Z. Phys. B – Condensed Matter 71, 37–42 (1988)

Condensed Matter
Zeitschrift für Physik B

The effect of low-temperature electron irradiation on the transition temperature of $YBa_2Cu_3O_{7-\delta}$ superconductors

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Received February 15, 1988

Measurements of the complex susceptibility $\chi = \chi' - i\chi''$ of electron-irradiated $YBa_2Cu_3O_{7-\delta}$ show a strong influence of the electron irradiation dose, $\Phi \cdot t$ on the transition temperature T_c. For irradiation doses of $\Phi \cdot t = 2.2 \cdot 10^{19}$ e$^-$/cm^2 we find a damage rate of $\Delta T_c / \Delta(\Phi \cdot t) = -1.6 \cdot 10^{-19}$ K/(e$^-$/cm^2). It is assumed that the decrease of T_c is mainly a bulk effect due to the production of atomic defects like vacancies and interstitials in the Cu–O–Cu chains and in the basal planes of the unit cells.

I. Introduction

High-temperature superconductivity was discovered at the IBM Rüschlikon Research Laboratory by Müller and Bednorz [1]. The experimental work is now focused on the identification, separation of phases and structural characterization of the YBaCuO compounds as well as on the detection of superconductivity by measuring the resistance, the susceptibility, the Meissner effect and the diamagnetic shielding. Tunnelling, infrared and point contact measurements are performed to elucidate the microscopic properties of these materials (see e.g. review paper of Rietschel [2].

In this paper we report on measurements of the effect of electron irradiation on the zero-field transitions in $YBa_2Cu_3O_{7-\delta}$ and the annealing behaviour of this radiation damage. The experimental method applied consists of measuring the real and imaginary parts (χ' and χ'') of the magnetic susceptibility of the sample in an alternating magnetic field as the temperature is lowered or raised through the $s-n$ transition [3, 4, 5, 6]. This technique also has been used by other authors [7] for a study of the effect of an oxygen deficiency on the $s-n$ transition. Studies of the ac-susceptibility after radiation damage provide a valuable supplement to other methods to study changes of the microscopic and macroscopic properties of solids, and the phase transition occurring in them. Using this tool it should also be possible to probe the intricacies of the structure-sensitive properties of superconductors. Previous studies in neutron-irradiated $A15$ alloys [8, 9, 10] have shown that in these materials all intrinsic superconducting properties are sensitively influenced due to the one-dimensional character of for example the Nb-chains. It is suggested that also in YBaCuO-type superconductors low dimensionality effects play a central role in its extraordinary superconducting properties.

II. Sample preparation

The sample was prepared at the MPI für Metallforschung, Stuttgart, from the powdery oxides Y_2O_3, CuO, and Ba_2CO_3. The components were mixed and pressed at 7 kbar into a pellet of 1 cm diameter, subsequently the specimen was reacted in a furnace under flowing oxygen. The sample was held at 950 °C for 17 h and cooled to 700 °C for an additional annealing time of 2 h. After that treatment the sample was pulverized again and the annealing procedure was then repeated under flowing air. After that treatment the density of the material increases 10% to 5.4 g/cm^3. Figure 1 shows the microstructure of the polished pellets containing an agglomerate of grains. For the irradiation experiment and the ac-susceptibility measurements specimens of dimensions $1 \times 1 \times 6$ mm^3 were cut from the pellet.

The irradiation experiments were carried out at the Dynamitron accelerator of the University Stuttgart with 2 MeV electrons of an incident time inte-

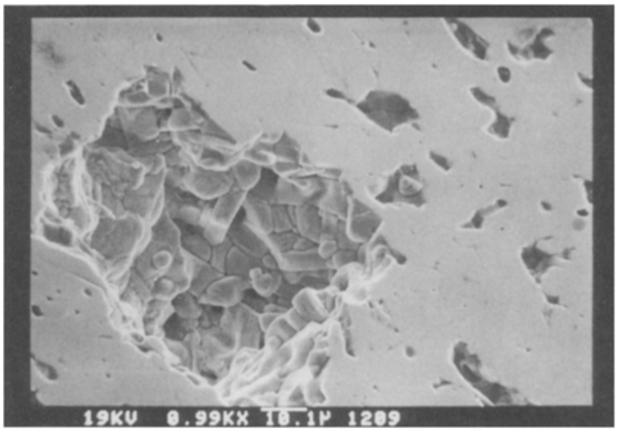

Fig. 1. Scanning electron-micrograph of the microstructure of $YBa_2Cu_3O_{7-\delta}$

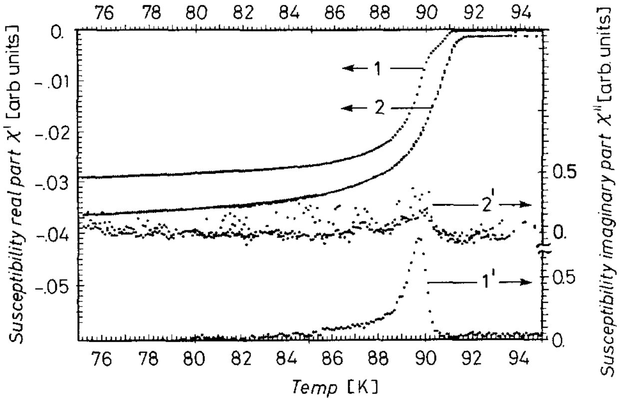

Fig. 2. Temperature dependence of the real part χ' and of the imaginary part χ'' of the initial susceptibility in arbitrary units of as-sintered $YBa_2Cu_3O_{7-\delta}$ (1) and of a sintered and subsequently grinded (powdery) sample (2)

grated flux density (fluence) of $\Phi \cdot t = 2.5 \cdot 10^{18}$ e^-/cm^2, of $5 \cdot 10^{18}$ e^-/cm^2, and at the van de Graaff accelerator of the KFA Jülich with $\Phi \cdot t = 2.2 \cdot 10^{19}$ e^-/cm^2 at 80 K.

III. Experimental procedure and results

3.1. *Measuring method*

The ac-susceptibility ($\chi = \chi' - \chi''$) measurements were performed with the LC oscillator technique [11]. The specimen is located inside the coil of the LC-resonant circuit at a frequency of 20 kHz and a magnetic field, $\mu_0 H = 2$ μT.

3.2. *Unirradiated specimen*

In a first temperature run the samples always were cooled down to 60 K under the ac measuring field, then measured up to 100 K and again cooled down to 60 K. Figure 2 shows the reversibility of the temperature dependence of the real part χ' and of the imaginary part χ'' of the ac-susceptibility of the nonirradiated as-sintered samples in arbitrary units.

In the nonirradiated sintered YBaCuO the onset of the transition is observed at 91 K (see Fig. 2 curve 1), where a diamagnetic magnetization results from superconducting shielding currents. The transition has passed half (midpoint) at 89.6 K, and the 10%–90% transition width, δT_c, is 3.1 K. It should be noted that this transition width is comparable to ac-susceptibility results found for $ErBa_2Cu_3O_{6+x}$ [12]. On warming and cooling both values of T_c are identical and the slope of the transition does not change independent of the direction of the temperature change characterized in the following by $\Delta T \gtrless 0$.

The characteristic temperature dependence of χ' can be described by a nearly linear region I between $90.1\ \mathrm{K} < T < T_c^{\mathrm{ONSET}} = 91$ K, a steep decrease in region II between $88\ \mathrm{K} < T < 90.1$ K, and a long tail to saturation in a region III $T < 88$ K.

The lower curve (1') in Fig. 2 shows the imaginary part χ'' of the ac-susceptibility with a maximum at 89.6 K and the onset, $T_c^{\mathrm{ONSET}} = 90.6$ K, which is 0.4 K lower than the onset of χ'.

To get information on the influence of the multiconnected grains on the complex susceptibility a sintered sample was grinded again. The powdery YBaCuO then was put into a quartz tube and introduced into the measuring coil. The results for the real and imaginary part (χ' and χ'') of the ac-susceptibility are represented in Fig. 2 (curves 2 and 2'). The onset of the transition to superconductivity as given by χ' occurs at 91.6 K and the 10%–90% transition width is $\delta T_c = 4$ K. The imaginary part χ'' now reveals (curve 2') only a hint of a maximum which probably results from still connected grains. This result agrees with measurement of Chen et al. [6] on the same material but does not correspond with the findings of Renker et al. [13] on $La_{1.85}Sr_{0.15}CuO_4$. These authors observed even in the powdery specimen a maximum at 35 K corresponding to the midpoint of the transition.

3.3. *Electron irradiated specimens*

After electron irradiation of the sintered specimens at 80 K the samples were transferred into the oscillator coil under liquid nitrogen. In Fig. 3a the transition

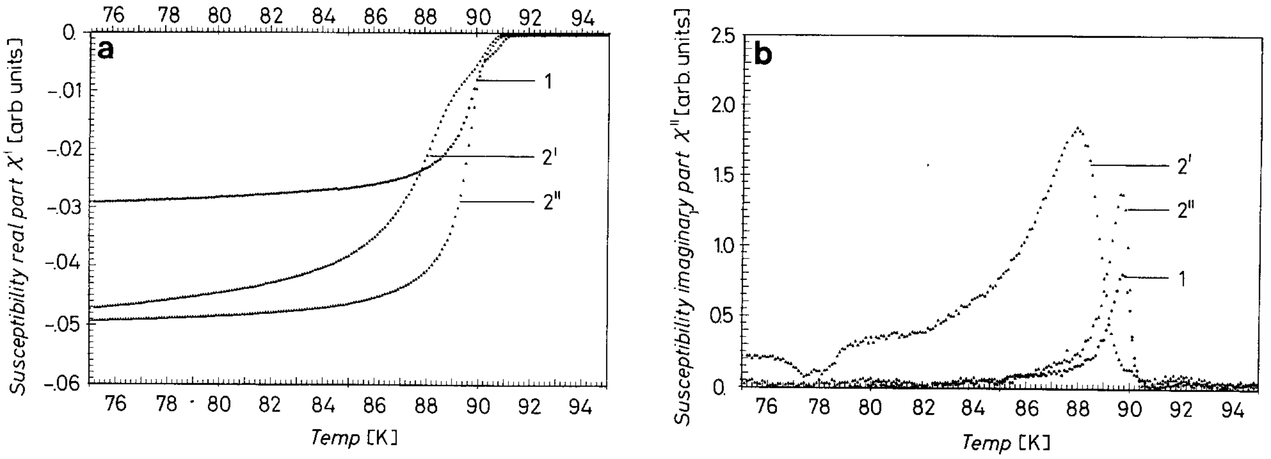

Fig. 3. **a** Temperature dependence of χ' of the untreated (1) and irradiated ($2.5 \cdot 10^{18}$ e$^-$/cm^2) (2) YBaCuO. (2') was measured for increasing temperature and (2'') for decreasing the temperature after heating up to 100 K. **b** As Fig. 3a, but for χ''

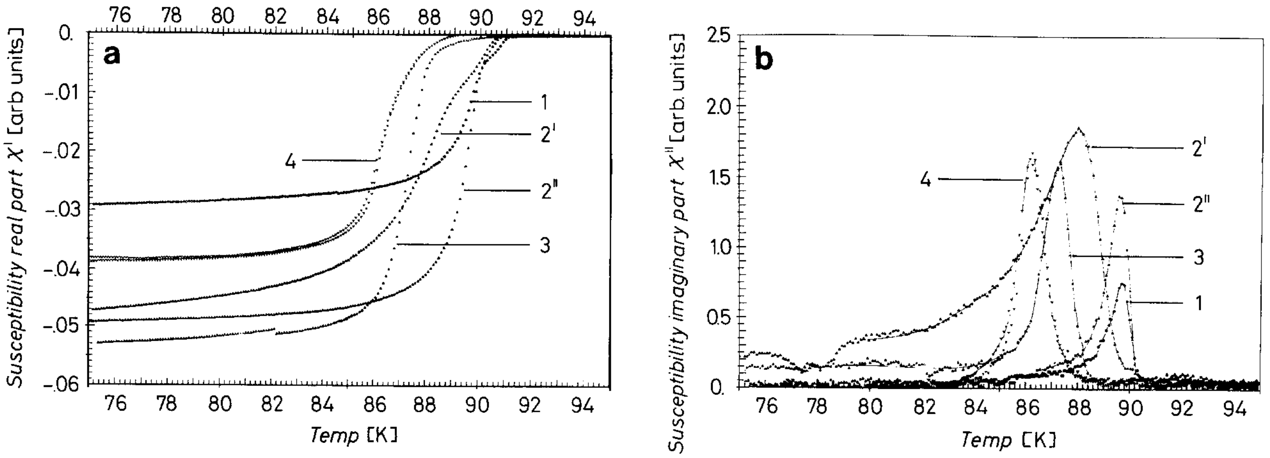

Fig. 4. **a** Temperature dependence of χ' of the nonirradiated YBaCuO (1, $\Delta T > 0$) and irradiated samples: $0.25 \cdot 10^{19}$ e$^-$/cm^2 (2', $\Delta T > 0$; 2'' $\Delta T < 0$), $0.5 \cdot 10^{19}$ e$^-$/cm^2 (3, $\Delta T > 0$), $2.2 \cdot 10^{19}$ e$^-$/cm^2 (4, $\Delta T > 0$). **b** As Fig. 4a, but for χ''

curve is shown after an irradiation dose of $2.5 \cdot 10^{18}$ e$^-$/cm^2. The onset of superconductivity with respect to the nonirradiated specimen is shifted by about 0.4 K and the χ' curves for $\Delta T \gtrless 0$ according to Fig. 3a show an irreversible effect. The characteristic behaviour in the above-defined three temperature ranges is preserved, but the range of the linear region I is changed: For heating ($\Delta T > 0$) $88.6\,\mathrm{K} < T < T_c^{\mathrm{ONSET}} = 90.8$ K is observed and for cooling ($\Delta T < 0$) we find $90\,\mathrm{K} < T < T_c^{\mathrm{ONSET}} = 90.8$ K. The slopes of these two parts are identical.

In the case of curve 2' ($\Delta T > 0$) in Fig. 3a the 10%–90% transition width is 5.2 K, the midpoint is at 88 K, and for curve 2'' ($\Delta T < 0$), the transition width is 2.7 K with the midpoint at 89.4 K. After cyclic measurements between 60 K and 100 K only curve 2'' is reproduced. The temperature dependence of χ'' is represented in Fig. 3b.

For a specimen irradiated by an e$^-$-dose of $5 \cdot 10^{18}$ e$^-$/cm^2 the linear part of χ' of region I has disappeared (compare Figs. 3a and 4a). The onset of the transition starts at 91.0 K and the 10%–90% width is 2 K and the midpoint is at 87.2 K as shown in Fig. 4a. The curve remains identical even after a cyclic cooling and warming procedure up to 100 K.

An irradiation dose of $2.2 \cdot 10^{19}$ e$^-$/cm^2 leads to a further decrease of the transition temperature (see Fig. 4a). The onset of χ' is shifted by 2.0 K to lower temperatures in respect to the nonirradiated specimen (91.0 K to 89.0 K) and the midpoint by about 3.4 K (89.6 K to 86.2 K). The 10%–90% transition width δT_c is 2.6 K. For χ'' (see Fig. 4b) the onset is observed

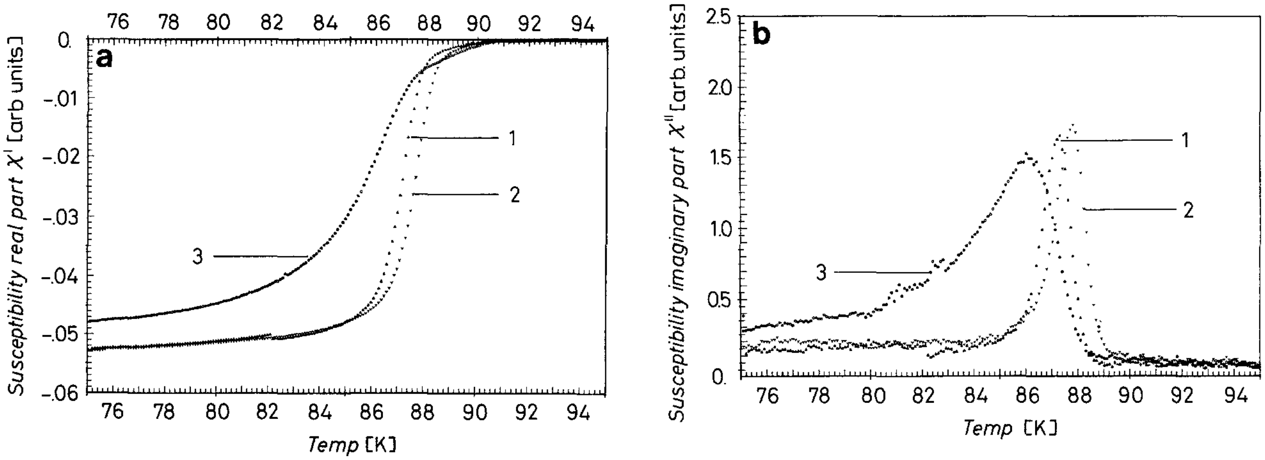

Fig. 5.a Temperature dependence of χ' of the irradiated YBaCuO ($0.5 \cdot 10^{19}$ e$^-$/cm^2) (1), thereupon annealed at $T_A = 300$ K (2), and after that annealed at $T_A = 400$ K (3). b As Fig. 5a, but for χ''

at 88.2 K which is 0.8 K lower than the onset of χ'. The maximum value of χ'' appears at 86.2 K corresponding to the midpoint of χ'. In Fig. 4a the high ($2.2 \cdot 10^{19}$ e$^-$/cm^2)-, medium ($5 \cdot 10^{18}$ e$^-$/cm^2)-, and low ($2.5 \cdot 10^{18}$ e$^-$/cm^2)-dose irradiated specimens as well as the nonirradiated sintered sample are represented for comparison.

Warming up the specimen irradiated with an e$^-$-dose of $5 \cdot 10^{18}$ e$^-$/cm^2, to 300 K for one hour, annealing effects lead to an increase of T_c^{ONSET} of only 0.4 K whilst the characteristic transition width δT_c doesn't change. A further annealing treatment at 400 K for one hours in He atmosphere reduces T_c^{MID} (midpoint) drastically to 86 K and increases the transition width δT_c to 5.2 K as shown in Fig. 5.

IV. Discussion

4.1. *Bulk and grain boundary effects*

The magnetic response of a homogeneous superconducting material e.g. Nb shows for the real part χ' of the complex susceptibility a monotonic change (Meissner effect) as the temperature passes the $n-s$ transition. The imaginary part χ'' decreases from its finite level in the normal state due to the eddy current losses and approaches zero in the superconducting state [3]. For non-homogeneous superconductors of a filamentary or of a granular structure like the oxidsuperconductors the imaginary part, χ'', reveals a maximum [3, 4, 12] (Figs. 2, 3b, 4b, 5b) just below T_c^{ONSET}. The origin of the imaginary part of the susceptibility are the eddy current losses induced by the ac magnetic field. Similar to normal conductors the maximum of χ'' is the result of two mechanisms: On cooling the sintered sample in an applied ac magnetic field eddy currents will flow along a percolating network passing a number of random contacts. More and more links become superconducting as the temperature decreases. The average conductivity rises leading to an increased dissipation which results in a higher value of χ''. At lower temperatures the second counter-acting mechanism starts: The diamagnetic shielding dominates and expels the magnetic field and thereby the eddy currents to a layer of a thickness of the London penetration depth. This finally gives lower losses and reduces χ''.

The shielding currents are suppressed when the grains are separated by grinding the sample. The Josephson junctions are destroyed and macroscopic shielding currents can no longer flow. This finally gives a nearly constant temperature dependence of χ'' as shown in Fig. 2.

According to these considerations and with respect to the two-phase model of Ishida et al. [12] we ascribe the lower onset of χ'' as compared to χ', (see Fig. 2) to the coupled grains (phase I). The higher onset of χ' points to the bulk effect of the grains (phase II).

4.2. *Damage rates of T_c*

After a radiation of the specimen by a dose of $2.2 \cdot 10^{19}$ e$^-$/cm^2 which corresponds to the production of an atomic concentration of about 2.5–$8.0 \cdot 10^{-4}$, the onsets of the real and imaginary part are thereafter shifted by nearly the same value to lower temperatures. The difference of the onsets of χ' and χ'' is about 0.5 K for the nonirradiated specimen (see Fig. 2) and about 0.8 K for the irradiated (maximum fluence) specimen (see Figs. 4a and 4b). This points to the fact that the same defects are produced in both phases. The defects created are assumed to be vacancies and interstitials of oxygen and copper atoms, which cause a reduction of the onset of T_c, $\Delta T_c^{\mathrm{ONSET}} = 2\%$ and of the midpoint of T_c, $\Delta T_c^{\mathrm{MID}} = 3.4\%$. This corresponds to a damage rate of $\Delta T_c^{\mathrm{MID}}/\Delta(\phi \cdot t) = -1.6 \cdot 10^{-19}$ K/(e^-/cm^2), or to a relative damage rate of $(\Delta T_c^{\mathrm{MID}}/T_c)/\Delta(\Phi \cdot t) = -1.8 \cdot 10^{-21}$ K (e^-/cm^2). Recently it has been reported [7] that there also exists a strong dependence of T_c on oxygen vacancies and the possibility to recover T_c by changing the oxygen stoichiometry. Takumoto et al. [16] report on a reduction of the transition temperature, $\Delta T_c = 35$ K in respect to the atomic concentration Δc of extracted oxygen atoms $= 0.029$ from the stoichiometric value of 6.8. With a density of the superconductor of 5.4 g/cm^3 this gives $\Delta T_c/\Delta c = -5.8 \cdot 10^{-21}$ (K/atom). To compare these findings with the results of the radiation damage we calculated the density, c_d, of displacements of atoms (dpa) produced by the electron irradiation using the relation [21]

$$c_d = \phi \cdot t \cdot c_0 \cdot \sigma_d \cdot \bar{v}$$

which causes a shift of $\Delta T_c^{\mathrm{MID}}$ of the transition to superconductivity.

Here we have used the maximum fluence $\phi \cdot t = 2.2 \cdot 10^{19}$ e^-/cm^2, the number of atoms $c_0 = 6.34 \cdot 10^{22}$ per cm^3. Furthermore we have taken for the threshold displacement energies $E_d = 20$ eV and 40 eV and the maximum energy $E_m = 814$ eV which can possibly be transferred to an oxygen atom. By means of these values the cross sections $\sigma_d = 1.2 \cdot 10^{-23}$ cm^2 ($E_d = 20$ eV) and $5.1 \cdot 10^{-24}$ cm^2 ($E_d = 40$ eV) were calculated. The factor $\bar{v} = 1.9$ takes into account the production of subsequent displacements. This gives for the number of displaced atoms $c_d = 3.2 \cdot 10^{19}$ and $1.35 \cdot 10^{19}$ (dpa/cm^3). With the shift of the midpoint of $\Delta T_c^{\mathrm{MID}} = 3.4$ K we find $\Delta T_c^{\mathrm{MID}}/c_d = -1.1 \cdot 10^{-19}$ and $-2.5 \cdot 10^{-19}$ (K/atom).

Comparing these results with those obtained for the oxygen non-stoichiometry we get $\{\{\Delta T_c^{\mathrm{MID}}/c_d\}/\{\Delta T_c/\Delta c\}\} = 19$ and 43 which reveals higher sensitivity of T_c with respect to the electron irradiated samples. This may result from the fact that by electron irradiation not only oxygen atoms are displaced but also copper atoms which could be responsible for the stronger irradiation effect. Within the framework of the bipolaron model were the phase transition is described by a Bose-Einstein condensation of bipolarons [2, 22], built up of $\mathrm{Cu{-}O_6}$ octahedra with $\mathrm{Cu^{3+}}$ and $\mathrm{Cu^{2+}}$ ions, it seems reasonable that a displacement of the Cu ions would influence sensitively the critical temperature.

After low-dose irradiation ($2.5 \cdot 10^{18}$ e^-/cm^2) we observe a reduction of T_c^{MID} and a remarkable difference between the χ'-curve 2′ ($\Delta T > 0$) and 2″ ($\Delta T < 0$) of Fig. 3a. We ascribe the lowering of T_c to the formation of Frenkel-type defects. The complete recovery of T_c after a moderate annealing at 100 K is ascribed to the correlated annihilation of the vacancy and interstitial type defects.

In the case of higher fluences ($5 \cdot 10^{18} - 2.2 \cdot 10^{19}$ e^-/cm^2) the layers and/or chains obviously are irreversibly damaged. After an annealing treatment at $T_A = 300$ K for 10 min (after an irradiation with $5 \cdot 10^{18}$ e^-/cm^2) T_c increases only slightly indicating that the primary structure cannot be fully recovered, probably due to uncorrelated recovery processes conserving vacancy type defects on O and Cu sites up to 300 K. A further increase of T_A to 400 K reduces T_c again. This result is surprising, because no further recovery is observed. We assume therefore that the annealing carried out under He atmosphere reduces the oxygen concentration leading to this effect. Similar behaviour has been observed by Tarascon et al. [7] on the $\mathrm{La_{1.85}Sr_{0.15}CuO_{4-\delta}}$ system. In their work, measurements of the ac-susceptibility after annealing under vacuum revealed a decrease of T_c which recovered after reannealing the superconductor under oxygen atmosphere. Obviously the deficiency of oxygen is compensated by this treatment. An explanation for the irreversible change of T_c by the damage of the weak links between the grains (phase I) leading to a possible isolation of the grains is not applicable in the case of e^--fluences of at most $2.2 \cdot 10^{19}$ e^-/cm^2 used in this experiment. A rough estimation of the contact area of a grain with its surroundings using Fig. 1 gives $1.35 \cdot 10^{-11}$ m^2, and with a contact layer of 1000 Å we get a contact volume of approximately $1.35 \cdot 10^{-19}$ m^3 corresponding to $8 \cdot 10^8$ unit cells ($a = 3.884$ Å, $b = 3.822$ Å, $c = 11.675$ Å) [15]. From these, only about 7000 unit cells are damaged. This number, however, seems not to be high enough to destroy these links and therefore phase I remains preserved. A similar conclusion has been drawn by Geerk et al. [14] from He-ion irradiation experiments of LaSrCuO. Accordingly it is assumed that the decrease of T_c results from an intragrain radiation damage affecting intragrain superconducting properties. It seems likely that the production of defects like vacancies and interstitials in the basal plane and within the Cu−O−Cu chains of the grains influence the behaviour of the ac-susceptibility and are responsible for the decrease of T_c. It is of interest to note that defect densities with distances as small as 10–20 lattice constants have a significant effect on T_c. This clearly indicates that the electronic microstructure responsible for the high T_c properties must be influenced by a long-range interaction phenomenon. It will be the aim of further detailed experiments to compare these results with current models of high T_c superconductors, e.g., resonating valence bond state (RVB) model – with the physical picture of n.n. singlet pairs resonating between different spatial pair configurations [17], exciton [18] and plasmon models [19] or bipolaron models [20].

The authors gratefully acknowledge Dr. I. Ferreira for critically reading the manuscript and Dr. Dworschak of the KFA, IFF Jülich for performing the high dose e$^-$-irradiation experiment.

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