IRRADIATION ENHANCEMENT OF SUPERCONDUCTIVITY. A MULTIHARMONIC STUDY*

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Received September 26, 2005

We have found in multiharmonic magnetic susceptibility experiments that neutron irradiation of high temperature superconductors produces a depression of the superconducting characteristics (critical temperature and Meissner screening) at moderate fluence 0.98×10^{17} neutrons/cm^2 and an unexpected enhancement of the intragranular superconducting properties at 9.98×10^{17} neutrons/cm^2. In contrast, the intergranular properties support a continuous suppression. We assume that this behavior is the result of the change of the nature of defect distribution at high fluence, when the uniform distribution of defects starts to develop space instabilities as a result of the subtle interplay of the in-cascade rate of interstitial loops production, cascade collapse of the vacancy loops, and the excess network bias.

Key words: neutron irradiation, radiation damage, multiharmonic susceptibility, $YBa_2Cu_3O_7$.

1. INTRODUCTION

Defects in superconductors are a topic of peculiar interest because their structure, size and dimensionality trigger the current carrying capacity, hence, one major application of superconductors. Therefore, tailoring the defect structure is one of the most important challenges in high temperature superconductors (HTS) from experimental point of view.

It is recognized that the defects has the key role in the pinning of the vortices driven by the transport current. Their motion generates dissipation in superconductors. Generally, it is accepted that in superconductors, efficient defects are those ones of size comparable to the Ginzburg-Landau coherence

* Paper presented at the National Conference of Physics, 13–17 September, 2005, Bucharest, Romania.

length ξ_{ab}. In HTS, ξ_{ab} is of the order of the lattice parameter and, consequently, their production with a homogeneous distribution is a complicated task.

One way to create such uniformly distributed pinning centers is the use of irradiation with nuclear particle. Charged particles, however, are valuable only for low size systems (films and whiskers) because of their short path within materials. Therefore, the most promising method is the use of neutrons of any energy which, due to their electrical neutrality, possess a long mean free path, $\lambda \approx 1 \div 10$ cm, which is comparable with the sample size.

HTS displays a structure with multiple sublattices each one populated with ions whose atomic masses are spanned from oxygen to barium. Moreover, there is also a free charge with a very anisotropic distribution. Therefore, the result of the interaction of HTS with the neutron is extremely complex and sometimes gives rise to surprising results.

The primary defects, vacancies and interstitials, created by irradiation have in solid a different kinetics due to their different mobility. Additionally, their diffusion and recombination is strongly controlled by the peculiar structure, temperature and pre-irradiation defects. The coupled nonlinear equation which depicts the whole process possesses a bifurcation point where the homogeneous solution could become spatially unstable and develop special distribution of the defects [1–6].

Most experiments report a continuous degradation of the critical temperature T_c and an enhancement of the critical current density J_c subsequent irradiation. However, there are also papers claiming an enhancement of the critical temperature for fluences around 10^{16} cm^{-2} associated with a slight decrease of the critical current density [7, 8]. The effect was attributed to the prevalence of radiation stimulated recombination rate of the pre-irradiative defects over the defect generation [9].

For the first time, we report the evidence of the self-organizing of the damages observed in magnetic susceptibilities at neutron fluences higher than 5×10^{17} cm^{-2}.

2. EXPERIMENTAL

$YBa_2Cu_3O_{7-x}$ ceramics were produced by solid state reaction from high purity reagents: Y_2O_3, CuO, and $BaCO_3$. The reagents were calcined at 930°C for 20 hours, The product was reground, pressed in bar shapes of $2.7 \times 2.9 \times 9$ mm^3, and sintered in flowing oxygen for 16 hours at 936°C. X-ray diffraction patterns samples reveal the pure orthorhombic phase but small amounts of $BaCuO_2$, are also present.

In the case of HTS, the use of thermal neutrons has a draw back arising from the small effective cross section σ of the atomic constituents. This disadvantage can be overwhelmed by inserting high σ atoms within superconducting matrix [10]. The main requirement is the absence of any deleterious effect on superconductivity of the inserted atoms. The best candidates are lithium [11–14] and uranium [15–17], which display a very large cross section and match well with HTS materials. Therefore, a small amount of lithium fluoride LiF (2 at. % Li) was added in the process of synthesis of the compound.

The pellets were sealed in quartz ampoules and irradiated in standard aluminum blocks suspended in the center of the channel 36/6 of the reactor VVRS from the IFIN-“HH” Magurele with a neutron flux density of 2.13×10^{13} cm^{-2}sec^{-1}. Immediately after irradiation, the sample activity was between 1.8 μR and 80 μR. For that reason, the samples were stored for seven days in the hot chamber. It is to note that $YBa_2Cu_3O_{7-x}$ shows the lowest activity among all rare earth cuprates [18] after neutron irradiation.

The dependence of the electric resistance on temperature was measured by four point method and the critical temperature was determined at the inflection point of the normal superconducting transition. For the virgin sample we obtained $T_c = 93.6$ K.

The *ac*-susceptibility, including the higher harmonics, was measured with a home made susceptometer with an *ac* driving magnetic field of amplitude equal to 0.6 mT at a frequency of $f = 1070$ Hz. The temperature was measured with a platinum thermometer (PT100) in thermal contact with the samples. The measurements were performed on sweeping the temperature at a rate of 0.3 K/min up to a temperature greater than the zero field critical temperature. The induced signal has been measured with a multi-harmonic EG&G lock-in amplifier. The *dc* magnetic field was in the range from 0 to 2 Tesla. Both *ac* and *dc* fields were applied parallel to longest size of the sample.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the evolution of the critical temperature under neutron irradiation as obtained from resistance *R vs.* temperature *T* measurements. The critical temperature decreases constantly with more than 1 K when the fluence increases from zero to 4.9×10^{17} cm^{-2}. Surprisingly, T_c increases again with 0.5 K for a further increase of the fluence up to 9.98×10^{17} cm^{-2}, Even though this increase is small, it is unexpected at highest fluence where the creation of damages is supposed to reach a maximum if only the generation-recombination processes of the defects are considered.

For a further insight, we proceeded to an investigation of the response of the samples in *ac*-magnetic field which is able to provide simultaneously information on both *intragrain* and *intergrain* modifications under irradiation.

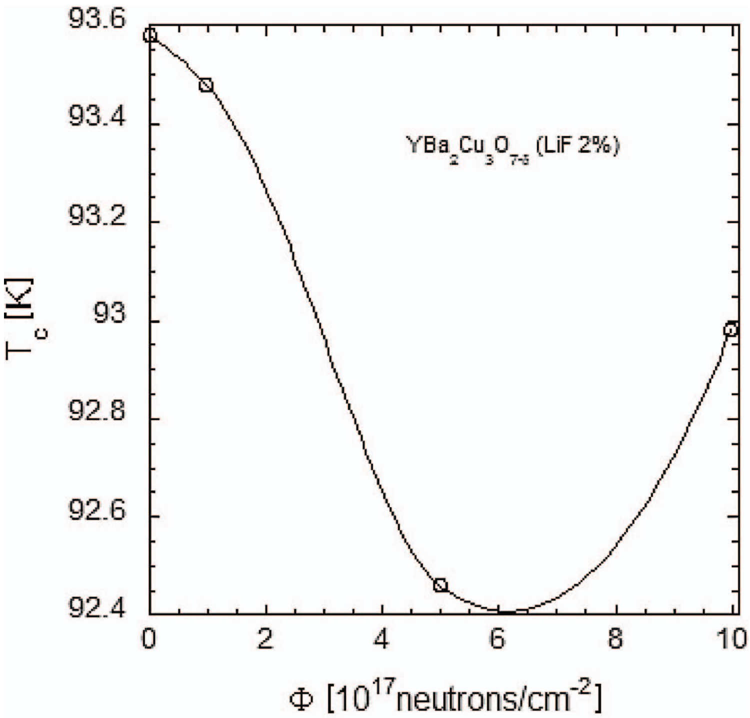

Fig. 1. – The dependence of the critical temperature T_c of irradiated polycrystalline Li-doped $YBa_2Cu_3O_{7-x}$ on the neutron fluence Φ. The solid line is guide for the eye.

The imaginary part of the fundamental harmonic χ_1'', which reflects the loss of energy during one *ac*-cycle, is presented in Fig. 2 for the virgin (unirradiated) samples for different *dc*-fields between zero and 2 T. The effect of field is to remove the overlapping of the inter- and the intragranular signals. This is the result of the different robustness of the superconductivity in the two contributions. Indeed, the superconductivity within grains has the upper critical field H_{c2} extremely high, thus, it is difficult to suppress the nucleation of the superconductivity. The *ac*-field penetrates up to the center of the grains and gives rise to the maximum dissipation only very close to T_c. The increase of the field shifts slightly the intragranular peak toward lower temperatures in agreement with the slow T_c *vs.* field dependence for $H << H_{c2}$. Specifically, the intragranular peak, marked with arrows in Fig. 2, shifts with almost 8.5 K for an increase of the field of 2.0 T.

The intergranular response reflects the response of space connecting grains which consists of weak or nonsuperconducting material. The structural and electronic characteristics of this material display a broad distribution which is

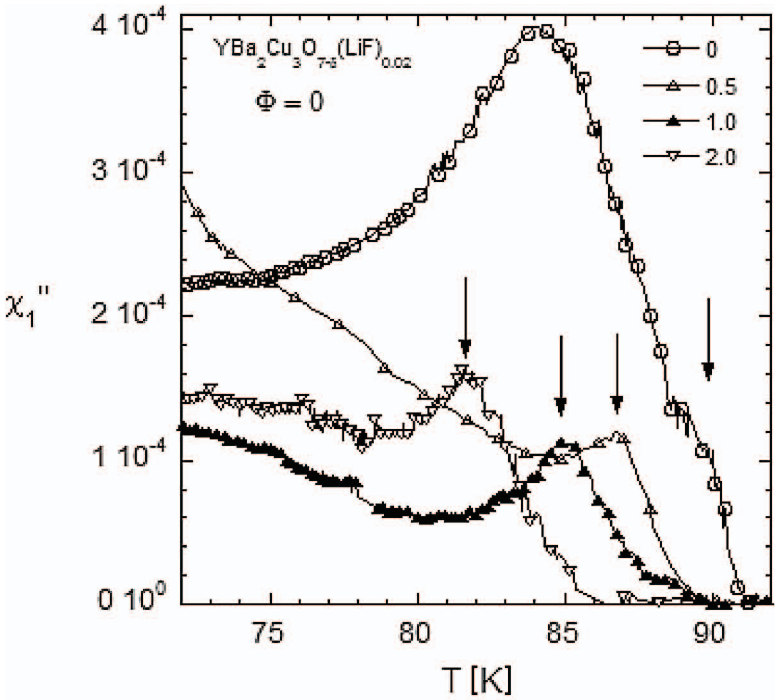

Fig. 2. – The imaginary component χ_1'' of the fundamental harmonic of the *ac*-susceptibility of the unirradiated polycrystalline Li-doped $YBa_2Cu_3O_{7-x}$ ceramics as a function of temperature *T* for the following *dc*-fields: 0; 0.5; 1.0, and 2.0 T. The arrows point to the intragranular peak.

reflected in the breadth of the intergranular, large peak seen at 84 K and zero *dc*-field. Due to the Josephson connections, the penetration of the field is denied at low temperature, but at higher temperature the *ac*-field penetrates up to the center of the sample (at the peak temperature of the intergranular response). However, the field penetration is still denied within grains. *DC*-magnetic fields smaller than the upper critical fields ($H_{c2}(0) \sim 10^2$ T), but much higher than the amplitude of *ac*-field ($h_{ac} \sim 10^{-4}$ T), are able to destroy the Josephson connections and penetrate the sample even at low temperature. Therefore, the intragranular peak is continuous shifted to very low temperatures as the *dc*-field increases. In Fig. 2, the intragranular peak is noticed at nonzero fields only as an increasing tail which extends below the 72 K, the limit of our measurements. The dissimilar shifts of the inter- and intragranular peak permit a better discrimination between the two kind of responses which becomes more and more obvious at higher field. To be specific, in zero field, the intragranular peak emerges only as a shoulder at high temperature but develops into a well defined peak at the highest field used in our measurements (2T).

Neutron irradiation at a fluence of 0.98×10^{17} cm^{-2} emphasizes the effect of the magnetic field. As can be seen in Fig. 3, the response at any *dc*-field shows an improved separation of the intragranular peak. Nevertheless, the peaks are larger, with the amplitude reduced almost three times, except in zero field where it is roughly constant. The fact that the irradiation conjugate with the field putting emphasis on the intergranular response could be the results of the inserted damages predominantly in the region between grains. However, the reduction of the amplitude of the intragranular peaks and their slight broadening in comparison to the unirradiated case suggests that disorder is induced also within grains.

A further increase of the neutron fluence to 9.98×10^{17} cm^{-2} turns out a considerable change in the intragranular response (Fig. 4). The corresponding peaks recover almost the whole amplitude displayed by the virgin samples. Additionally, the width of the peaks is narrower than at lower fluence and very well discriminated from the intergranular background.

Fig. 5 shows the third harmonic $|\chi_3|$ of the unirradiated sample at different applied magnetic field. By comparison with the first harmonics and its

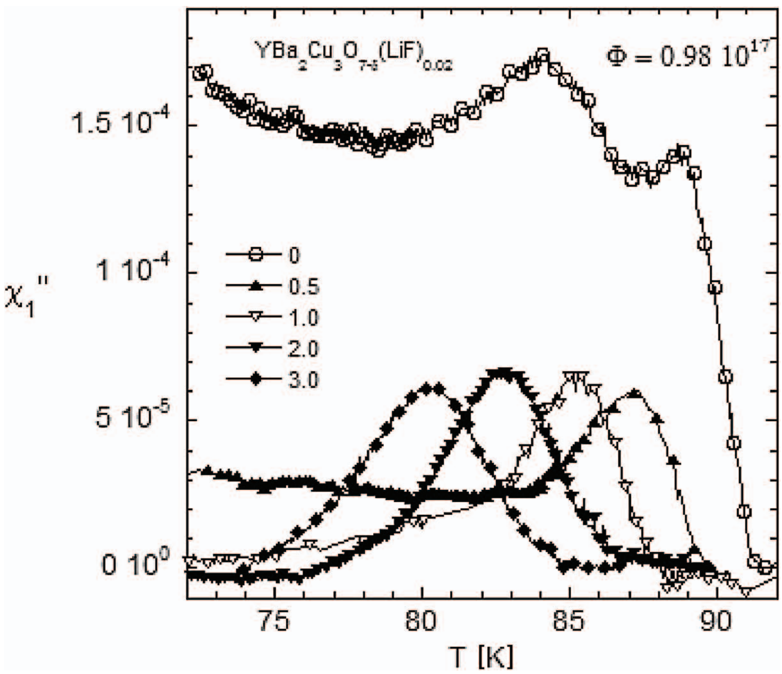

Fig. 3. – Temperature dependence of the imaginary component χ_1'' of the fundamental harmonic of the *ac*-susceptibility of polycrystalline Li-doped $YBa_2Cu_3O_{7-x}$ ceramics irradiated with neutrons at a fluence of 0.98×10^{17} cm^{-2} as a function of temperature T for the following *dc*-fields: 0; 0.5; 1.0; 2.0, and 3.0 T.

dependence on the magnetic field, we are able to attribute the small peak at high temperature to the intragranular response and the larger one to the intergranular response. When the field increases, the signal is depressed and the peaks are shifted to lower temperatures.

The higher harmonics reflects the non-sinusoidal reaction of the magnetization to a sinusoidal applied field. The non-harmonic response is inherent to HTS due to the nonlinear resistivity generated by the flux diffusion in a pinning landscape. There is no analytic model to describe the third harmonics even though a large number of papers have considered the topic [19–21]. However, it is accepted that the irreversible processes are better reflected in $|\chi_3|$ than in χ_1. The field suppression of $|\chi_3|$ is the result of the changes in the flux profile, hence, in the dependence of the pinning energy on the current density.

After the submission to the neutron irradiation at the fluence of 0.98×10^{17} cm^{-2}, the third harmonic is reduced more than two times (Fig. 6). Differently from the fundamental signal, the intragranular peaks become less separated from the intergranular response getting the appearance of a shoulder.

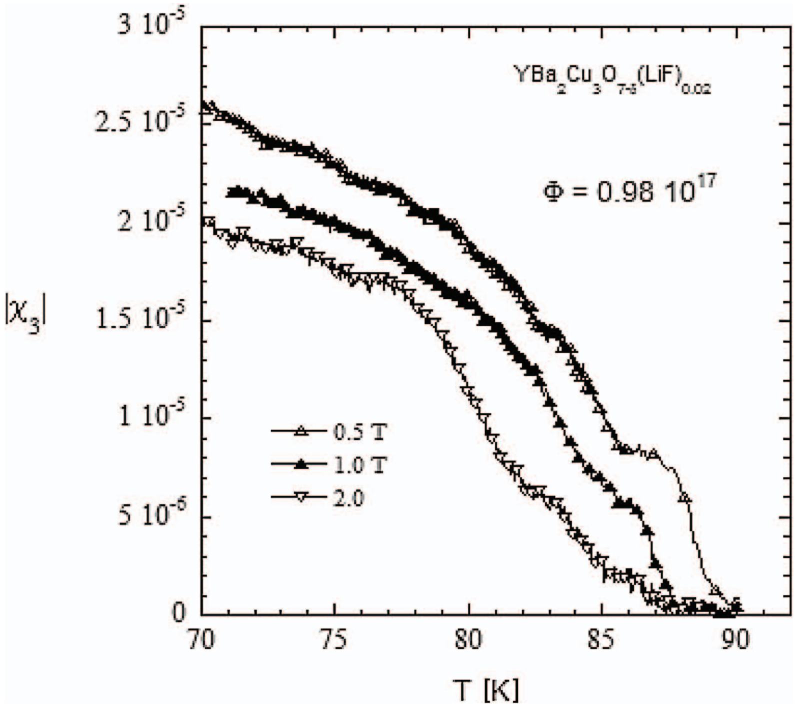

Fig. 6. – Temperature dependence of the third harmonic of the *ac*-susceptibility of polycrystalline Li-doped $YBa_2Cu_3O_{7-x}$ ceramics irradiated with neutrons at a fluence of 0.98×10^{17} cm^{-2} as a function of temperature T for the following *dc*-fields: 0.5; 1.0; and 2.0 T.

Increasing the neutron fluence to 9.98×10^{17} cm^{-2}, $|\chi_3|$ is emphasized and reaches amplitude comparable to the virgin sample. The intragranular peak shows a spectacular two times increase relative to the unirradiated state (Fig. 7). Additionally, its separation relative to the intragranular background is also improved $|\chi_3|$ for all fields.

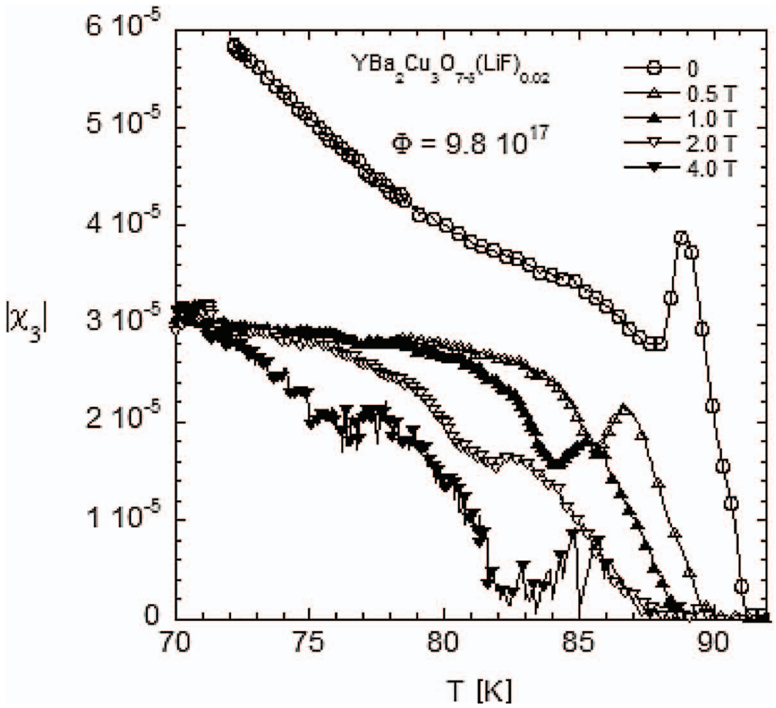

Fig. 7. – Temperature dependence of the third harmonic of the *ac*-susceptibility of polycrystalline Li-doped $YBa_2Cu_3O_{7-x}$ ceramics irradiated with neutrons at a fluence of 9.98×10^{17} cm^{-2} as a function of temperature T for the following *dc*-fields: 0; 0.5; 1.0; 2.0, and 4.0 T.

The inspection of the above data shows that there is a kind of improvement of the superconducting properties within grains at fluences of order 10^{18} cm^{-2} in contrast with the depression of these properties after irradiation at fluences of order 10^{17} cm^{-2}. The fluence dependence of T_c and χ_1'' advocates for an improvement relative to the damaged sample irradiated at 0.98×10^{17} cm^{-2}, but the changes in the third harmonics suggest improvements even relative to the unirradiated sample. The intergranular contribution displays a different dependence on fluence.

The contrasting behaviour of the two contribution suggests that the almost uniform degradation of the samples irradiated up 0.98×10^{17} cm^{-2} (better to say up to 4.9×10^{17} cm^{-2} as it results from T_c *vs.* Φ data) evidenced in susceptibility experiments crosses over into a nonuniform one at 9.98×10^{17} cm^{-2}. The latter distribution can be depicted as an accumulation of the defects in the intergranular space causing a rapid degradation of the Josephson connections, hence, shifting the intragranular peak at very low temperatures, and a "cleaning" of the intragranular area leaving large defectless areas within grains.

Such a transition of the defect distribution was predicted by the theory of diffusional reactions applied to irradiation damages [1–6]. The nonlinear equation describing the complex process of generation, diffusion, and annihilation of the defects possesses a bifurcation point where the homogeneous distribution could become unstable leading to a self-organization of the defect distribution [3]. The self-organization of defects, including pattern formation, occurs when, besides the mobile defects, *i.e.*, vacancies and interstitials, less mobile clusters of vacancies are also produced due to the higher value of the diffusion constant of interstitials relative to vacations.

It is expected that at the grain border should be the sink with the highest strength and bias factor. The point defects, which are absorbed by the border sinks, contribute to the increase of the effective thickness of the intergrain Josephson junction, hence, to the decrease of the sample connectedness. This is a consequence of the exponential decrease of the intragranular lower critical field when the barrier widens.

The diffusion of defects towards all strongly biased sinks leaves back large, defectless areas displaying a local improved superconductivity. It was shown by numerical simulation that a key role in the development of the nonuniform distribution of defects is provided by the material anisotropy [6].

In conclusion, using magnetic susceptibility experiments, we have evidenced, for the first time, that a spatially inhomogeneous distribution of the irradiation damages is built in at fluences of order 10^{18} cm^{-2}.

Acknowledgements. The research was supported in part by the European Community under the TARI contract HPRI-CT-1999-00088 and by Romanian Ministry of Education and Science in the framework of the MATNANTECH project 260/2004.

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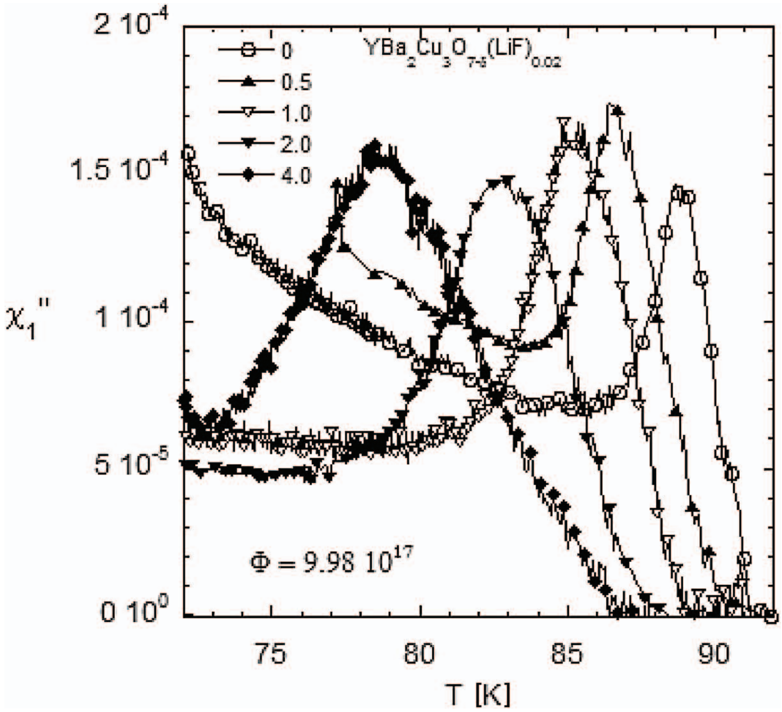

Fig. 4. – Temperature dependence of the imaginary component χ_1'' of the fundamental harmonic of the *ac*-susceptibility of polycrystalline Li-doped $YBa_2Cu_3O_{7-x}$ ceramics irradiated with neutrons at a fluence of 9.98×10^{17} cm^{-2} as a function of temperature T for the following *dc*-fields: 0; 0.5; 1.0; 2.0, and 4.0 T.

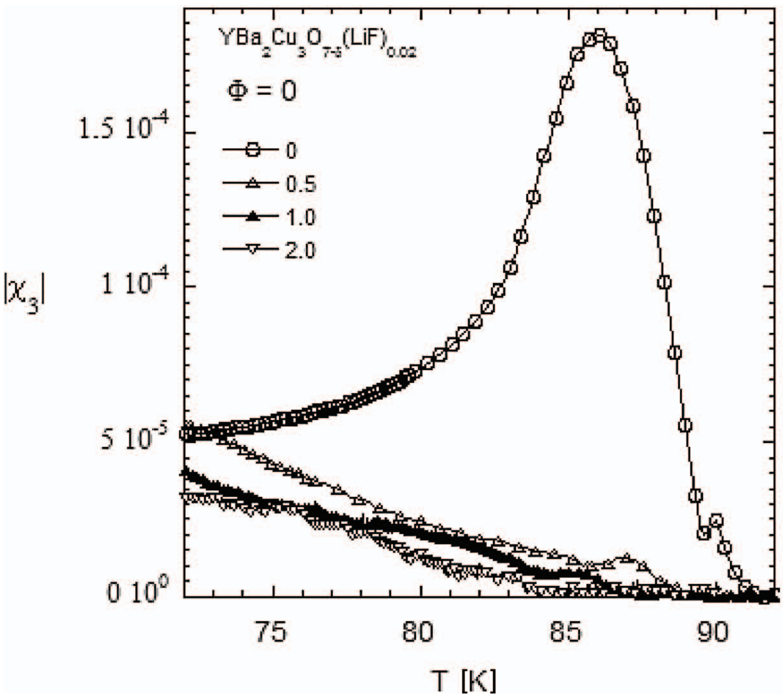

Fig. 5. – The third harmonic of the *ac*-susceptibility of the unirradiated polycrystalline Li-doped $YBa_2Cu_3O_{7-x}$ ceramics as a function of temperature T for the following *dc*-fields: 0; 0.5; 1.0, and 2.0 T.