

Self-doping caused by oxygen displacements in heavy-ion-irradiated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ crystals

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Detailed irradiation and annealing experiments on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ single crystals of widely different doping levels confirm the mechanism of self-doping of oxygen by heavy-ion irradiation in bulk samples. The self-doping occurs in two steps: the initial expulsion of up to ten percent of the oxygen ions from the amorphous region, which can be partially suppressed by performing the irradiation at low temperature, and the subsequent slow diffusion of oxygen along the *ab* planes into the matrix. The diffusion process well describes the ion-dose dependence of the critical temperature and the aging of irradiated samples.

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I. INTRODUCTION

The remarkable influence of amorphous columnar defects (CD's) created by high-energy heavy-ion irradiation in high- T_c superconductors (HTSC's) has provoked a great deal of interest. Most investigations have been concerned with the exploration of vortex pinning, flux flow, and novel vortex matter phase transitions due to the introduction of CD's.¹⁻⁵ It has often been reported that the heavy-ion irradiation caused a modification of T_c , but this effect, as well as the effect of heavy-ion irradiation on other superconducting parameters and material properties, has not been studied in great detail. Only recently evidence was obtained that an important part of the T_c change of high- T_c $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_n\text{O}_{2n+4+x}$ ($n = 1, 2$) thin films after heavy-ion irradiation is due to the motion of oxygen and self-doping of the samples.⁶ In fact, a similar mechanism has been suggested to explain the variation of T_c in neutron-irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) samples, as being closely related to the change of the concentration of oxygen vacancies at the Cu-O chain sites.^{7,8} In underdoped HTSC's, the irradiation induced doping leads to an increase in T_c , at odds with the commonly accepted notion of a systematic decrease of T_c through some unidentified degradation process. The idea of self-doping has important consequences both as far as "applications" are concerned, in the sense that theoretical pinning models of the pinning potential of a columnar defect should be revisited in the light of the presence of the oxygen "piles" around the defect core, as well as for the mechanism of track formation itself. The high sensitivity of the superconducting material's physical properties, notably the critical temperature T_c , on the oxygen doping means that the latter can serve as an intrinsic probe which allows one to measure the change in chemical composition of the amorphous region following the ion impact. It is therefore important to quantify the phenomenon on bulk crystals, in which the effect of oxygen diffusion from the atmosphere are less important than in films.

In this paper, we investigate the modification of T_c in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (Bi-2212) single crystals at different doping levels irradiated with widely varying ion doses at room

temperature (RT, 298 K) and low-temperature (LT, ~ 80 K), respectively. Our results definitely show that heavy-ion irradiation at room temperature always introduces more oxygen ions into the matrix. The insensitivity of further annealing experiments to the gas atmosphere in which these are carried out, as well as the dose dependence of T_c , indicate that this oxygen originates from the amorphous regions. The extra oxygen ions produce a positive or a negative modification of T_c , depending on the initial doping state of the sample and the parabolic relation between T_c and hole doping.⁹ We have also found a long-term effect of the doping modification, namely T_c , evolves as function of storage time and temperature. In remarkable contrast to the room-temperature irradiation, we find that the effect of the doping modification is largely suppressed in samples that were irradiated at low temperature. A simple diffusion model describes the observations well.

II. EXPERIMENTS

Single crystals of Bi-2212 were grown using the traveling solvent floating-zone method.¹⁰ We have realized various doping levels by growing the crystals at low partial oxygen pressure (25 mbar) and post annealing them for several days. Underdoped (UN) crystals were homogenized by annealing in flowing nitrogen gas at 700 °C, optimally doped (OP) crystals were obtained by annealing crystals at 750 °C in air, and post-annealing at 400 °C in air produced overdoped (OV) crystals. Due to the slightly different partial oxygen pressures during the annealing treatments, we have obtained several series of underdoped samples with different T_c , named UN65, UN75, and UN77, respectively. Table I shows the denotation of these samples and their initial T_c . Before irradiation, all the crystals were checked for homogeneous flux penetration by the magneto-optical technique in order to ensure the absence of extended defects.

Heavy-ion irradiation was performed at the Grand Accélérateur National d'Ions Lourds (GANIL, Caen, France) with 5.8-GeV Pb ions with the ion beam directed parallel to the *c* axis of the samples. The irradiation produces continuous

TABLE I. Denotation of the different Bi-2212 single crystals according to their doping level before irradiation ($n=0$) and their initial T_c values.

Samples	UN65- n	UN77- n	OP- n	OV- n	UN77-LT- n	UN75-LT- n
$T_{c,ref}(K)$	65	77.6	87.5	84.5	77.6	75.4

amorphous tracks of radius ~ 5 nm which traverse the whole thickness of the sample. During the irradiation the ion beam also traverses a $1\text{-}\mu\text{m}$ -thick Ti film in front of the sample. The secondary electron emission from this Ti film is used to continuously monitor the ion flux during the irradiation. Before starting each run, the ion flux is calibrated using a Faraday cup placed between the Ti film and the sample. This allows an accurate control the total ion fluence of each sample. The ion beam continuously sweeps across the target area ($3 \times 2 \text{ cm}^2$) using a asynchronous vertical (3 Hz) and horizontal (1 kHz) ac drive field. Differently doped Bi-2212 single crystals were irradiated with widely different ion fluences n ranging from 5×10^{13} ions/m² to 2×10^{15} ions/m². The irradiation rate is about 2×10^{11} ions/m²s. Samples denoted UN65- n , UN77- n , OP- n , and OV- n were irradiated at room temperature under vacuum (10^{-5} mbar). The irradiation of crystals UN77-LT- n and UN75-LT- n were specially performed in vacuum while cooling the sample holder with a liquid nitrogen flow yielding a irradiation temperature of about 80–100 K. If n is not specified, we refer to a series of samples with different doses.

The critical temperature T_c was measured using two different experiments. The global ac susceptibility was measured on crystals UN65- n , OP- n , OV- n , and UN75-LT- n , using a commercial superconducting quantum interference device (SQUID) magnetometer with an ac magnetic field (1 G) of frequency 171 Hz, applied parallel to the crystals' c axes. The linear extrapolation of the $\chi'(T)$ data from full screening to zero is used to define T_c . The second experiment concerned the ac transmittivity measured for the crystals UN77- n and UN77-LT- n by a Hall local probe magnetometer. A miniature Hall sensor of dimension $10 \times 10 \mu\text{m}^2$ is placed on the center of sample top surface. Both are subjected to an ac field of amplitude of 1 G and frequency of 7.75 Hz. The detailed measurement was described elsewhere.¹¹ The ac Hall voltage V_{ac} was measured as function of temperature and applied dc field H_a . From V_{ac} , the first and third harmonic components of the transmittivity were determined. We defined the irreversibility field $H_{irr}(T)$, or $T_{irr}(H_a)$, as the temperature at which the third harmonic component first becomes distinguishable from the background noise. T_c was defined as the T_{irr} measured with zero applied dc field. Though there is a small difference in the T_c values obtained from the above two experiments (less than 1 K), both experiments are comparable in that they both measure the vanishing of the ac screening current.

III. EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of the ac susceptibility (χ' and χ'') of UN65- 10^{15} and OP- 10^{15} in com-

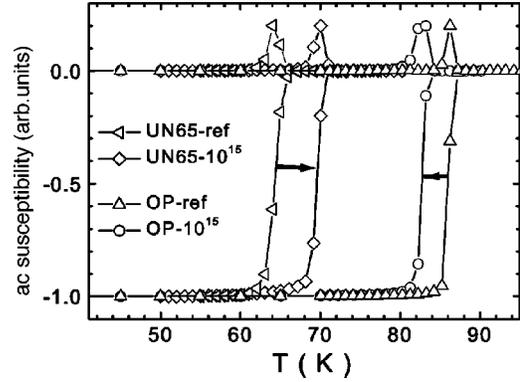


FIG. 1. The ac susceptibility of the samples UN65- 10^{15} (\diamond) and OP- 10^{15} (\circ), measured 30 days after irradiation, compared to that of the unirradiated reference samples UN65-0 (\triangleleft) and OP-0 (\triangle).

parison to the UN65-0 and OP-0 reference samples; both were measured 30 days after the irradiation. It is seen that the RT irradiation caused an increase of T_c ($\delta T_c \sim +5$ K) for the sample UN65- 10^{15} in contrast to the decrease of T_c measured in the initially optimally doped OP- 10^{15} ($\delta T_c \sim -3.5$ K).

Figure 2 shows the ac susceptibility of the UN75-LT- n samples measured five days after the LT irradiation. Within the experimental accuracy, T_c of all the samples were found to stay identical to that of the pristine sample. In order to demonstrate that columnar defects were effectively produced in these samples, we measured the reversible magnetization and found that it exhibited the same behavior as for the optimally doped crystals irradiated at room temperature.³ However, the local ac transmittivity of UN75-LT- n showed an increase of T_c when it was measured half a year after the LT irradiation, having been kept at room temperature in nitrogen for 90 days and in air for another 90 days. As shown in Fig. 3, the increase of T_c is smaller than that of UN77- n , irradiated at room temperature and also measured six months after the irradiation.

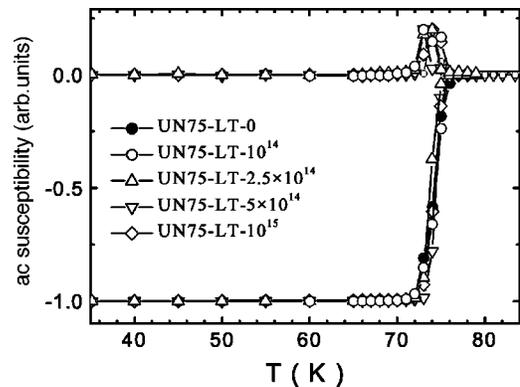


FIG. 2. The ac susceptibility of samples UN75-LT-0 (\bullet), UN75-LT- 10^{14} (\circ), UN75-LT- 2.5×10^{14} (\triangle), UN75-LT- 5×10^{14} (∇), UN75-LT- 10^{15} (\diamond), irradiated at $T \approx 80$ K and measured five days after the irradiation. Within experimental accuracy, the T_c of these samples are identical.

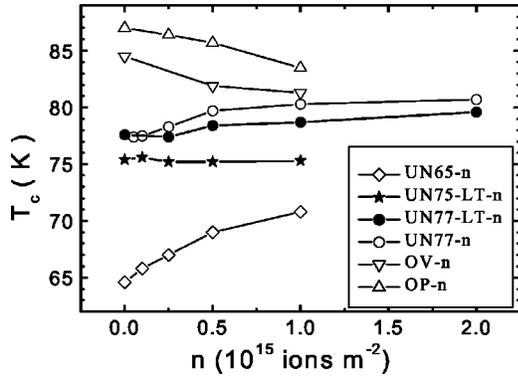


FIG. 3. Evolution of T_c as function of the ion fluence n for the samples irradiated at room temperature (RT) and low temperature (LT), UN65- n (\diamond), UN75-LT- n (\star), UN77-LT- n (\bullet), UN77- n (\circ), OP- n (\triangle), and OV- n (∇). The crystals UN77- n and UN77-LT- n were measured six months after irradiation. The three series of samples UN65- n , OP- n , and OV- n were measured one month after RT irradiation while the crystals UN75-LT- n were measured five days after LT irradiation.

The evolution of T_c with ion fluence n is plotted in Fig. 3 for all the RT- and LT-irradiated samples, including UN65-, UN77-, UN75-LT, UN77-LT-, OP-, and OV- n . A clear modification of T_c has been produced by the irradiation in all these samples except for UN75-LT- n whose T_c 's are identical. T_c of the initially optimally doped OP- n and overdoped OV- n samples decreases, in accordance with results reported in the literature. The result for the initially underdoped crystals, UN65-, UN77- n , and even UN77-LT- n , is opposite: T_c is found to increase after RT irradiation.

Moreover, we found a long-term effect, namely, T_c changes further with longer storage time for all samples of all doping levels, after they were stored in air. As an example Fig. 4 shows the ac susceptibility for UN65- 10^{15} measured at different times. The T_c of this crystal increased from 70 to 72 K after having been kept in air for 300 days. For OP- 10^{15} and OV- 10^{15} we found that T_c has decreased about 1 K more after having been kept in air for one year. The T_c of the

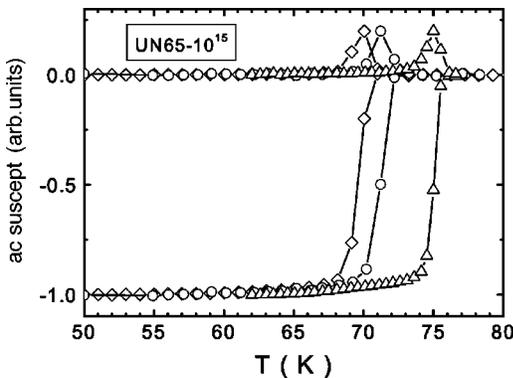


FIG. 4. History dependence of the ac susceptibility of sample UN65- 10^{15} after irradiation, (\diamond) after 30 days at room temperature, (\circ) after 330 days at room temperature, (\triangle) after 510 days at room temperature and annealing in flowing nitrogen gas at 200°C for 15 minutes.

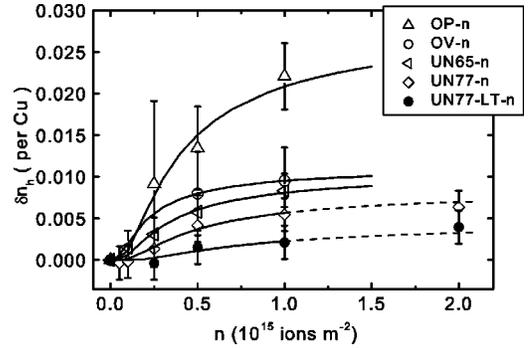


FIG. 5. The calculated modified hole density δn_h as function of ion fluence n for the RT-irradiated samples UN65- n (\diamond), OP- n (\triangle), and OV- n (\circ), together with that of UN77- n (∇) and UN77-LT- n (\bullet). The lines are fits to Eq. (3) with fitting parameters S and x_{d1} as given in Table II. The error bars are calculated in accordance to Eq. (1) by using $\Delta T_c = \pm 0.5$ K.

unirradiated reference samples did not change during this time.

A somewhat higher storage-temperature promotes the change of T_c . We annealed crystal UN65- 10^{15} at 200°C in flowing nitrogen gas for 15 min after the sample had been stored in air for 330 days and found its T_c to increase from 72 to 75 K (see Fig. 4). The same treatment performed on the unirradiated samples did not produce any change of T_c . Apparently the heavy-ion irradiation has dislodged oxygen ions into the crystal matrix that slowly diffuse further into the crystal.

IV. DISCUSSION

To analyze the modification of T_c , we first recall the well-established parabolic relationship between T_c and the hole concentration n_h , described by⁹

$$T_c/T_c^{max} = 1 - 82.6(n_h - 0.16)^2, \quad (1)$$

where n_h is the number of holes per Cu and T_c^{max} is the maximum value of T_c at optimal doping. (Note here the unit of n_h . There are $1/a^2 \approx 6.93 \times 10^{18}$ Cu's per m^2 , where $a = 0.38$ nm is the a -axis lattice parameter for Bi-2212.) After having determining n_h from the measured T_c values we plot the calculated hole density $\delta n_h = n_h - n_{h,ref}$ of the RT-irradiated samples versus irradiation dose n in Fig. 5. ($n_{h,ref}$ is the hole density of the unirradiated reference sample.) Obviously, the RT irradiation produces a positive modification of the hole concentration for all the irradiated samples, the higher the irradiation dose, the greater the increase of n_h . For underdoped samples the increase of n_h gives rise to an increase of T_c , while for the optimally and overdoped samples T_c decreases. Note that in Fig. 5 the error bars for the OP- n crystals are much bigger than for the UN65- n and OV- n samples since the T_c 's are closer to the peak position in the parabolic relation between T_c and n_h according to Eq. (1).

The radiation damage processes accompanying the passage of an energetic heavy ion are likely to encompass energy deposition into the electron gas of the target, the transfer

of the energy from the electron gas to heat the lattice ions, the transport of heat in the lattice, and the phase change and defect formation which accompanying the rapid heating and quenching of the lattice. In the avalanchelike process a huge number of atoms is displaced, leading to local melting of the crystals, and resulting in the creation of columnar defects throughout the whole thickness of the samples. Oxygen, as the most mobile component in the system, is expected to contribute the largest fraction of the additional radiation-generated interstitials. This process has been well described for neutron-irradiated samples.^{7,8}

The increase in n_h may originate from a change in cation composition or oxygen content. Electron energy-loss spectroscopy (EELS),¹² performed on heavy-ion irradiated YBCO films, showed that there was no noticeable difference in the cation composition of the amorphous core region of the CD's and the surrounding crystalline matrix. Instead, a remarkable change was observed across the damaged area in the fine structure of the oxygen K -edge absorption spectrum, more precisely, the prepeak of the K -edge. The integrated intensity of the prepeak is a direct measure of the hole density near the Fermi level. Though such experiments have not yet been reported on Bi-2212 samples, we assume that similar results hold for other heavy-ion irradiated HTSC's copper oxides and therefore we believe that the increase in hole density is mainly coming from oxygen ions expelled from the amorphous cores of the CD's, ignoring the possible influence of displacements of cation atoms which may also have some contribution to change of T_c or some other properties, such as the formation of a kind of Cu-rich plane fault observed in YBCO thin films.¹³

We suggest the following explanation for our experimental data. We assume that during the passage of the swift heavy ion the oxygen is expelled from the area of the ion track and piles up around the core. The impact causes a hot spot which drives the oxygen from the track into the crystal matrix. Since the diffusion is very anisotropic, D_{ab} (along the ab plane) being many orders of magnitude larger than D_c (in the c direction),^{14,15} the diffusion process can be described by a two-dimensional diffusion equation. Although the diffusion in the ab plane is known to be anisotropic as well ($D_a \approx 6D_b$),^{14,15} we ignore this fact and assume for simplicity isotropic diffusion in the ab plane. The temperature and duration of the initial diffusion process is not known, but we assume that it can be characterized by a diffusion length x_{d1} which we can determine from our data. (For isothermal diffusion we could have written $x_{d1} = 2\sqrt{D_1 t_1}$, but under the irradiation conditions we have no clue which value of D_1 or t_1 we would have to take.) For each track an oxygen diffusion profile thus extends into the matrix with corresponding hole density profile $\delta n_h(r)$. We assume that each oxygen ion in the CuO_2 plane yields two holes. This means that the source term S representing the number of holes around each track per CuO_2 layer, can be as large as 2200 for a track radius of $r_{cd} \approx 5$ nm and a -axis lattice parameter of 0.38 nm. The solution of the two-dimensional diffusion equation yielding δn_h around each track is¹⁶

TABLE II. Fit parameters of Eq. (3) for the data obtained on both the RT- and LT-irradiated samples.

Samples	UN65- n	OP- n	OV- n	UN77- n	UN77-LT- n
S	105 ± 15	253 ± 44	183 ± 35	85 ± 10	18 ± 6
$x_{d1}(\text{nm})$	30 ± 4.5	28 ± 6	38.5 ± 5	25 ± 3.5	19 ± 10

$$\delta n_h(r) = \frac{S}{\pi x_{d1}^2} \exp\left(-\frac{r^2}{x_{d1}^2}\right), \quad r > r_{cd}, \quad (2)$$

where r is the distance in the ab plane from the center of the track, S is the total number of holes per CuO_2 layer expelled from each columnar defect during the irradiation. The final result of the irradiation is a random distribution of tracks with an average distance $d = n^{-1/2}$ and corresponding oxygen profiles around them.

In order to connect the hole density modulation with the change in T_c we determine δn_h at the midpoint of two typical CD's that happen to be at a distance d from each other. Although the shape of the hole density profiles for all the doped samples are the same, there are two kinds of T_c profiles due to the parabolic relation between T_c and n_h : (i) for an underdoped crystal, the local T_c value is lowest at $r = d/2$; (ii) for an optimally or overdoped sample, the local T_c value is highest at $r = d/2$. In fact the measured T_c depends on when screening sets in, i.e., on when a superconducting network is produced that can sustain supercurrents over length scales of order of the penetration depth. It means that upon cooling an irradiated underdoped crystal superconducting islands will start to grow around the tracks, followed by the growth of a superconducting network which will be fully established when T is close to the T_c corresponding to δn_h at $r = d/2$. For optimally doped and overdoped samples the highest local T_c almost coincides with the temperature at which a network is formed. We expect that for the first case (underdoped) the measured T_c is slightly higher than the value determined by δn_h at $r = d/2$, but we believe that the differences are negligible since the superconducting transition is sharp. Therefore we can compare the T_c data of all our samples with the change of hole density at $r = d/2$ given by

$$\delta n_h = \frac{2S}{\pi x_{d1}^2} \exp\left(-\frac{d^2}{4x_{d1}^2}\right). \quad (3)$$

In Fig. 5, this equation is fitted to the data (as we will show below one month storage at room temperature did not noticeably change δn_h), yielding the values for x_{d1} and S given in Table II. The magnitude of S for the RT-irradiated samples, UN65- n , OP- n , and OV- n , in Table II, corresponds to the number of oxygen ions per CuO_2 layer expelled from an ion track during irradiation, and determines the asymptote of δn_h for large ion dose. An average value of $S \sim 180$, which is about 10% of the total number of holes per CuO_2 layer in the cores (~ 2200 in accordance to the above calculation), was expelled from each track during the irradiation.

Meanwhile we notice that for the different doping levels the other fitting parameter x_{d1} , which describes the spatial decay of the oxygen ‘‘pile’’ profile, is almost the same within the experimental error bar, denoting a comparable mean displacement of diffusing oxygen ions in the differently doped matrices.

The hole density profile created during the irradiation is expected to evolve further with storage time, as illustrated by the aging effect seen for UN65-10¹⁵ in Fig. 4. Due to this slow oxygen diffusion process, there is an additional change of hole density $\delta n_{hs}(t_s)$ at $r=d/2$ which depends on storage time t_s and storage temperature T_s . The estimation of δn_{hs} is more complicated in comparison to the above calculation for δn_h since at the onset there exists a complex oxygen density distribution $n_h(r,0)$ in the matrix. Nevertheless, if t_s is long enough, the hole density $n_h(r,t_s)$ approaches a final average density \bar{n}_h for which the oxygen ions distribute completely homogeneously, where $\bar{n}_h \approx n_{h,ref} + S/d^2$. We assume that the absolute value of the relative change $|n_h(r,t_s) - \bar{n}_h|/|n_h(r,0) - \bar{n}_h|$ decays exponentially with t_s , i.e.,

$$|\bar{n}_h - n_h(r,t_s)| = |\bar{n}_h - n_h(r,0)| \exp\left(-\frac{t_s}{\tau}\right) \quad (4)$$

where τ is the diffusion time over a typical distance $d/4$, i.e., $\tau \approx (d/4)^2/D_s$, with $D_s \approx D_{ab}$ the oxygen diffusion constant. Therefore the change of hole density $\delta n_{hs}(r,t_s)$ at $r=d/2$ can be described as

$$\delta n_{hs} = n_h\left(\frac{d}{2}, t_s\right) - n_h\left(\frac{d}{2}, 0\right) \approx [\bar{n}_h - n_h(0)](1 - e^{-t_s/\tau}). \quad (5)$$

This result holds, for example, at room temperature at which $\tau \approx 75$ months for UN65-10¹⁵. From the values of S , t_s , and D_s , we can estimate the aging effect for UN65-10¹⁵ shown in Fig. 4. We use $D_{ab}(T) \sim 1.7 \times 10^{-9} \times \exp(-0.93 \text{ eV}/k_B T)$ m²/s which was obtained by oxygen tracer diffusion investigations.¹⁴ According to Eq. (5), 30 days of storage at room temperature leads to $\delta n_{hs} \approx 1 \times 10^{-4}$ which corresponds to a change of T_c of less than 0.1 K. For 330 days at 298 K we get $\delta n_{hs} \approx 1.2 \times 10^{-3}$ corresponding to $\delta T_c \approx 1$ K which is a little lower than the measured value (~ 2 K). After 510 days at room temperature we compute $\delta n_{hs,1} \approx 1.7 \times 10^{-3}$ and after annealing at 473 K for 15 min we obtain $\delta n_{hs,2} \approx 3.9 \times 10^{-3}$, leading to a total of $\delta n_{hs} = \delta n_{hs,1} + \delta n_{hs,2} \approx 5.7 \times 10^{-3}$ corresponding to a change of T_c from 70 to 74 K. This compares reasonably well with the obtained increased T_c from 70 to 75 K. It is remarkable that Eq. (5) works so well to predict the data for the aging effect.

Since the T_c 's of the samples UN77- n were measured six months after the irradiation, the doping modification was affected by two oxygen diffusion processes, namely, during the

irradiation and afterwards through slow oxygen redistribution. We first estimate the aging effect of room-temperature storage by using Eq. (5) and the value of $[\bar{n}_h - n_h(0)]$ for UN-65-10¹⁵. For UN77-10¹⁵ we estimate a small change $\delta n_{hs} \sim 7 \times 10^{-4}$; the effect is considerably larger for UN77-2 $\times 10^{15}$ ($d \approx 23$ nm) leading to $\delta n_{hs} \sim 4 \times 10^{-3}$ corresponding to $\delta T_c \geq 2$ K. Therefore we fit Eq. (3) to the data of the UN77- n with $n \leq 10^{15}$ (without UN77-2 $\times 10^{15}$) in Fig. 5, yielding the fitting parameters S and x_{d1} shown in Table II. The values for S and x_{d1} are very close to the results for the other RT-irradiated underdoped crystals UN65- n . For the data of the LT-irradiated samples UN77-LT- n we follow the same procedure by fitting Eq. (3) to the data for $n \leq 10^{15}$ ignoring the data point at $n = 2 \times 10^{15}$. The resulting values for S and x_{d1} are also given in Table II. Especially S is significantly lower than the value for the other samples. It implies that the low-temperature condition in the irradiation process greatly reduces the expulsion of oxygen from the cores, but also decreases the average diffusion length x_{d1} . However, it is not clear why for the other series UN75-LT- n we did not observe a noticeable variation in T_c (see Fig. 2). It might be that for some unknown reasons the superconducting network is not connected well though there exist superconducting islands around the columnar defects.

It seems that the oxygen diffusion model cannot well explain the experimental data of those irradiated samples with a very high irradiation dose ($n > 10^{15}$). We suspect that there is an additional damaging effect influencing the critical temperature in the crystal with a large density of amorphous areas.⁶

V. CONCLUSION

In conclusion, we have experimentally shown that heavy-ion irradiation in Bi-2212 single crystals always produces an increase of the hole density around the columnar defects. This is caused by a two-step process: first, oxygen ions are expelled from the CD's and, second, the surplus of oxygen ions diffuses into the matrix. The resulting modification of T_c strongly depends on the irradiation temperature and the storage time and temperature. We have shown that irradiation at low-temperature partially suppresses the expulsion of oxygen from the CD's. A simple diffusion model could well explain the experimental data and the physical origin of the doping modification. We think that the scenario of oxygen diffusion may also play a role to explain the change of T_c in neutron-irradiated YBCO samples.⁷

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