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ENHANCEMENT OF CRITICAL TEMPERATURE UP TO 100K OF YBCO OZONE ANNEALED PELLETS BY DEUTERIUM ABSORPTION

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ABSTRACT

In this paper we report preliminary results about transition temperatures of $YBa_2Cu_3O_7$ pellets loaded with high pressure deuterium gas. After the gas loading non–superconducting phases were not detected by X–ray diffraction. The complex magnetic AC susceptibility has been measured as a function of the temperature. One D–YBCO pellet exhibited a magnetic critical temperature (T_c) as high as 100K and the absence of a significant weakening of the superconducting grain coupling. Another sample, with T_c of 95.8K in free air, showed a T_c onset as high as 102K under 35bar of deuterium gas pressure.

1. INTRODUCTION

The effects of hydrogen and deuterium on superconducting properties of metals have been deeply analyzed in the past, showing in particular a large inverse isotopic effect in the Pd–[H,D,T] systems [1,2].

The effects of hydrogen of YBCO has been studied by some Authors [3–10] and it has been shown that hydrogen can decrease [5] or increase [3,4] the critical temperature depending on its stoichiometry and on the kind of bonds with Cu. The hydrogen atoms preferably occupy oxygen vacancies in sites on Cu(1)O plane and Cu(2)O_2 plane [4] or only Cu(2)O_2 plane [5]. However , a general worsening of the superconducting grain coupling is observed [7]. The effects of deuterium have not been deeply analyzed.

In a previous work [11], dealing with "Cold Fusion" researches, some of the Authors explored the effects of large deuterium concentration in appropriate metallic compounds (Pd, Ti, Ti–Al, YBCO). For this purpose, looking for neutron emission (if any) during non–

equilibrium conditions, different loading procedures have been tested. After a 35 bar loading procedure [11], the superconducting transition temperature T_c of deuterated YBCO (D–YBCO) pellets was equal to T_c=95.8K, in comparison with the usual T_c of 92K. At 77K the susceptibility measurements showed a weaker shielding properties compared with the same pellet before deuterium loading. This probably means that the non–superconducting phase in the samples was increased, due to hydrides in a solid solution with YBCO [4].

In this paper we show preliminary results about transition temperatures of YBCO pellets prepared and loaded with high pressure deuterium gas in two different procedures. In section II the two different experimental apparatus are described. In section III improvements to the sample preparation, the deuterium loading procedures and experimental data are reported and discussed.

2. – EXPERIMENTAL SET–UP

In order to have the possibility of testing the superconducting features both in equilibrium and high pressure thermodynamic non–equilibrium conditions, the samples were characterized by measurements of AC shielding properties using two experimental set–up.

In the first set–up the AC magnetic susceptibility is measured using a two–coils coaxial susceptometer. The external coil generates the AC magnetic field, the inner one is the pick–up coil. The reported measurements have been obtained after subtraction of instrumental blank, stored in the data–acquisition computer. The blank measurements have been performed by substituting the superconducting sample with a teflon disk of the same geometrical dimensions. In spite of the higher sensitivity of a bridge configuration, the simpler two–coils system avoids the frequency dependent balance; moreover, the large volume of the pellets do not require, in our measurements, high signal sensitivity. In order to detect χ' and 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 5208). The susceptometer calibration, and in particular the real part χ' of the susceptibility, has been previously obtained (at 4.2K) by means of lead samples with the same shape of the pellets. Measurements has been performed with a 1G amplitude of the AC magnetic field at 107 Hz. The local earth magnetic field was shielded at 0.2G. The temperature is measured by a silicon diode (DT470SD12, Lake Shore Cryotronics), in good thermal contact with the sample, through an high–resolution temperature controller (DR91C, Lake Shore Cryotronics). Starting from room temperature, the samples are cooled down to T=77K with a decreasing rate of 15 K/min under the AC applied magnetic field (Field Cooling, FC). After at least one hour at 77 K the measurements have been performed with a warming up rate of 0.3 K/min, up to room temperature.

In the second experimental set–up, in order to test the transition temperature in high pressure thermodynamic non–equilibrium conditions, a simpler susceptometer has been used by means of the "inductance–variation method". Due to the small dimensions of the high pressure gas cell we have used a single–coil, driven with 1G AC at 1KHz, containing the sample. The coil inductance has been measured by a LCR meter (HP4262A) and its dependence

from the temperature has been measured with an heavy–duty j type thermocouple (Fluke). The measurements were acquired during the warming up.

All measured quantities are recorded by a computer–controlled acquisition system by HP–IB bus.

In the following, the transition temperature T_c is defined as the temperature corresponding to a value of χ' equal to the 10% of the complete shielding value. Analogously, the transition width ΔT_c is defined as the difference between T_c and the temperature corresponding to a value of χ' equal to the 90% of the complete shielding value. The thermal equilibrium of both measurement systems has been checked by means of measurements of transition temperature of non–deuterated YBCO samples: they showed a T_c of 91–92K depending on the sample quality.

3. – LOADING PROCEDURES AND EXPERIMENTAL RESULTS

We performed the deuterium loading by using superconducting high quality pellets. YBCO pellets have been prepared with a modified citrate pyrolysis procedure and only two subsequent thermal treatments (calcination and sinterization) in ozone enriched atmosphere [12]. The samples are quite similar (within ±5%) in shape among them (diameter 20 mm, height 5 mm). The pellets quality has been checked by X–ray diffraction and AC susceptibility: spurious phases are not detectable within 5% accuracy. All the samples fabricated in the same batch and measured at 0.2, 1, 10G at 107Hz showed a similar diamagnetic behaviours.

For the first loading procedure we have used pellets prepared in our standard way [12].

The deuterium loading procedure [11] can be summarized as following:

a) the sample was put into a stainless steel vessel filled with high pressure (35 bar) deuterium gas (99.8% pure) at room temperature;

b) the vessel and the sample temperature was raised by a controlled heater, up to 90^0C, until the pressure decrease was at least 1 bar: higher temperatures, although reduce deuterium loading time, can lead to an irreversible damage of the sample;

c) soon after, in order to avoid excessive self–heating, we decreased the temperature of the heater down to 80^0C and we waited until the pressure decrease was over;

d) at this time, we lowered the temperature quite abruptly down to 20^0C to reduce the absorption process almost completely. We can estimate, by pressure drop in the cell, an average loading factor of deuterium of 0.5. The loading factor is an average value because, generally speaking, some gradients of concentration exist between the internal and external side of the sample and this effect can be expected in our dense and thick (6 mm) samples.

The shape of the samples does not significantly change after gas loading process.

The superconducting properties have been tested even under high pressure conditions of deuterium gas. Starting at room temperature, with the vessel at a D_2 pressure of 35bar, the sample was cooled down to 77K. During the cycle from 77K to 300K, we measured the transition temperature by the "inductance-variation method". As shown in Fig.1 we observed that the onset temperature was as high as 102K.
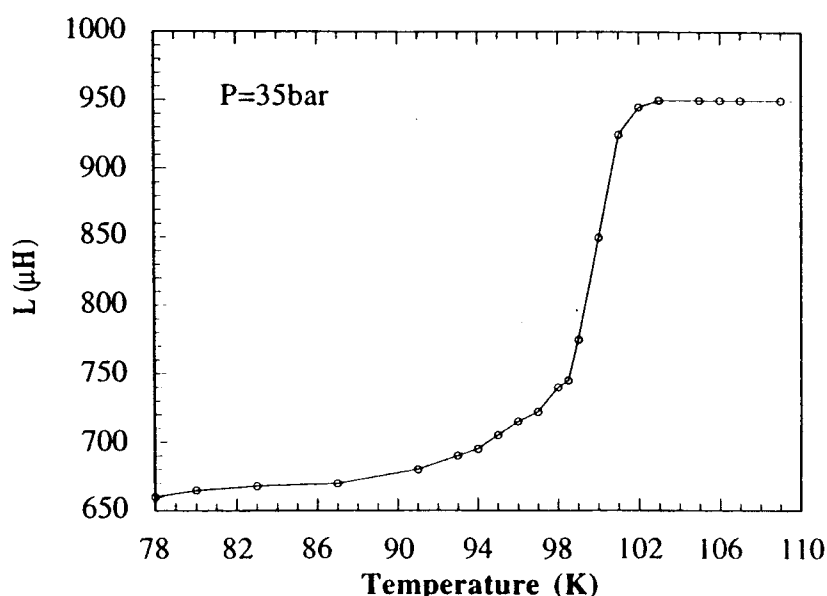
FIG. 1 – Diamagnetic behaviour of the sample (Series DYBCO-101) under 35bar D_2 pressure by self-inductance variation method. The onset temperature is 102K.

However, the large enhancement of T_c is unstable: the sample afterwards measured at room pressure shows a transition temperature of about 95.8 K.

The instability before described forced us to try some changes both to the sample preparation and to the gas loading procedures.

We operated as following:

I) basically we did not vary the preparation procedure [11], except for the atmosphere used during the "calcination" process: instead of using ozone-enriched oxygen atmosphere, we used clean dry-air enriched with 1-2% of O_3. Following some Authors [8], the N_2 gas atmosphere (~77% concentration) does not directly influence the sample preparation but it changes the dynamic processes during the calcination. The sinterization is made under a pure O_2 atmosphere with 5% enrichment of O_3;

II) we made two thermal cycles at different deuterium gas loading pressures, shown in Figs. 2,3: we performed a second slightly modified cycle.

In the first gas loading cycle, at the beginning, the pellets were exposed to D_2 gas at a pressure of P=40bar. After the heating up to 95^0C–97^0C, when the reaction cell pressure was decreased of at least 2bar, we switched off the heater and we waited for the pressure stabilization. Then, we filled the cell again with D_2 gas up to P=42bar at 40^0C.

In the second gas loading cycle, when the deuterium pressure went down, we refilled the cell with D_2 gas up to P=53bar and we kept for 200 min. the pellets at 95^0C, then we switched off the heater. In this procedure the loading factor has been measured by weighing the sample

before and after the loading. The deuterium loading factor was 0.23 in the first cycle and about 1 in the second one.
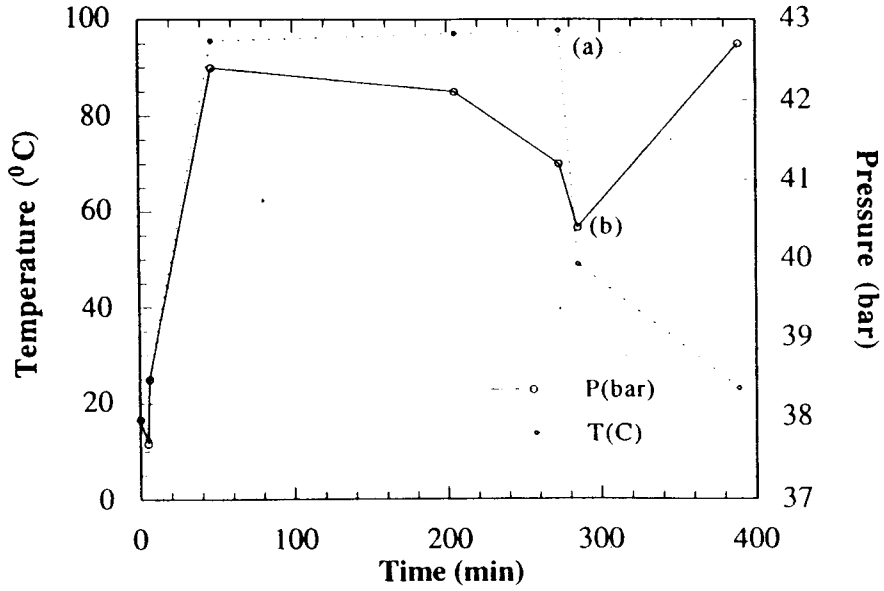

FIG. 2 – First D_2 gas loading procedure for the DYBCO–201 samples. In (a) we switched off the heather, in (b) we refilled the D_2 gas.
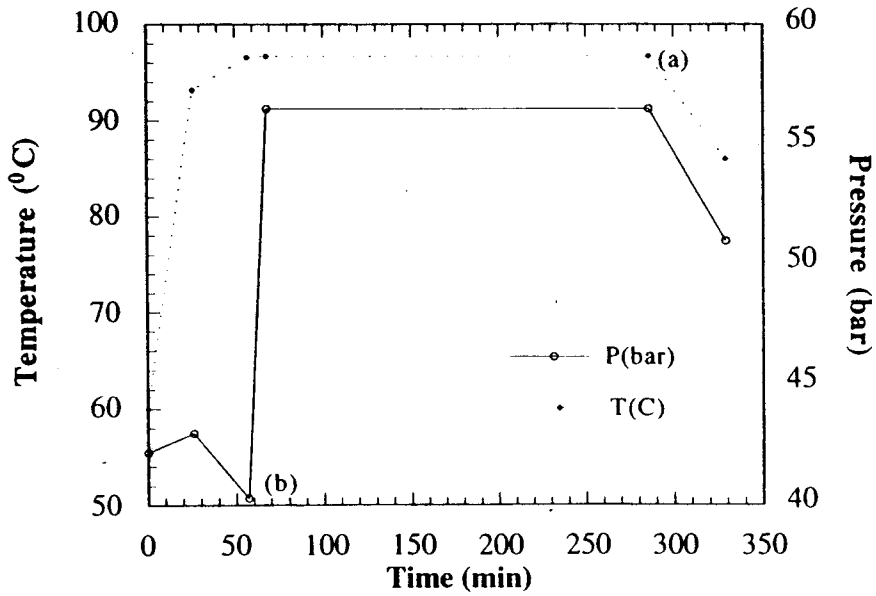

FIG. 3 – Second D_2 gas loading procedure for the DYBCO-201 samples. In (a) we switched off the heather, in (b) we refilled the D_2 gas.

The superconducting properties of these samples have been measured by the susceptometer described in the section II. The temperature dependences of the real part of AC susceptibility χ' of the loaded samples are shown in the curves β and γ of Fig. 4. For comparison, we show in the same figure the behaviour of a non–deuterated sample (α): we can observe that the transition temperature is 92.3K and the transition width is 2K for a 2 years–old aged sample. This plot shows two features:

1) the onset transition temperatures of samples β and γ are respectively 97.8K, 100K;

2) χ' values at the superconducting state were almost the same before and after deuterium loading. This denotes that, in the deuterium loading of these specific samples, no large fraction of intergrain volume becomes non–superconductive.
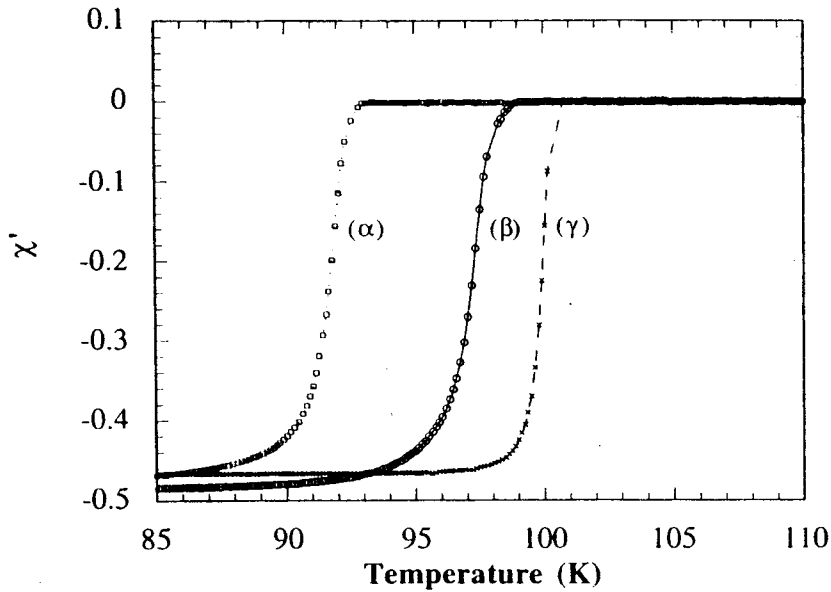

FIG. 4 – Real part of the magnetic susceptibility (χ') for 3 YBCO samples (Series DYBCO-201). (α) YBCO pellet before D_2 loading; (β, γ) YBCO pellets after D_2 loading.

In Fig. 5 the temperature dependences of χ'' is shown. This plot shows the following features:

1) the onset transition temperatures are corresponding to the ones of χ';

2) the FWHM (Full Width Half Maximum) of the peaks of β and γ are very similar while the FWHM of the sample α is lower;

3) the peaks heights of the samples β and γ are greater than the one of the sample α.

If the deuterium loading would generate spurious phases, these ones would precipitate on the grain boundaries. These phases would reduce the Josephson coupling among the grains and, as a consequence, the critical current of the samples. This would lead to:

1) a broadening of the superconducting transition, with lower values of $|\chi'|$ if compared with the corresponding ones before the loading and an incomplete shielding even at 77K;

2) a broadening of the peak of χ'', a lowering of the value of this peak and value of χ'' at 77K higher than the one in the normal state.
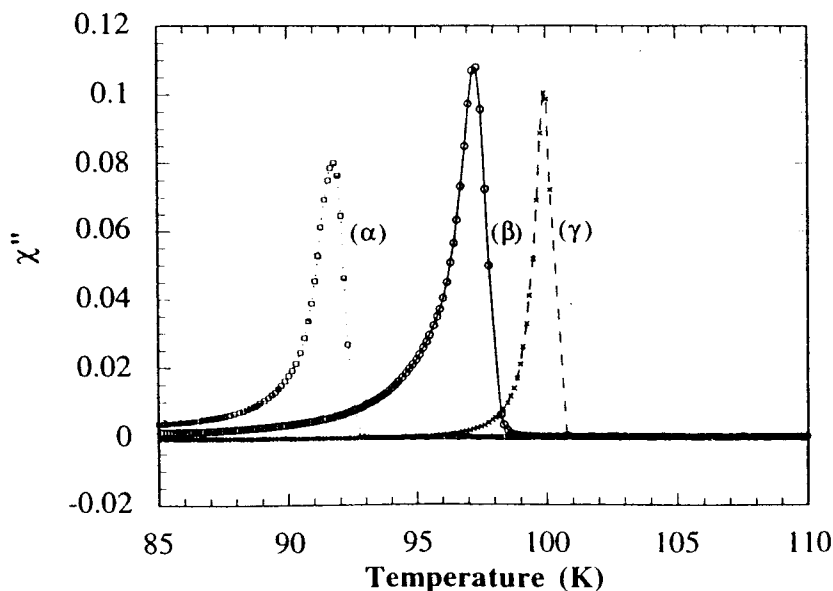

FIG. 5 – Imaginary part of the magnetic susceptibility (χ') for 3 DYBCO-201 samples. (α) YBCO pellet before D_2 loading; (β, γ) YBCO pellets after D_2 loading.

These statements are usually reported in literature [3] where, typically, the effects of deuterium loading are the increase of the critical temperature and the worsening of the intergranular coupling, of the order of 40% and more. As previously described in the Fig. 4 and 5, we observe a nearly opposite behaviour: our deuterium loading did not generate a weakening of the intergranular coupling and, as a consequence, it did not generate spurious phases on the grain boundaries.

We checked the stability of the superconducting properties in air for 1 year: this long time did not lead to the decomposition of the sample [10] or to loss of superconducting properties. However, after 2 thermal cycles 300–77–300K, we experienced a large reduction of the superconducting temperature down to about 91K, very close to the value measured before the deuteritation. After the last measurements we checked the quality of the composite again by X-ray diffraction: we did not find any spurious phases and any significative variations in the lattice parameters.

In conclusion we obtained a D–YBCO ozone stabilized pellets of good superconducting properties. The maximum value of the magnetic T_c was 100K. We loaded YBCO pellets even with hydrogen: we obtained a maximum T_c of 97.5K. Anyway we remark that all these data are preliminary and a systematic work, about the dependence of T_c from the loading conditions and the comparison between the deuterium and hydrogen loading, will be published in the next future.

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