Transport properties, phase transition, and recovery near 200 K of proton-irradiated $YBa_2Cu_3O_7$ thin films

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Irradiation of thin $YBa_2Cu_3O_7$ films with protons at 4.2 and 77 K causes distinct changes of the resistivity ρ_0, T_c, the transition width δT_c, and the formation of new phases in different fluence regions. At low fluences, T_c and δT_c are not affected, while ρ_0 and the thermal part of the resistivity, ρ_{th}, increase. This behavior is quite different from that of previous "high-T_c" superconductors. At large fluences, a semiconducting phase developed, revealing a dose-dependent activation energy. About 60% of the irradiation-induced changes recover during annealing above 200 K.

The superconducting properties of materials are strongly affected by chemical and structural disorder. Particle irradiation is often used to produce intrinsic damage in a controllable fashion in order to study the influence of disorder on the superconducting properties in a wide damage concentration range up to levels where phase transformations, e.g., amorphization, occur. Previously, the change of the critical temperature T_c as a function of the irradiation fluence was accompanied by an increase of the residual resistivity $\Delta\rho_0$. A universal behavior, depending on whether the Fermi level E_F was located in a peak or valley of the electronic density of states (DOS), was deduced from these data. Lattice defects lead to a lifetime broadening of electronic states, and thus, to a smearing of the peaks in the DOS. Under the assumption that the electron-phonon coupling constant λ was proportional to the density of states at E_F, T_c was calculated as a function of $\Delta\rho_0$.[1] Some results on the effects caused by irradiation and implantation of the new superconducting oxides have already been published (Refs. 2–4, and references therein). In general, it is found that the critical temperature of these materials is rather sensitive to radiation damage. T_c decreased below 4.2 K at damage levels of about 2×10^{-2} displacements per atom, dpa (1 eV/atom). The T_c suppression occurred in the same dpa region after irradiation with H, He, and Ar ions, which deposit quite different energy densities into nuclear and electronic collisions. From this result, it was concluded that the observed changes of T_c were due to damage of collisional nature rather than to electronic excitations which produce defects in isolating ceramics.[3] Increasing the damage level to about 0.04 dpa led to an orthorhombic-to-tetragonal phase transformation,[3] accompanied by a transition from metallic to semiconducting behavior. A transformation into an amorphous phase was observed at damage levels above 0.1 dpa.[2,3]

It is well known that the oxygen concentration and oxygen ordering play important roles for the high-T_c superconductors. The oxygen atoms are rather mobile and diffuse even in a near-room-temperature plasma oxidation process.[5] Thus, it is conceivable that displaced oxygen atoms may recombine with neighbored vacancies below 300 K. Therefore, in this study, the irradiations were performed at 4 and 77 K in order to study the recovery stages below 300 K. The existence of such stages was observed previously in electron-irradiated bulk samples.[6]

Thin superconducting films of $YBa_2Cu_3O_7$ have been prepared by magnetron sputtering on single-crystal $SrTiO_3$ substrates at 800 °C and were heated subsequently *in situ* at 430 °C in pure O_2 atmosphere. The preparation process is described in detail elsewhere.[7] The resistively measured T_c-midpoint value typically was at 89 K, and the transition width was less than 2 K. The layers show the full superconducting transition at 88 K. The films were single crystalline, aligned with the c axis perpendicular to the substrate surface as shown by channeling and x-ray measurements. From irradiation experiments of such high-quality films it was hoped to obtain reliable information on the relationship between radiation-induced changes of T_c and ρ_0. The experimental setup for the low-temperature irradiation consists of a 350-keV heavy-ion accelerator and a liquid-He cryostat. The irradiation equipment is described in more detail in Ref. 8. The transition temperature was taken as the temperature at half the value of the residual resistance obtained by a standard four-probe arrangement. The irradiations have been performed with protons of 300 keV with a beam scanned horizontally and vertically over the target area. The penetration depth of the protons ($\simeq 2$ μm) was larger than the thickness of the $YBa_2Cu_3O_7$ films (0.5 μm).

The observations depended on the applied fluence. Irradiations at 77 K in the low-fluence region ($<1\times10^{16}$ H^+/cm^2) cause an increase of the resistance R, but do not affect T_c to a great extent. This behavior is demonstrated in Fig. 1 where R vs T curves are shown. Curve (a), the curve with the lowest resistance, is that of the sample before irradiation. Curve (b) is obtained for a sample which was irradiated with 1.5×10^{15} H^+/cm^2 and annealed to room temperature. After annealing to room temperatures, the R-vs-T curve is completely reversible as indicated by arrows. Curve (c) with the highest resistance is the annealing curve obtained after irradiation with a total fluence of 5×10^{15} H^+/cm^2 and slowly warmed up (0.3 K/min) to room temperature. It is clearly seen that the

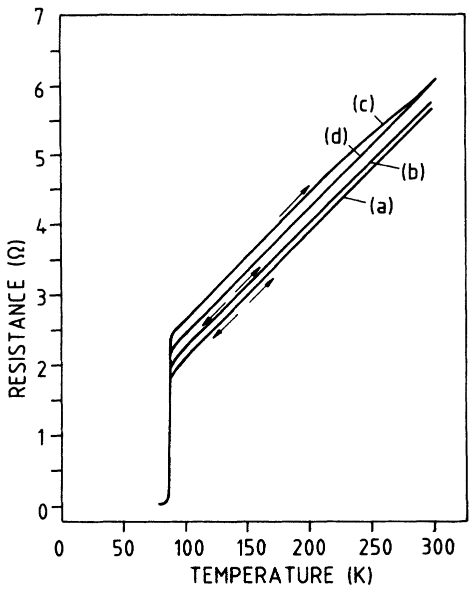

FIG. 1. Resistance as a function of temperature: (a) cooling and heating curve of a sample before irradiation; (b) cooling and heating curve of this sample, previously irradiated with 1.5×10^{15} H^+/cm^2 and annealed to room temperature; (c) annealing curve of this sample after irradiation with a total dose of 5×10^{15} H^+/cm^2 at 77 K; and (d) cooling and heating curve of sample (c).

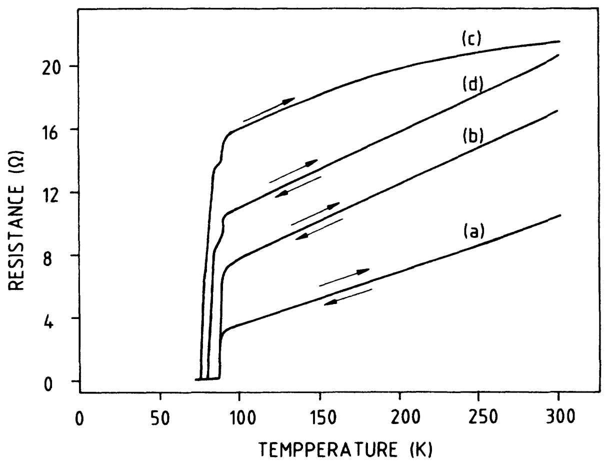

FIG. 2. Resistance as a function of temperature: (a) cooling and heating curve of the sample before irradiation; (b) cooling and heating curve of this sample previously irradiated with 1.3×10^{16} H^+/cm^2 and annealed to room temperature; (c) annealing curve of this sample after irradiation with a total dose of 2.3×10^{16} H^+/cm^2 at 77 K; and (d) cooling and heating curve of sample (c).

deviation from the linear increase of the resistance starts at about 200 K, indicating that a certain fraction of the radiation-induced disorder starts to anneal at this temperature. Curve (d) is that obtained by cooling and heating after the irradiated sample has been annealed to room temperature. From the difference of curves (c) and (d) normalized to the difference of the R values at 100 K, the recovery stage can be extracted. The slope, $d\rho/dT$, T_c and δT_c are not affected in this fluence region.

For fluences larger than 1×10^{16} H^+/cm^2, in addition to an increase of R, a decrease of T_c is noted as is demonstrated in Fig. 2 by the R-vs-T curves (c) and (d). In these curves, the initial T_c value is still indicated by small steps, due to the fact that the irradiating beam is slightly shadowed from totally reaching the voltage contacts. It should be noted that the disorder causes a nearly parallel shift of the transition curve to lower temperatures. This result points to a remarkably homogeneous damage distribution caused by the proton irradiation. The annealing curve (c) of the sample irradiated with 2.3×10^{16} H^+/cm^2 reveals two steps in the transition region. After warming up to room temperature, the lower one of these steps annealed indicating that the disorder which recovers at temperatures above 150 K [see curve (c)] also causes a decrease of T_c. Curve (d) is reversible in cooling and heating cycles and the recovery stage can be extracted as described above. The recovery stage covers a broad temperature region suggesting that more than just a single activation energy is involved in the recovery process. It can be seen in Fig. 2 that the slope $d\rho/dT$ of the sample increases in this fluence region from (a) 1.9 $\mu\Omega$ cm/K to (d) 2.4 $\mu\Omega$ cm/K after annealing to room temperature.

For fluences above 7×10^{16} H^+/cm^2, in addition to the R increase and the T_c decrease, a transition into a second phase is clearly seen in Fig. 3 [curve (c)]. Here, especially at temperatures below 10 K, a strong increase of the resistance with decreasing temperature is noted after irradiation with 7.8×10^{16} H^+/cm^2 at 4.2 K. Since the increase of the resistance could be described by an expression of the form $R=R_0\exp(-E_g/2kT)$, we conclude that this phase is semiconducting. From the fit an activation energy E_g of 0.44 meV could be deduced. After warming up

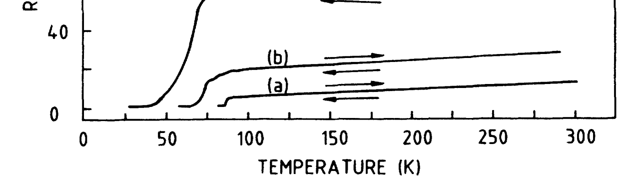

FIG. 3. Resistance as a function of temperature: (a) cooling and heating curve of the sample before irradiation; (b) cooling and heating curve of this sample, previously irradiated with 4.3×10^{16} H^+/cm^2 and annealed to room temperature; (c) annealing curve of this sample after irradiation with a total dose of 7.8×10^{16} H^+/cm^2 at 4.2 K; and (d) cooling and heating curve of sample (c).

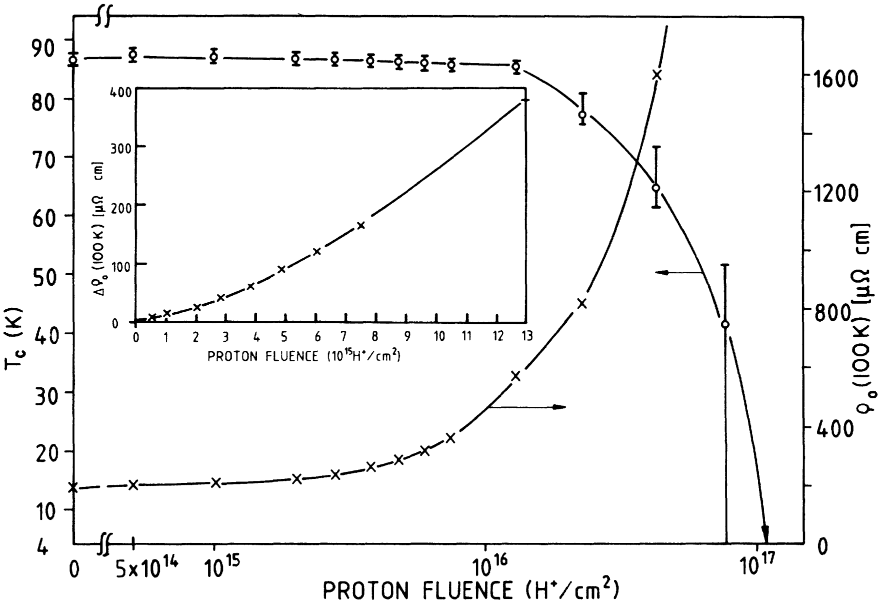

FIG. 4. Superconducting transition temperature, transition width, and resistivity as a function of the proton fluence irradiated and measured at 77 K.

to room temperature [curve (c)] most of the semiconducting phase anneals out although a slight increase of R with decreasing T is still seen in curve (d). The rather broad transition width of curve (d) also indicates that a mixture of phases still exists. An increase of the fluence up to 1.1×10^{17} H^+/cm^2 at 4.2 K, results in an activation energy of 2.6 meV, indicating that by increasing the damage level above 2×10^{-2} dpa the gap becomes wider. In this state of disorder, the superconducting phase no longer exists above 4.2 K. During annealing to room temperature, again a strong recovery is noted although the superconducting phase does not form a continuous network, as the zero resistance is not reached.

For a convenient discussion the T_c midpoint values, the transition widths δT_c, and the resistivities at 100 K are shown in Fig. 4 as a function of the proton fluence ϕ. Further, the radiation-induced increase of the resistivity, $\Delta\rho_0[\Delta\rho_0=\rho(100\text{ K},\phi)-\rho(100\text{ K},0)]$ as a function of ϕ is given in the inset of Fig. 4. Several features are noted which are quite different from the behavior of former irradiated high-T_c superconductors, which will be discussed in more detail. In the low-fluence region up to about 1×10^{16} H^+/cm^2, it is seen that T_c and δT_c change only slightly while ρ increases from 190 to 570 $\mu\Omega$ cm. This could be attributed to defects being inhomogeneously distributed having an undamaged network of high-T_c material. For this case, one would expect a broadening of δT_c which is, however, not observed. Further, the R vs T curves show a linear behavior in this fluence region which also points to homogeneously distributed defects. In the medium fluence region, the total transition curve shifts almost parallel to lower temperature after irradiation and to higher temperature after annealing (Fig. 2). This provides not only additional evidence of a homogeneous defect distribution but also of the homogeneity of our single crystalline starting material. In irradiation experiments of polycrystalline material of less quality, T_c depressions were accompanied by a broadening of the transition curves. We therefore believe that our observations are an intrinsic property of the material rather than grain-boundary effects.

Since defects are electron-scattering centers, normally the number of defect centers, and thus $\Delta\rho_0$, is proportional to ϕ at low fluences and reaches a saturation at large fluences. However, for $YBa_2Cu_3O_7$, $\Delta\rho_0$ increases stronger than linear with ϕ, as shown in the inset of Fig. 4, which points to an enhanced electron-scattering effect. This is supported by the observed increase of $d\rho/dT$ from 1.9 to 2.4 $\mu\Omega$ cm/K. For normal high-T_c superconductors the thermal part of the resistivity $\rho_{th}=\rho_{RT}-\rho_0$ was found to decrease immediately with ϕ at low fluences. This was attributed to a decrease of λ_{tr}, the electron-phonon coupling transport constant which is closely related to λ. For $YBa_2Cu_3O_7$ in contrast, ρ_{th} is even found to increase slightly, T_c, however, is not affected. This different behavior of $YBa_2Cu_3O_7$ is clearly demonstrated in Fig. 5 where the relative T_c decrease, T_c/T_{c0}, is presented as a function of $\Delta\rho_0$ in comparison to other superconductors. Previously, λ was assumed to be proportional to $N(E_F)$ and T_c was calculated as a function of $\Delta\rho_0$.[1] Even for low-T_c transition metals and transition-metal compounds, the increase of T_c with increasing $\Delta\rho_0$ could be attributed to an increase of $N(E_F)$ and therefore, of λ.[13] For the high-T_c $YBa_2Cu_3O_7$, such relationships do not exist, which may indicate a different pairing mechanism.

For fluences above about 7×10^{16} H^+/cm^2, a strong decrease of T_c and a strong increase of the transition width is noted. As demonstrated in Fig. 3(c), this behavior is accompanied by the appearance of a semiconducting phase. Assuming that all the energy is dissipated to oxygen atoms well distributed in different unit cells, the semiconducting volume fraction ($YBa_2Cu_3O_6$) is estimated to

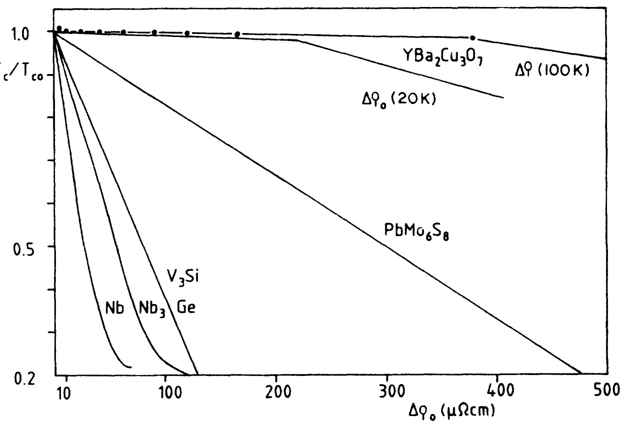

FIG. 5. Reduced T_c values as a function of the radiation-induced increase of the residual resistivity $\Delta\rho_0$ for Nb (Ref. 9), V_3Si (Ref. 10), Nb_3Ge (Ref. 11), $PbMo_6S_8$ (Ref. 12), and $YBa_2Cu_3O_7$. T_{c0} is the T_c midpoint before irradiation.

be 10 vol% as an upper limit. Since the transition to superconductivity does not reach zero resistivity, we conclude that a continuous network of the semiconducting phase exists, embedding the superconducting material. During annealing to room temperature the semiconducting phase partly retransforms to the superconducting phase probably due to the recombination of close oxygen-vacancy pairs. The semiconducting network then becomes discontinuous and the superconducting phase prevails. Thus, it appears that the decrease of the residual resistivity ratio below 1.0 is due to the presence of the semiconducting phase and cannot be attributed to the superconducting phase. With an increasing proton fluence, the volume fraction of the semiconducting phase as well as the activation energy increase.

In conclusion, a broad recovery stage has been observed at about 200 K in low-temperature irradiated YBaCuO thin films. About 60% of the radiation-induced damage recovers together with the changes caused by the irradiation in the different fluence regions. This refers to the T_c decrease, to the increase of the resistance, of the transition width and of the volume fraction of the semiconducting phase. We therefore conclude that all changes are due to the same type of defect which is believed to consist of displaced oxygen atoms, mainly. Previous results obtained for the former high-T_c superconductors, especially for transition metals and transition-metal compounds, revealed a universal behavior between T_c and δT_c and the radiation-induced changes of the residual resistivity and the thermal part of the resistivity. These changes could mainly be attributed to variations of the electronic band structure at the Fermi level. The results reported here for $YBa_2Cu_3O_7$ are quite different. At low fluences, T_c and δT_c are not sensitive to rather large radiation-induced changes of the residual resistance. This is an intriguing effect which so far was observed in single crystalline films only and may be due to a special defect structure which deserves further investigations. The fact that T_c does not immediately decrease with increasing electron scattering on point defects in the high-T_c oxide superconductor could, in principle, be due to the fact that the T_c decrease is canceled by an increase of λ_{tr} and thus of λ. We, however, argue that electron scattering on imperfections in the energy range of kT at the Fermi surface does no longer occur in an energy range which is important for the pairing mechanism. Then the results would indicate that the pairing energy is larger than kT in agreement with theoretical estimations.[14]

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[1]L. F. Mattheiss and R. L. Testardi, Phys. Rev. B **20**, 2196 (1979); Phys. Rev. Lett. **41**, 1612 (1978).

[2]G. J. Clark, A. D. Marwick, R. H. Koch, and R. B. Laibowitz, Appl. Phys. Lett. **51**, 139 (1987).

[3]B. Egner, J. Geerk, H. C. Li, G. Linker, O. Meyer,. and B. Strehlau, Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 2141 (1987).

[4]Y. Quéré, in Proceedings of the Twelfth International Conference on Atomic Collisions in Solids, Okayama, Japan, 1987 (unpublished).

[5]B. G. Bagley, L. H. Greene, J.-M. Tarascon, and G. W. Hull, Appl. Phys. Lett. **51**, 622 (1987).

[6]B. Stritzker, Fall Meeting of the Materials Research Society, Boston, Massachusetts, 1987 (unpublished).

[7]H. C. Li, G. Linker, F. Ratzel, R. Smithey, and J. Geerk, Appl. Phys. Lett. **52**, 1098 (1988).

[8]P. Ziemann and O. Meyer, Z. Phys. B **35**, 141 (1979).

[9]G. Linker, in *Proceedings of the Fourth International Conference on Superconductivity in d- and f-Band Metals, Karlsruhe, 1982,* edited by W. Buckel and W. Weber (Kerforschungszentrum, Karlsruhe, 1982), p. 367.

[10]O. Meyer and G. Linker, J. Low Temp. Phys. **38**, 747 (1980).

[11]J. Pflüger and O. Meyer, Solid State Commun. **32**, 1143 (1979); J. Pflüger, Ph.D. thesis, Universität Karlsruhe, 1980 (unpublished).

[12]G. Hertel, H. Adrian, J. Bieger, C. Nölscher, L. Söldner, and G. Saemann-Ischenko, Phys. Rev. B **27**, 212 (1983).

[13]R. Schneider, G. Linker, and O. Meyer, Phys. Rev. B **35**, 55 (1987).

[14]P. A. Lee and N. Read, Phys. Rev. Lett. **58**, 2691 (1987).