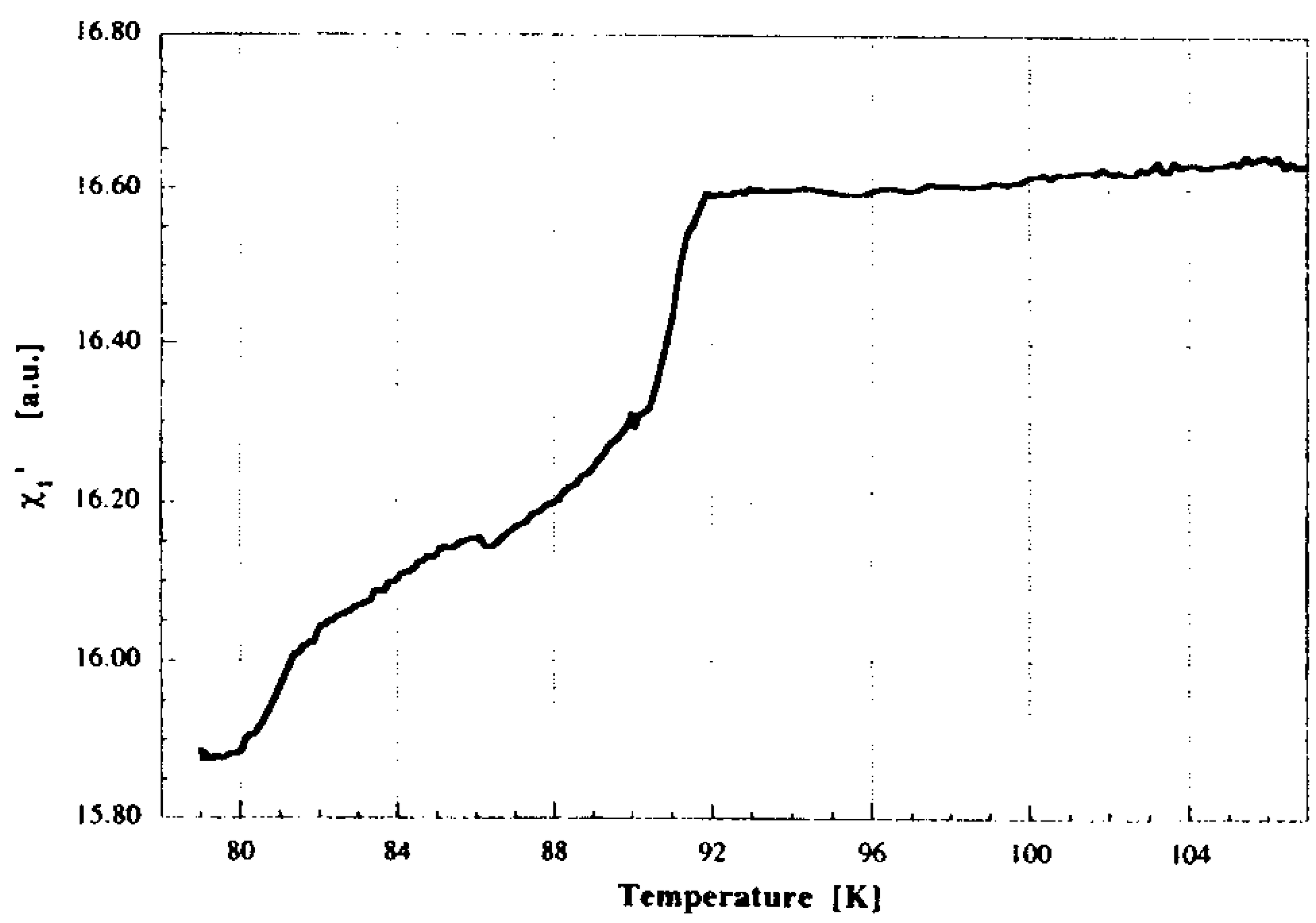

Fig. 1. Behaviour of the real part χ' of the unloaded YBCO sample, $H_{ac} = 7$ G and $f = 1070$ Hz.

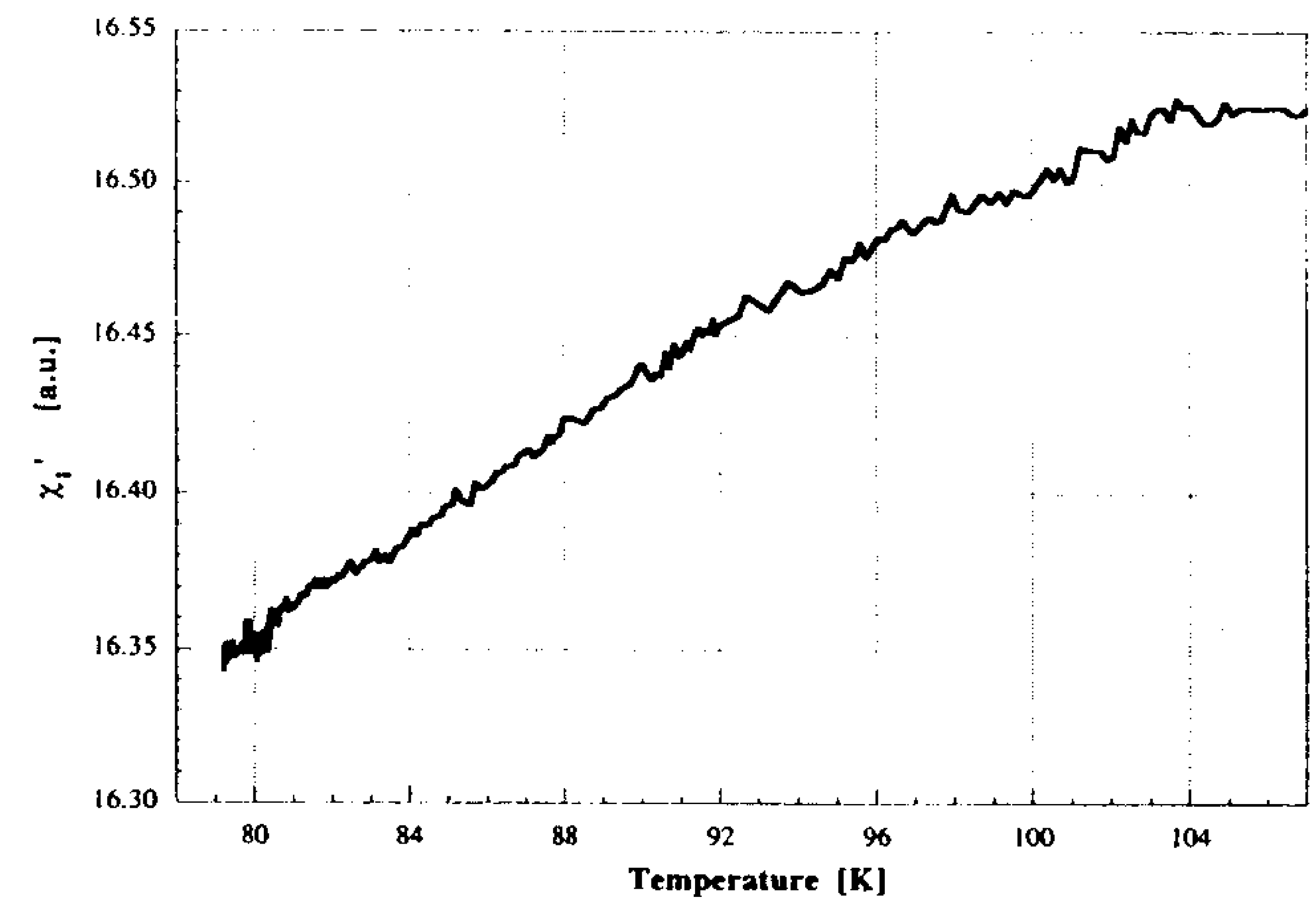

Fig. 3. Behaviour of the real part χ' of the loaded H-YBCO (α) sample, $H_{ac} = 7$ G and $f = 1070$ Hz.

have been measured before and after hydrogenation, in order to compare changing of behavior.

The unloaded YBCO shows (Figs. 1, 2) two phases: an intra-grain phase with T_{on} of χ' and T_{peak} of χ'' at 92 K and an oxygen deficient intra-grain phase with T_{off} of χ' and T_{peak} of χ'' at a temperature of 80 K. This sample shows no good oxygen stoichiometry for both phases, because the $T_{on} - T_{off}$ spread seems to be very large for them.

The loaded sample HYBCO (α) shows (Figs. 3, 4) a very significant change of behavior: the χ' and χ'' T_{on} increase up to 104 K, but the phase at 92 K seems to have disappeared, therefore the oxygen deficient phase at 80 K is still present.

The other sample HYBCO (β) shows (Figs. 5, 6) a more interesting behavior: a very significant χ' and χ'' T_{on} increasing up to 105 K. Moreover, the particular behavior of susceptibility seems to have a convolution at least of four phases: two phases have the same behavior of the unloaded sample while the other two occur after the hydrogenation. These four phases have χ'' peaks at different temperatures, 82 K and 92 K (old phases), 95 K [5] and 103 K [4] (new phases).

With respect to another hydrogen gas loading [3] (H/YBCO up to 50%), in our loading procedure the achieved H/YBCO mean ratio is much lower (H/YBCO roughly 10%).

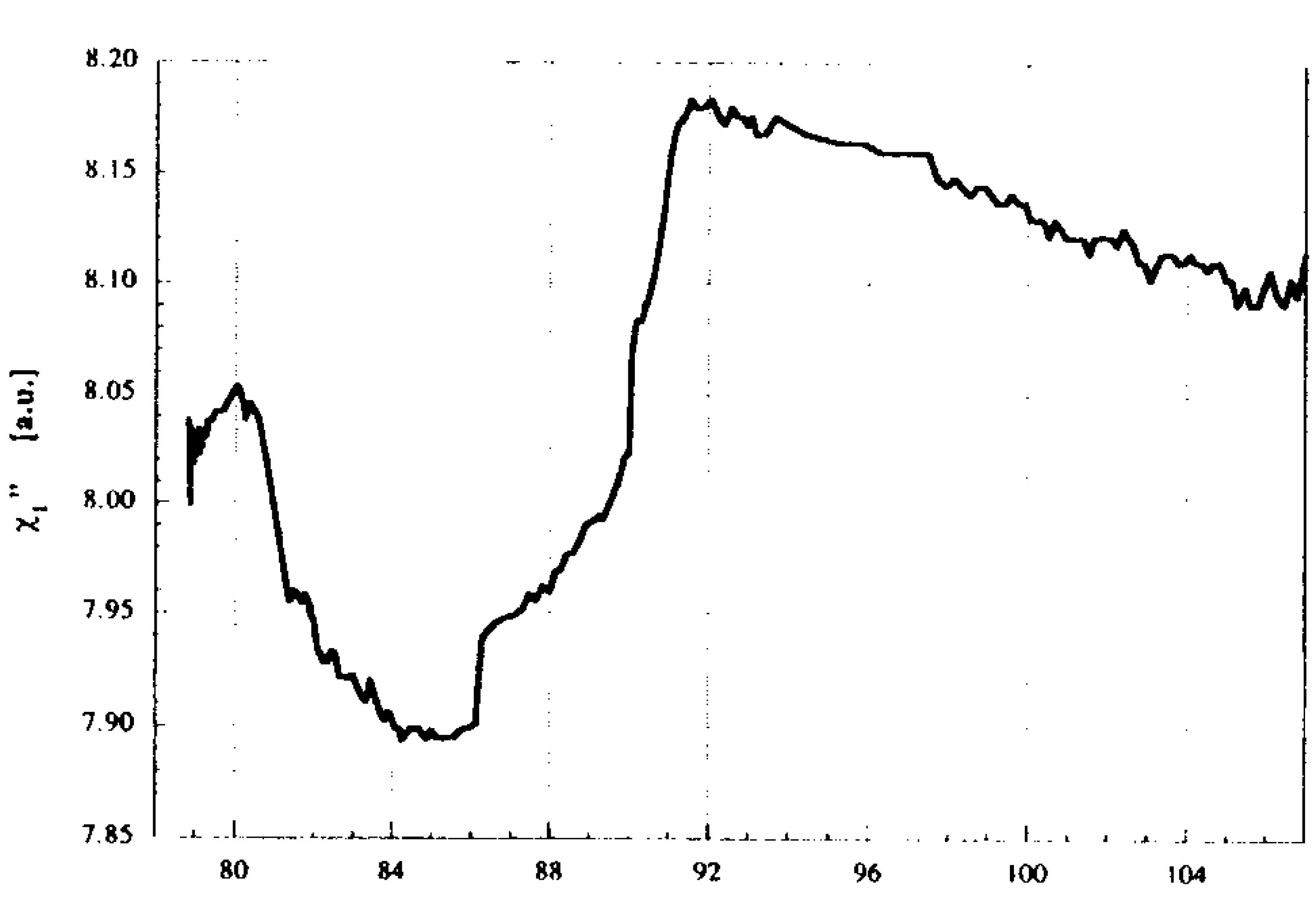

Fig. 2. Behaviour of the imaginary part χ'' of the unloaded YBCO sample, $H_{ac} = 7$ G and $f = 1070$ Hz.

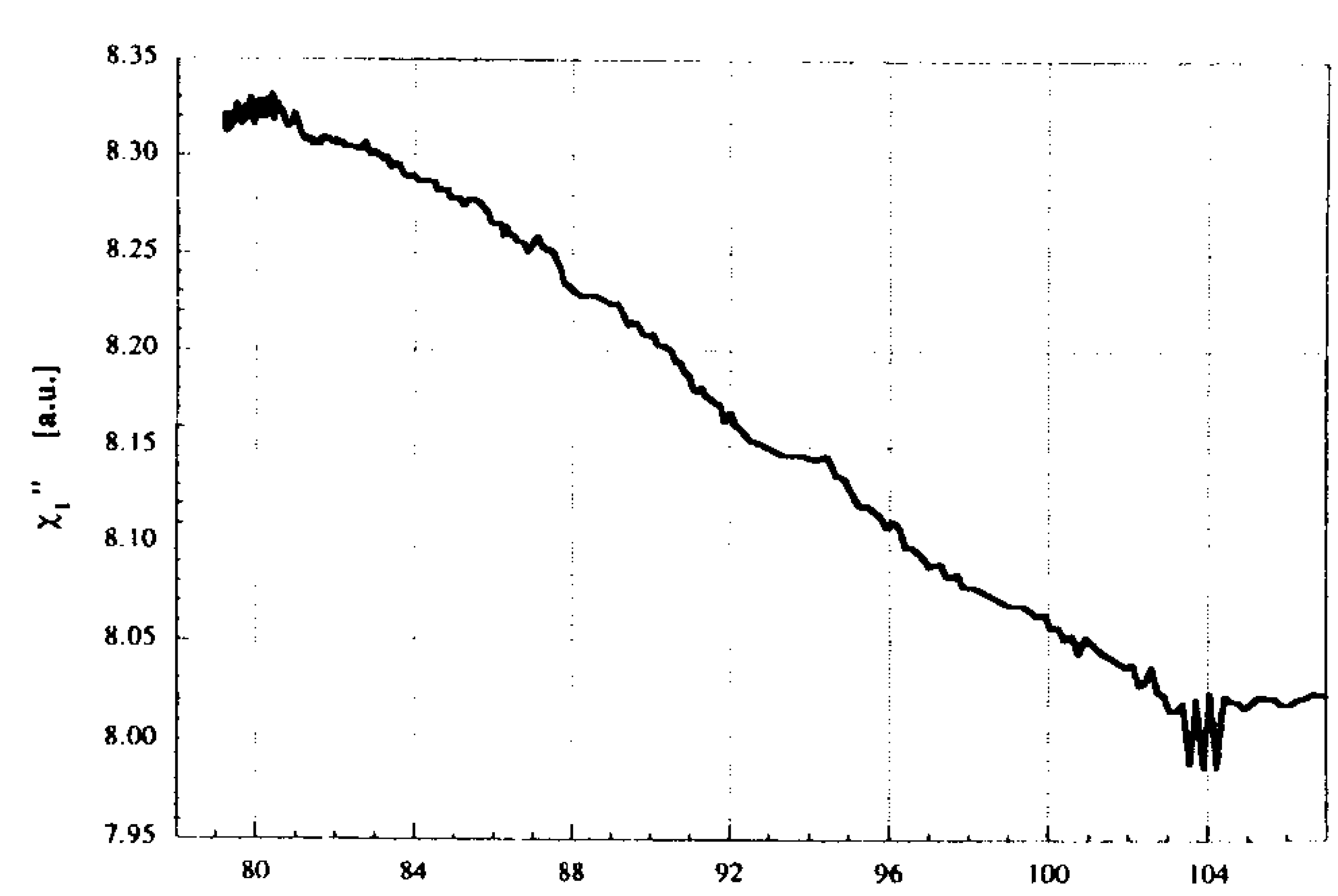

Fig. 4. Behaviour of the imaginary part χ'' of the loaded H-YBCO (α) sample, $H_{ac} = 7$ G and $f = 1070$ Hz.

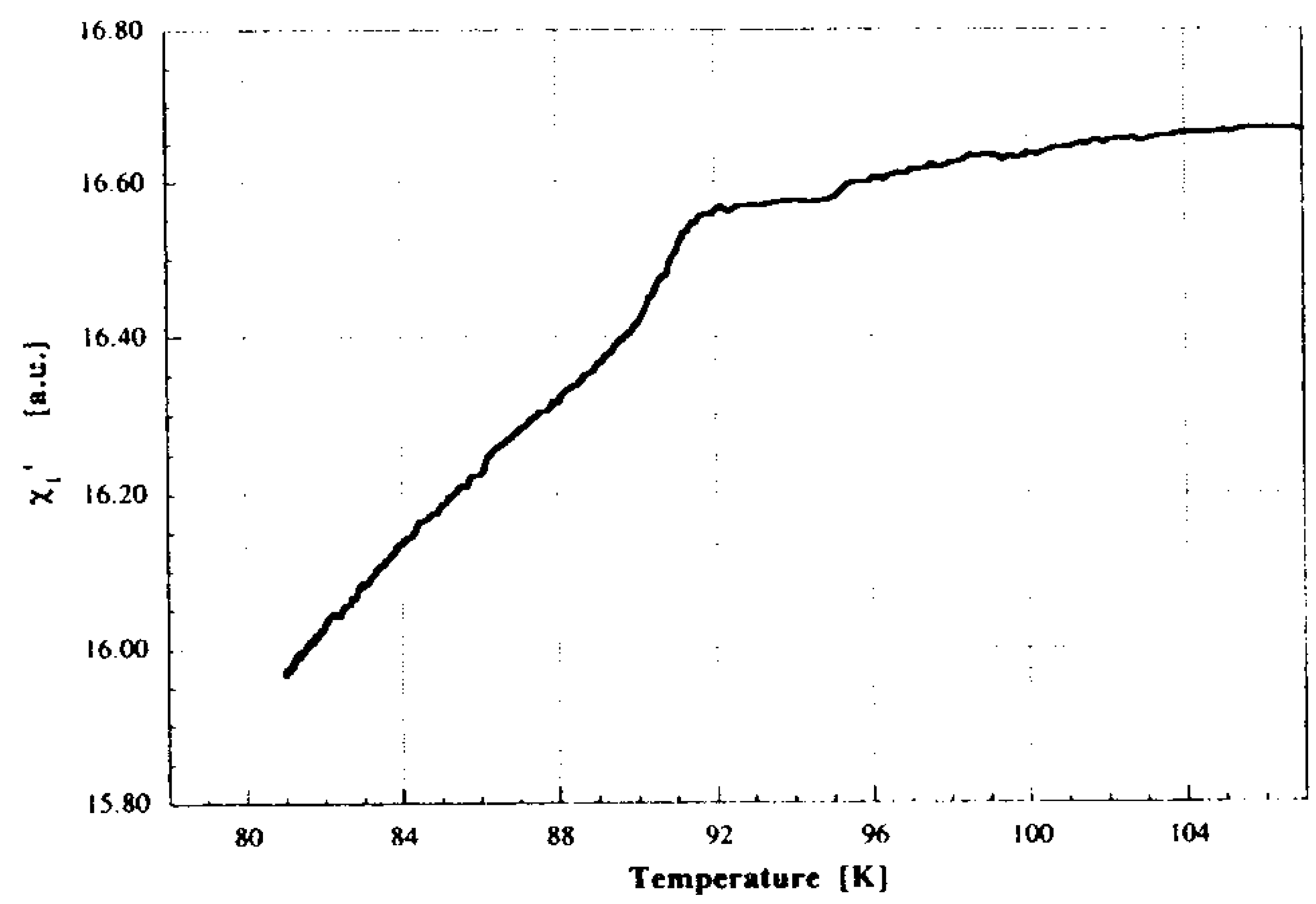

Fig. 5. Behaviour of the real part χ' of the loaded H-YBCO (β) sample, $H_{ac} = 7$ G and $f = 1070$ Hz.

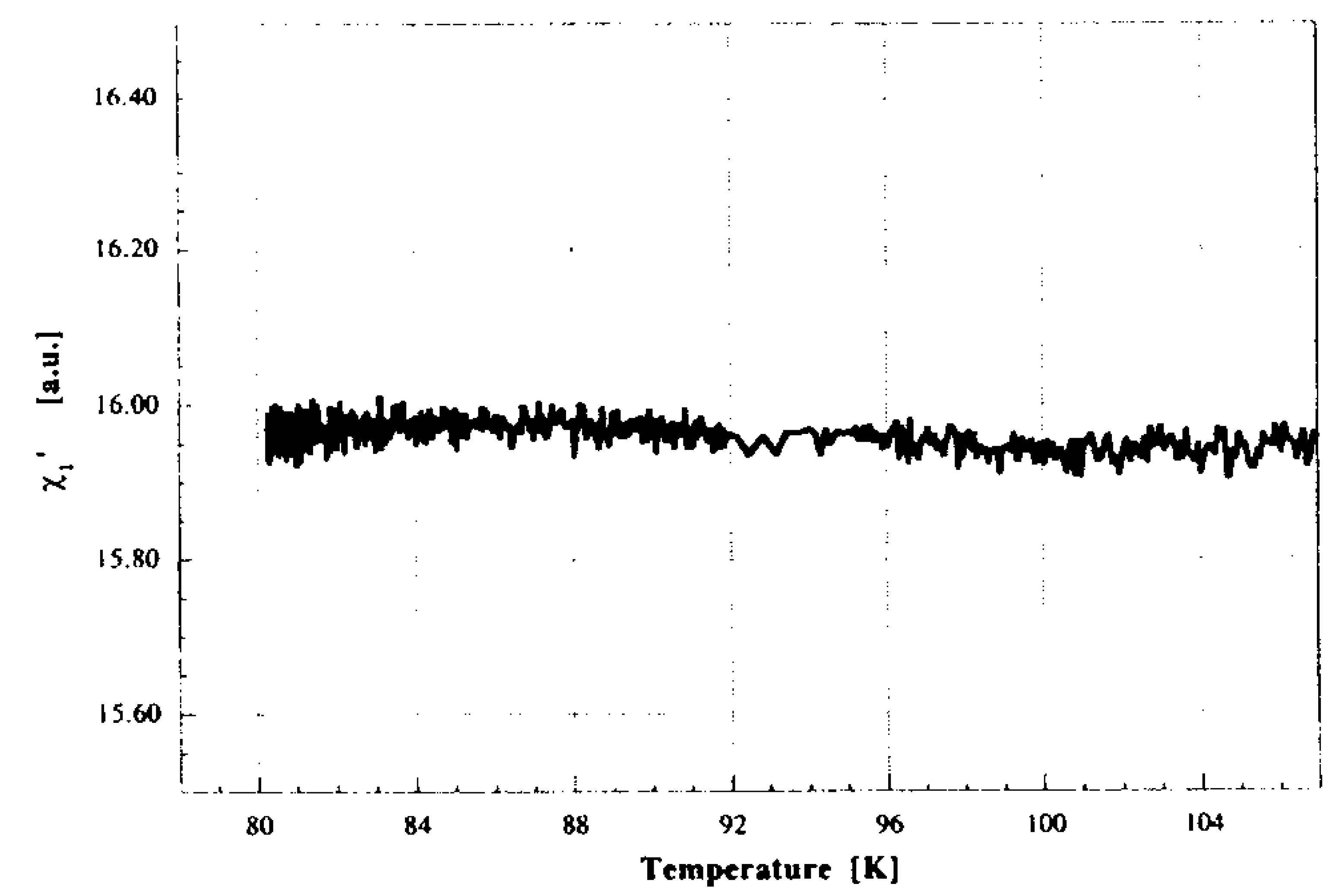

Fig. 7. Behaviour of the real part χ' of the loaded H-YBCO sample, $H_{ac} = 7$ G and $f = 107$ Hz, which shows only normal behaviour with loss of superconductivity after thermic cycles.

Using this very high pulse electrolytic current and very low mean electrolytic current, the sample reaches a high superficial hydrogen concentration in a very short time. This operation is indicated in order to fill fairly the hydrogen into the yttrium sites [11] even if it could distort the tetragonal YBCO structure with consecutive change of the T_{on} susceptibility. In our case, the value of $T_{on} - T_{off}$ of the susceptibility is quite large (20 K) and this means that the sample is still poorly oxygen compounded.

An explanation of this effect can be that we filled with hydrogen the yttrium nearest free sites, and a narrow deformation of CuO planes.

This behavior completely disappears after the operation of two thermal cycles (300 K–77 K–300 K) and the superconducting property also (Figs. 7, 8); only the normal state properties are present. This could mean that during the spontaneous hydrogen deloading (because of the thermal stress), the oxygen stoichiometry is decreased.

This hydrogenation does not damage the samples in an evident way.

In conclusion, these measurements have confirmed that also hydrogen loading in melted YBCO produces a similar enhancement of T_{on} like already verified in sintered YBCO [5].

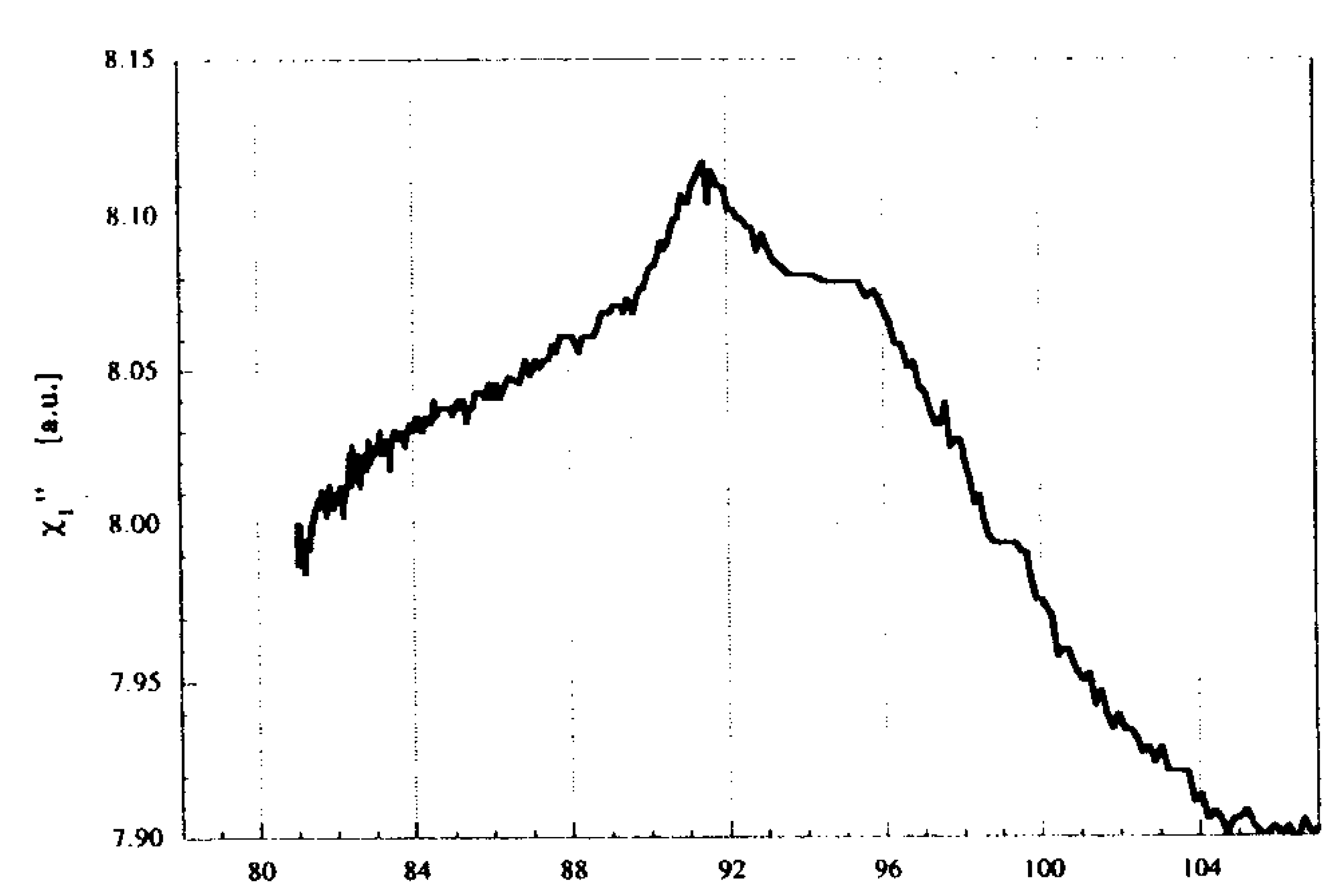

Fig. 6. Behaviour of the imaginary part χ'' of the loaded H-YBCO (β) sample, $H_{ac} = 7$ G and $f = 1070$ Hz.

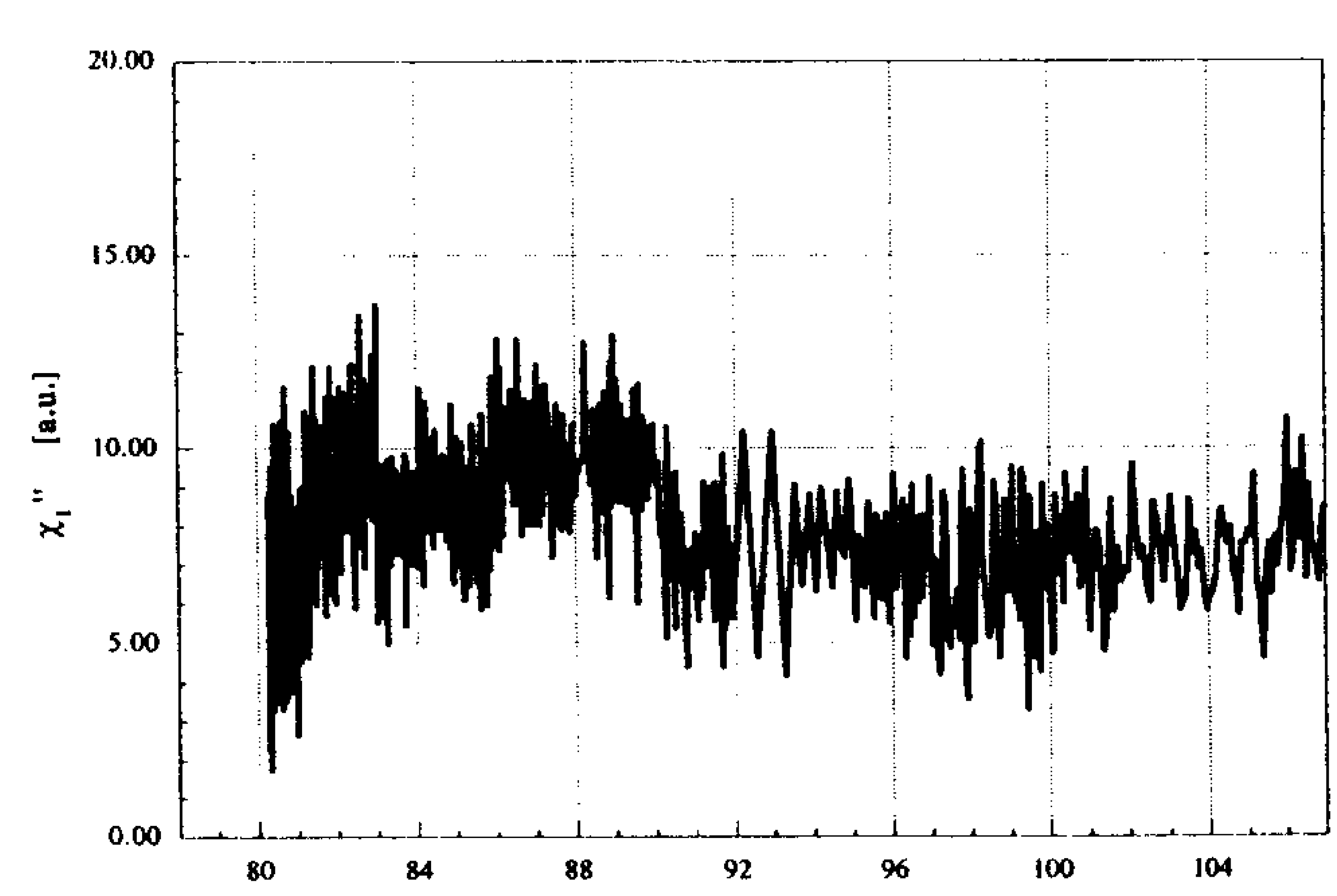

Fig. 8. Behaviour of the imaginary part χ'' of the loaded H-YBCO sample, $H_{ac} = 7$ G and $f = 107$ Hz, which shows only normal behaviour with loss of superconductivity after thermic cycles.

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