Effect of Proton Irradiation and Annealing on
the Critical Current Density in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Single Crystals

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FEB 14 1996

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Physical Review B

jmc

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*Work supported by the U.S. Department of Energy, BES-Materials Sciences under contract #W-31-109-ENG-38 (HKV, MAK, PB, GWC) and the National Science Foundation--Office of Science and Technology Centers under contract #DMR 91-20000 (UW, JG, WCL).

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Effect Of Proton Irradiation and Annealing On The Critical Current Densities in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Single Crystals.

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(Received

Abstract

We have studied the effect of annealing up to 350°C on the critical current densities in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals that were irradiated with 3.5 MeV protons to a fluence of $1 \times 10^{16} \text{ p}^+/\text{cm}^2$. Large enhancements in the critical current densities, determined from DC-magnetization measurements, were observed immediately after irradiation at all temperatures for magnetic field orientations both parallel and perpendicular to the c-axis. These crystals were then annealed at room temperature, 100, 200, 300, and 350°C, and the critical current densities were determined after each annealing step. The annealing above room temperature resulted in a reduction of the critical current densities for both directions of the magnetic field. The transition temperatures, determined from low field DC-magnetization measurements at each stage of the measurement sequence, decreased by about 0.5 K following the irradiation and recovered to their original value after annealing at higher temperatures. We propose a defect model to explain the observed pinning and its anisotropy observed in this work and earlier work on electron and neutron irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals.

INTRODUCTION

Radiation damage has been traditionally used to introduce pinning centers in the superconducting materials, simultaneously altering the existing defect structure and the critical current density in these materials[1]. The results show a broad variety of effects and depend on the type of material subjected to the radiation, on the pre-irradiation defect structure and on the type of radiation. Irradiations with neutrons[2,3], electrons[4] and protons[5-7] have significantly enhanced the critical current density in single crystals and polycrystals of the high transition temperature superconductors. More recently large enhancements in the critical current density have been observed at high temperatures and high fields upon irradiation with heavy ions in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals[8,9].

Although the critical current density has been significantly enhanced by introducing new defect structure by irradiation, only recently has consideration been given to the identification and the stability of these artificial pinning centers. Recent results from measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals electron irradiated at room temperature suggest that the displaced copper atoms and their clusters are responsible for observed enhancements in J_c for $H \parallel c$ -axis[4]. Those defects disappeared upon annealing at temperatures up to 200°C leading to a recovery of the critical current density to its original value[10]. Very recently, annealing effects in neutron irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were studied[3]. The results indicated the presence of different kinds of defects, some of which were stable and some that annealed out causing a decrease in J_c from the irradiated value. The authors concluded that both point defect clusters and defect cascades were responsible for the observed enhancement when the field was applied parallel to the c -axis. The defect cascades were not destroyed by annealing to 300°C and contributed to the remaining pinning observed after the final anneal. The decrease of the critical current density upon annealing was attributed to the disappearance of the point defect clusters. It was also found that the defect cascades by themselves did not contribute to the pinning of the vortices when the field was parallel to the ab -plane.

Earlier work has reported an order of magnitude enhancement in the critical current density at 77 K in a field of 1 T after irradiation near room temperature with 3 MeV protons to a dose of $1 \times 10^{16}/\text{cm}^2$ [11]. Using an estimate[12] for the defect density necessary to account for the observed value of the critical current density, they argue that the relevant sources of pinning in the irradiated crystal are the TEM-invisible point defects. However, the specific point defects responsible for the observed pinning were not identified.

Information regarding the types of defects produced in a material under a certain irradiation condition can be obtained from an examination of the recoil energy spectra of the elements in the material. The integral recoil fraction for a certain recoil energy is defined as the fraction of the total recoils with energies below the chosen recoil energy and above a threshold energy often chosen to be 20 eV[13]. A knowledge of the fraction of primary recoils, those atoms which are directly displaced from their lattice sites by the incoming particle, is useful for a comparison of the types of defects produced under different irradiation conditions. Possible point defect mobility at the irradiation temperature also results in extended defect structure (clusters of point defects).

The integral recoil fractions of the primary recoils as a function of recoil energy for copper atoms under 1 MeV electron, fast neutron ($E_n > 0.1$ MeV) and 3.5 MeV proton irradiations are shown in figure 1. The primary recoil energies were calculated using SPECTER[14] for neutron irradiation, by the McKinley-Feshback expression for electron irradiation[15] and by TRIM for proton irradiation[16]. These calculations are accurate for copper atoms in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as long as only the primary recoil parameters are considered. All primary recoils for defect production in copper with 1 MeV electron irradiation fall between 20(threshold energy) and 70 eV(maximum recoil energy). Thus, the recoil energies induced by electron irradiation are all low, initially producing a random dispersion of point defects.

At the opposite extreme in the distributions of recoil energies is that of the neutrons for which the primary recoils are governed by nearly isotropic nuclear scattering with all recoil energies equally probable up to the maximum allowed by hard sphere scattering dynamics. Thus, besides the point defects produced by the low energy recoils(approximately 20-100 eV), there are the defect cascades that are produced by the primary high energy ($E > 30$ KeV) recoils and visible under Transmission Electron Microscopy[TEM].

The primary recoil distribution for the 3.5 MeV protons lies between the distributions for the electrons and the neutrons. This recoil spectrum is dominated (75%) by the low energy recoils that initially produce a high density of point defects. In addition, a low density of the TEM-visible defect cascades are produced by the high energy recoils (<1%) similar to those produced in the case of neutron irradiation. The recoils of intermediate energies may be expected to produce defects that vary in size depending on the

energy of recoil. Defects formed due to the recoils of intermediate energies probably include small defect cascades.

The defect structure produced by proton irradiation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals has been investigated using conventional Transmission Electron Microscopy (TEM) of irradiated crystals and in situ irradiation experiments [13,17]. Most of the visible defect sizes range from 2 to 5 nm. Many of the defect strain fields have been found to be highly anisotropic, more recent evidence for this is shown in Figure 2. The anisotropy of many defect strain fields is demonstrated by the fact that two to three times as many defects are visible in diffraction vector [200] (Fig. 2b) than in [020] (Fig. 2a). Those few defects which show visibility in both diffraction vectors are almost certainly the defect cascades associated with the highest recoil energies, which produce the greatest local structural disorder and strain in both directions. These cascade defects are the same as those produced to a greater fraction by neutron irradiation and also investigated by TEM [18, 19]. However, the majority of visible defects which show strain only in [200] are now believed to be of a different structure which results from the clustering of mobile point defects [17]. Other features in Figure 2 include the broad light and dark bands, parallel with the foil edges at the top, which are thickness contours due to the effect of dynamical diffraction extinction, and the nearly vertical, more narrow light and dark bands (fringes), which are caused by dynamical diffraction effects from the 45° tilted twin boundaries.

To summarize, there appear to be three general types of defects produced by proton irradiation at room temperature. They are (1) a relatively high concentration of point defects on all the sublattices, (2) clusters of point defects including the TEM-visible defects with highly anisotropic strain fields, and (3) the more isotropic defect cascades that vary in size depending on the value of the recoil energy, the larger ones (recoil energies > 30 keV) being visible under conventional TEM.

We present the results from DC magnetization measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals irradiated at room temperature with 3.5 MeV protons to a dose of 1×10^{16} p^+/cm^2 . The critical current densities were determined using the anisotropic Bean model [20]. To gain a better understanding of the nature of the radiation induced defects the irradiated crystals were annealed at room temperature, 100, 200 and 300°C . The critical current densities and the transition temperatures were determined after irradiation and after each anneal.

EXPERIMENTAL DETAILS

A. Sample Selection and Transition Temperature

Three thin plate-like twinned crystals with typical dimensions of $1 \times 0.8 \times 0.035$ mm³, with the smallest dimension along the c-axis, were chosen for this study. Their transition temperatures, T_C , defined as the temperature for the onset of superconductivity, were determined from DC magnetization measurements made in a non-commercial low field SQUID magnetometer [21]. The crystals were cooled in zero-field to about 70 K and a field of 1 Oe was applied parallel to the c-axis. The moments were measured every 0.1 K as the crystals passed through the transition to the normal state. One of the crystals, V15, was grown in a Zirconia crucible[22] and had a T_C of 91.2 K. Two other crystals, V10 and V6, grown in a gold crucible[23] had T_C 's of 92.3 K and 90.3 K, respectively. All transition widths were less than 1 K.

B. Irradiation

The crystals were irradiated to a fluence of 1×10^{16} p⁺/cm² at a rate of about 1.4×10^{12} p⁺/cm²/sec. This fluence was chosen because it produced the maximum critical current density at 77 K in earlier work[11]. The irradiations were performed at room temperature in the TANDEM accelerator at Argonne National Laboratory. The crystals were irradiated with 3.5 MeV protons with the ion beam at about 10° off the c-axis to prevent the channeling of the incident protons. The range of the protons of this energy in this material is about 55 μm which is larger than the thicknesses of the crystals. This ensures a nearly uniform defect density through thicknesses of the crystals of about 35 μm.

C. DC magnetization Measurements

The DC magnetization measurements were made in a commercial Quantum Design SQUID magnetometer with a sensitivity of 1×10^{-6} emu. For measurements with $H \parallel c$ -axis each crystal was first glued with varnish to a flat glass plate with the ab-plane of the crystal parallel to the plane of the plate. The glass plate was then mounted with varnish in a horizontal slot cut at the center of a vertical cylindrical quartz tube. The magnetic field is then applied parallel to the axis of the tube and to the c-axis of the crystal.

It has been observed that magnetization measurements for fields nearly in the ab-plane of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals are very sensitive to the angular alignment of the field with the ab-plane[20, 24]. To ensure that the ab-plane is aligned parallel to the field careful mounting procedures were used. A quartz fiber was glued with varnish to the flat face (ab-plane) of the crystal. A non-magnetic weight was attached to one end of the fiber. A copper wire glued to the other end was used to suspend the fiber, the assembly being held vertical by gravity. The angular alignment was verified by measuring the slope of the magnetization as a function of the applied field in the Meissner state every time the sample was remounted. This procedure has been described elsewhere[3].

For the DC magnetization measurement, the field was cycled from 0 to 5 T and back to 0 T and the moment was measured every 0.5 T. To overcome the relaxation associated with the magnet, the data were taken 120 seconds after every field change to allow for the stabilization of the field. Scan lengths of 4 cm were used to ensure field uniformity better than 0.1%. An average of three scans was used for the final value of the moment at every field. The time taken for the three scans at each field was approximately 6 minutes. The relaxation of the sample was checked from the values of the individual scans. At 10 K, the scans were reproducible to within 2% at all fields. However, at higher temperatures (70 K) and at higher fields (> 2 T) the third scan was smaller than the first scan by up to 50%. This indicates that there is a strong relaxation of the magnetization within the sample at higher temperatures and at higher fields. At the present time we ignore this problem by using the same waiting time for all our measurements. Thus, the values of the critical current densities reported here are the average values over a time of about 8 minutes after the application of the field.

The field dependence of the magnetization was measured at 10, 40, and 70 K for $H \parallel c$ -axis and for $H \parallel ab$ -plane before the crystals were irradiated and the measurements were repeated after irradiation. Two crystals, V10 and V15, were remeasured 8 weeks after irradiation, having been stored at room temperature (20°C). These crystals were then annealed in air for 8 hrs at 100, 200 and 300°C and their DC magnetizations were measured after each anneal at 10, 40 and 70 K for both orientations of the magnetic field. Crystal V15 was further annealed at 350°C in air for 8 hrs. and the critical current densities were again determined from DC magnetization measurements. The transition temperatures of the two crystals were measured at each stage of the experiment. The maximum annealing temperature was chosen to avoid any loss of oxygen based on the oxygen tracer diffusion coefficient in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals reported by Rothman et al.[25]. The third

crystal, V6, was stored at room temperature in air and the DC magnetization was measured after 6 months($H \parallel ab$ -plane and $H \parallel c$ -axis) and about 12 months($H \parallel c$ -axis) after irradiation. This crystal was then broken into two halves, one half being used for the annealing studies of the critical current density and the other for TEM. It was then annealed at 100, 200 and 300°C and the DC magnetization was measured with $H \parallel c$ -axis after each anneal. TEM results on this crystal are not available as yet.

RESULTS

1. Effects due to Irradiation

Following irradiation with protons a decrease in the transition temperature by about 0.5 K was observed for all the crystals. Such decreases in the transition temperatures have been observed in $YBa_2Cu_3O_{7-\delta}$ single crystals irradiated with neutrons[3] and electrons[4] to fluences which produce a maximum in the critical current density. Decreases up to 2 K following irradiation with 3 MeV protons to a fluence of $2 \times 10^{16} / \text{cm}^2$ have been observed[5]. Systematic increases in T_c 's were observed when the crystals were annealed in air for 8 weeks at room temperature and 8 hours at 100, 200 and 300°C. The changes in the transition temperatures are shown in Figure 3.

The anisotropic Bean model[20] developed for a rectangular parallelepiped was used to extract the critical current density from DC magnetization measurements. The critical current densities are determined from the equations $\Delta M = (J_c^{ab} l_1 / 20) \{1 - (l_1 / 3l_2)\}$ and $\Delta M = (J_c^c l_1 / 20)$ for $H \parallel c$ -axis and $H \parallel ab$ -plane, respectively[3]. J_c^{ab} is the critical current density in the ab-plane when the field is applied parallel to the c-axis and J_c^c is the critical current density along the c-axis when the field is applied parallel to the ab-plane. l_1 and l_2 are the dimensions of the crystal in the ab-plane.

A large increase in the width of the hysteresis loop is observed upon irradiation with protons for both directions of the magnetic field. The results indicate a strong anisotropy in flux pinning between the two orientations of the magnetic field. Therefore, in this section, we will deal with the results for the two directions separately.

$H \parallel c$ -axis. DC magnetization measurements for each sequence at 10 and 70 K for crystal V15 are shown in figures 4a and b, respectively. The critical current densities at 10 and 70

K, determined from the width of the hysteresis loop, are shown in figures 5a and b, respectively. It is easily seen that there is an increase in the critical current density, J_c^{ab} , upon irradiation at both measurement temperatures.

Figures 6a and b show the field dependencies of the critical current densities at 70 K for the three crystals before and after irradiation, respectively. Before irradiation crystal V6 has the highest value of J_c^{ab} while crystal V15 has the lowest value of J_c^{ab} . However, after irradiation the results are reversed with V15 having a higher critical current density (by a factor of 2.5 at 2 T) than V6 and V10 at all fields. Before irradiation crystal V10 had an intermediate value of J_c^{ab} up to 3 T and the highest value of J_c^{ab} above 3 T. After irradiation V10 has similar values of J_c^{ab} as V15 and is higher than the J_c^{ab} in V6 at all fields. The correlation of the critical current densities at 2 T before and after irradiation is presented in figure 7a. This figure shows that the crystals that have a lower critical current density before irradiation have a higher value of critical current density after irradiation.

A second important feature observed in the measurements at 70 K is the shift in the point of reversibility of the magnetization upon irradiation with protons. Before irradiation the magnetization at 70 K in crystals V10 and V6 is reversible above 4 and 3.5 T, respectively. The irreversibility field, H_{irr} , does not change after proton irradiation in the two crystals within the resolution of this measurement. However, in crystal V15, H_{irr} shifts from 1 T before irradiation (as seen by the closing of the hysteresis loop at 1 T in figure 4b) to a field greater than 5 T after proton irradiation. The changes in the irreversibility field, ΔH_{irr} , given by the difference in H_{irr} before and after irradiation is plotted against the values of H_{irr} before irradiation in figure 7b. Thus, crystals with a low H_{irr} have a large increase in H_{irr} after irradiation. Such shifts in the irreversibility field were not found in earlier measurements of proton irradiated $YBa_2Cu_3O_{7.8}$ single crystals[5].

The field dependencies of the critical current densities at 10 K are similar among the three crystals before irradiation[Fig. 8a] in contrast to the data at 70 K[Fig. 6a]. After irradiation the crystals have similar values of J_c^{ab} , the values varying within a factor 1.5 among the crystals[Fig. 8b]. We do not observe the same correlation in the critical current densities at 10 K before and after irradiation as we did for the critical current densities at 70 K in a field of 2 T.

The correlation of the critical current densities before and after irradiation and the dependence of the shift in the irreversibility field upon irradiation on its value before

irradiation will be explained below by the variations in the final defect structure among crystals. The interaction of mobile point defects with the pre-irradiation defect structure is important in determining the nature of the final pinning defect structure in the crystals.

H || ab-plane. The effects due to proton irradiation with the applied field parallel to the ab-plane in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals have been studied for the first time. The field dependencies of the critical current densities at 10 and 40 K, before and after irradiation with protons, are shown in figures 9 and 10, respectively. An increase in J_c^c is observed in crystals V10 and V15, with the highest value of J_c^c at 10 K in a field of 2 T being $5 \times 10^4 \text{ A/cm}^2$. Comparing the critical current densities of V10 and V15 at 40 K, crystal V15 that had a lower J_c^c before irradiation has the higher J_c^c after irradiation.

An interesting effect observed in this orientation before irradiation is that the crystal V6, which had the highest critical current density, J_c^{ab} , when the field was applied parallel to the c-axis had the lowest value of J_c^c when the field is applied parallel to the ab-plane. Moreover, this crystal had the smallest enhancement in the critical current density upon irradiation with protons for H || ab-plane similar to the results for H || c-axis.

ANNEALING RESULTS

The effect of annealing in air at room temperature, 100, 200 and 300°C on the critical current density can be used to characterize the defects responsible for the observed pinning. We report this effect as a recovery of the critical current density, R, defined as,

$$R = \frac{J_c^{\text{Irr}} - J_c^{\text{Ann}}}{J_c^{\text{Irr}} - J_c^{\text{Unirr}}}$$

Here, J_c^{Unirr} , J_c^{Irr} and J_c^{Ann} are the values of the critical current density before irradiation, after irradiation and after annealing, respectively.

Annealing at room temperature. The critical current densities and the transition temperatures in all the crystals were determined within four days after the irradiation. The crystals V10 and V15 were then stored at room temperature and the measurements were repeated after 8 weeks. For $H \parallel c$ -axis, the critical current density at 2 T decreased by about 5 % at all measurement temperatures compared to the value just after irradiation[Fig. 5]. The crystal V6 was stored at room temperature and the critical current densities were again determined 6 months after irradiation. A small decrease (6 % at 2 T) in J_c^{ab} at 10 K and no significant change at 40 and 70 K were observed. The critical current densities did not change when this crystal was measured about a year later.

The critical current density J_c^c ($H \parallel ab$ -plane) decreased by about 10 % at 10 K in a field of 2 T after the crystals were annealed in air at room temperature for 8 weeks[Fig. 11a]. However, unusual changes in the critical current density were observed at 40 K[Fig. 11b] in all the crystals, the magnitude varying among the crystals. J_c^c decreased at low fields by about 8 % while an increase was observed at higher fields. The magnitude of this increase in the critical current density increased with increases in the applied field (from about 8 % at 2 T to 60 % at 4.5 T in V15) as can be seen in figure 11b. Moreover, the critical current density was nearly independent of the applied field at higher fields(> 2 T) after the annealing at room temperature. These increases in the critical current densities at 40 K suggest the formation of a new defect structure with time. Apparently this change in the defect structure with time affects neither the critical current density at 10 K for $H \parallel ab$ -plane, nor the critical current density when the field is applied parallel to the c -axis for all measurement temperatures. Misalignment between measurements as a possible cause for the changes at 40 K for $H \parallel ab$ -plane can be ruled out as these changes were observed only at 40 K and not at 10 K. To additionally confirm that misalignment was not a problem in these measurements, hysteresis measurements were made in a fourth irradiated crystal. The measurements were repeated after 2 weeks without demounting the crystal. The second measurement showed an increase in J_c^c at 40 K at high fields and not at 10 K.

Annealing above room temperature. The critical current densities decreased systematically at all measurement temperatures upon annealing at 100, 200 and 300°C for both orientations of the magnetic field as can be seen in figures 5 and 11. The effect of annealing on the critical current densities can be studied from the recoveries calculated using the equation for R. The crystals V10 and V15 exhibit similar dependencies of the recovery, R, on the annealing temperature. The recoveries in the critical current densities at 2 T for crystal V15

for the two orientations of the magnetic field at 10 K are plotted as a function of the annealing temperature in figure 12a. From this figure it is evident that the recovery due to the annealing is different for the two orientations of the magnetic field. In general, the recovery R increases by equal increments with the annealing temperatures for $H \parallel c$ -axis and tends to saturate after the 300°C anneal. For $H \parallel ab$ -plane, there is a large recovery between 100 and 200°C with only a small additional recovery after the 300°C anneal. The differences in the recoveries for the two orientations of the magnetic field will be explained by differences in the type of the pinning defects.

The recoveries in J_c^{ab} for the three crystals at 10 K in a field of 2 T for $H \parallel c$ -axis are shown in figures 12b. The recoveries in J_c^{ab} are almost the same in V10 and V15 at all measuring and annealing temperatures. However, in crystal V6 the annealing in J_c^{ab} is slower between room temperature and 100°C and follows the behavior of V10 and V15 from 100 to 300°C. Moreover, the absolute value of R is less in V6 compared to V10 and V15 for all the annealing and measuring temperatures. We will explain this variation in the recoveries among the crystals by the difference in the final defect structure produced by the interaction of the radiation induced defects with the pre-irradiation defect structure.

DISCUSSION

Effects due to Irradiation

$H \parallel c$ -axis. The defects created by irradiation with protons are effective in pinning the vortices thus enhancing the critical current density at all temperatures as can be seen in figures 5a and b. However, the values of the critical current density and their variation with the temperature of measurement after irradiation are not the same in all the crystals. We observe a correlation between the critical current densities at 70 K before and after irradiation [Fig. 7a]. Crystal V6, which has the highest critical current density before irradiation and can be considered to be the most defective, has the lowest J_c^{ab} after irradiation. The least defective crystal, V15, characterized by an absence of a hysteresis in the magnetization at 70 K above 1 T before irradiation, has the highest value of J_c^{ab} after irradiation. This correlation of the critical current densities at 70 K before and after irradiation can be best explained by the formation of a pinning defect based on the clustering of mobile point defects produced by irradiation. This explanation involves the interaction of the mobile point defects with the pre-irradiation defect structure which is very important in determining the final defect structure and the critical current density in the crystals. This

description has been used to explain similar behavior of the critical current densities observed in electron[4,10] and neutron[3] irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ single crystals.

Irradiation with protons initially produces a high density of point defects (interstitial-vacancy pairs) by the low energy recoils and a lower density of the defect cascades by the higher energy recoils[Fig. 1]. The point defects probably include interstitials and vacancies on all the sub-lattices, some of which may be mobile at room temperature. It has been suggested from experiments on electron irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ single crystals that the mobile point defects which are important to pinning are formed by the displacements of copper[26]. By analogy with most metals and alloys, we will assume that the interstitials are more mobile than the vacancies[27]. This is consistent with recent TEM results which indicate that the strain fields exhibited by the cluster defects are of the interstitial type and not the vacancy type[17]. The migrating interstitials of copper can either cluster, recombine with vacancies, or be trapped by the defects present in the material before irradiation. The extent of the clustering of the interstitials and the recombination of interstitials with vacancies would depend on the density and type of the pre-irradiation defect structure. In more defective crystals like V6 and V10, the chances of the interstitials being trapped by the pre-irradiation defects such as dislocations or stacking faults far exceed the probability of the clustering and the recombination of the interstitials with vacancies. Such defective crystals would then have a low density of clusters but a high density of copper vacancies. In a clean crystal, as V15, the local instantaneous concentration of migrating copper interstitials will be greater due to the low sink density(pre-irradiation defect concentration) resulting in a higher probability for clustering and recombination with vacancies. The final defect structure in a clean crystal(V15) would then consist of a higher density of clusters and a lower density of vacancies due to enhanced recombination when compared to a more defective crystal(V6 and V10). The density of the defect cascades, formed by the recoils of energy > 30 keV, would not vary among the crystals as the formation of these defects is independent of the pre-irradiation defect structure.

Having proposed the types of defects formed in the crystals after irradiation, we can try to understand the effect of the various defects on the critical current density. The higher value of J_c^{ab} observed in V15 at 70 K after irradiation [Fig. 7a] can be attributed to the higher density of clusters in this crystal. The higher density of vacancies in V6 does not seem to be as effective as the clusters in V15 in pinning the vortices at 70 K. The critical current density observed at 70 K in V6 after irradiation could be primarily due to the defect cascades that are formed independent of the pre-irradiation defect structure. These results

are consistent with the results on crystal V10 which has a lower value of J_c^{ab} compared to V6 before irradiation[Fig. 6a] while after irradiation the critical current density in V10 is comparable to J_c^{ab} in V15 and higher than in V6[Fig. 6b]. We suggest that defects effective in pinning the vortices at 70 K are the clusters of copper interstitials and the defect cascades, but not the copper vacancies.

The arguments used to explain the correlation of the critical current densities before and after irradiation for $H \parallel c$ -axis can be used to understand the shift in the irreversibility field upon irradiation in V15. The clusters that enhance the critical current density in V15 at 70 K are also effective in shifting the irreversibility field H_{irr} in this crystal. The irreversibility field does not change in crystals V10 and V6 both of which have high values of H_{irr} before irradiation. These results are consistent with previous reports on electron[4] and neutron[3] irradiated $YBa_2Cu_3O_{7-\delta}$ single crystals. Large shifts in the irreversibility field after irradiation with electrons and neutrons have been observed only in $YBa_2Cu_3O_{7-\delta}$ single crystals that have a low value of H_{irr} prior to irradiation[3,4]. Changes in H_{irr} could not be detected in neutron irradiated crystals which have a high value of H_{irr} prior to irradiation, similar to crystals V6 and V10[3]. Moreover, defect independence of the irreversibility line has also been reported in $YBa_2Cu_3O_{7-\delta}$ single crystals irradiated with protons[5]. The hysteresis loops for these crystals were similar to those exhibited by crystal V6 at 70 K and did not show measurable changes in the irreversibility field after irradiation. Thus, the shift of the irreversibility field upon irradiation occurs only in crystals that have a low value of H_{irr} prior to irradiation.

Prior to irradiation the data at 10 K are similar to the data at 70 K where the most defective crystal V6 has the highest J_c^{ab} and the least defective crystal V15 has the lowest. Following irradiation, the critical current density in V6 at 10 K is comparable to the critical current densities in V10 and V15 unlike the data at 70 K. Thus, there exists some defect in V6 that is effective in pinning the vortices at 10 K to make J_c^{ab} in V6 comparable to the values in V10 and V15. However, this defect structure in V6 is ineffective in pinning the vortices at 70 K. Using the model developed earlier we suggest that crystal V6 is left with a higher density of vacancies compared to V10 and V15. Therefore, one may associate the additional pinning observed at 10 K in V6 to the excess vacancies produced in this crystal after irradiation. Hence, we suggest that the vacancies, clusters of copper interstitials and the defect cascades are all effective in pinning the vortices at 10 K.

$H \parallel ab$ -plane. The behavior of the critical current densities for $H \parallel ab$ -plane is different from that for $H \parallel c$ -axis. The correlation of the critical current densities before and after

irradiation observed among the three crystals for $H \parallel c$ -axis at 70 K is not observed for $H \parallel ab$ -plane. This is because the pre-irradiation defects that pin the vortices when the field is parallel to the c -axis in crystal V6 are ineffective in pinning the vortices when the field is parallel to the ab -plane. Furthermore, the defects created by irradiation in V6 are also ineffective in increasing the critical current density in this field orientation. However, significant increases in J_c^C are observed in crystals V10 and V15 when the field is applied parallel to the ab -plane. This enhancement of J_c^C in V10 and V15 can be attributed to the presence of the clusters in these crystals. The lack of enhancement in V6 upon irradiation suggests that the defect cascades and vacancies that are formed in this crystal after irradiation are ineffective in pinning the vortices when the field is parallel to the ab -plane. Results from neutron irradiated $YBa_2Cu_3O_{7-\delta}$ single crystals also suggest that the defect cascades do not pin the vortices when the field is applied parallel to the ab -plane.

Annealing Results

The recoveries for $H \parallel c$ -axis are similar at all temperatures with equal amounts of recovery at 100, 200 and 300°C with some indication of saturation of recovery at 350°C [Fig. 12a]. The recovery of the critical current density for $H \parallel ab$ -plane, reflecting the annealing of the interstitial clusters, is different from the recovery of the critical current density for $H \parallel c$ -axis. Preliminary TEM results on V10 (R at 10 K of about 90 % after final anneal at 300°C [28]) after annealing up to 300°C show that most of the TEM-visible defects have disappeared [17].

A comparison of the recovery of the critical current density for $H \parallel c$ -axis among the crystals shows least recovery in V6 [Fig. 12b]. This is due to the lower density of clusters in this crystal inferred earlier from the discussion of irradiation data and observed by TEM in this crystal before annealing. The annealing of the other crystals results in the break up of the clusters into copper interstitials which can then combine with copper vacancies in the CuO_2 planes. Thus, the recovery of the critical current density at 10 K for $H \parallel c$ -axis could be due to the loss of both clusters and vacancies. These results are completely consistent with similar annealing results on electron irradiated $YBa_2Cu_3O_{7-\delta}$ single crystals [10].

The recovery of the critical current density for $H \parallel c$ -axis between 300 and 350°C is probably due to the annealing of the smaller defect cascades produced by the recoils of intermediate energy (1 - 10 KeV). TEM [29] and annealing results [3] on neutron irradiated $YBa_2Cu_3O_{7-\delta}$ single crystals show that the larger defect cascades are stable upon

annealing up to 300°C. These stable defect cascades contribute to the unrecovered fraction of the critical current density for $H \parallel c$ -axis after the final anneal at 350°C.

CONCLUSIONS

The defects induced by irradiation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals with protons (3.5 MeV, $1 \times 10^{16} \text{ p}^+/\text{cm}^2$) are effective in pinning the magnetic flux vortices, enhancing the critical current density for magnetic field orientations both parallel and perpendicular to the c -axis. We observe a correlation between the critical current densities at 70 K before and after irradiation wherein, the crystal with the lowest critical current density, J_c^{ab} , before irradiation has the highest value of J_c^{ab} after irradiation. This correlation can be best explained by the formation of a pinning defect based on the clustering of mobile point defects produced by irradiation. The interaction of the mobile point defects with the preirradiation defect structure leads to a variation in the density of clusters and vacancies among the crystals. The density of the defect cascades should not vary among the crystals as their formation is independent of the pre-irradiation defects. Our results indicate that clusters of copper interstitials and the defect cascades are effective in pinning the vortices at 70 K for $H \parallel c$ -axis. The formation of copper interstitial clusters are also responsible for the large shift in the irreversibility field in V15 after irradiation. We associate the additional pinning observed in V6 at 10 K with the excess vacancies formed in this crystal upon irradiation with protons.

The effect of proton irradiation on the critical current densities for $H \parallel ab$ -plane has been studied for the first time. The defects that are effective in pinning the vortices for this field orientation are primarily the interstitial copper clusters while the defect cascades and the vacancies are not effective pinning centers in this field orientation.

The differences in the defects effective in pinning the vortices for the two orientations are evident in the recoveries of the critical current densities upon annealing at 100, 200 and 300°C. The recovery of the defect clusters that are the primary pinning defect for $H \parallel ab$ -plane tends to saturate at 200°C. The smaller defect cascades produced by the recoils of intermediate energy could recover above 200°C contributing to the recovery of J_c^{ab} for $H \parallel c$ -axis. The crystal, V6, with the lower fraction of clusters shows the smallest recovery in the critical current density for $H \parallel c$ -axis. The defect cascades that do not

disappear upon annealing contribute to the critical current density observed for $H \parallel c$ -axis after the final anneal at 300°C.

ACKNOWLEDGMENTS

One of the authors (MAK) would like to thank Professor Sir Peter Hirsch for the provision of laboratory facilities in the Department of Materials, University of Oxford and the British Science and Engineering Research Council for financial support. We would also like to thank M. C. Frischherz and B. M. Vlcek for useful discussions and J. Downey for providing the single crystals grown in a gold crucible. This work was supported by the U. S. Department of Energy, Basic Energy Sciences-Materials Science under contract No. W-31-109-ENG--38(H. K. V, M. A. K, P. B and G. W. C) and the National Science Foundation-Office of Science and Technology Center for Superconductivity, under contract No. DMR 91-20000(U. W, J. G, W. C. L).

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Figure Captions

- Figure 1. The comparison of primary recoil energy distributions in irradiated copper calculated for 1 MeV electrons, 3.5 MeV protons and fast neutrons (position H1 in the Missouri University Research Reactor) assuming an arbitrary threshold for defect production of 20eV.
- Figure 2. Adjacent twins irradiated with 3.5MeV protons to a dose of $2 \times 10^{16} \text{ cm}^{-2}$ in the bulk crystal before thinning for TEM. Micrograph a) is taken in dark field with diffraction vector 020 and viewed in approximately a [100] projection, and micrograph b), due to the twinned geometry, is taken in dark field with diffraction vector 200 and viewed in a [010] projection. Irradiation produced defects (2-5nm in size) can be observed most easily in areas adjacent to open parentheses, where TEM sample thicknesses (60-100nm) and diffraction conditions in the two separate twins are similar. The reason more defects are visible in b) is explained in the text.
- Figure 3. Transition temperatures of crystals V10 and V15 before irradiation, after irradiation and after annealing in air at room temperature for 8 weeks, and for 8 hrs at 100, 200 and 300°C.
- Figure 4. Hysteresis loops for all the measurements for $H \parallel c$ -axis for crystal V15 a) 10K and b) 70K.
- Figure 5. Critical current densities for all the measurements for $H \parallel c$ -axis for crystal V15 a) 10K and b) 70K.
- Figure 6. Field dependence of the critical current densities for the three crystals for the applied field parallel to the c-axis at 70 K a) before irradiation and b) after irradiation.
- Figure 7. a) Critical current density after irradiation ($H \parallel c$ -axis, 70 K, 2 T) is plotted against the critical current density before irradiation for the three crystals.
b) Change in the irreversibility field, H_{irr} , at 70 K, due to proton irradiation plotted against H_{irr} before irradiation for the three crystals.

- Figure 8. Field dependence of the critical current densities at 10 K for the three crystals for the applied field parallel to the c-axis a) before irradiation and b) after irradiation.
- Figure 9. Field dependence of the critical current densities at 10 K for the three crystals for the applied field parallel to the ab-plane a) before irradiation and b) after irradiation.
- Figure 10. Field dependence of the critical current densities at 40 K for the three crystals for the applied field parallel to the ab-plane a) before irradiation and b) after irradiation.
- Figure 11. Field dependence of the critical current densities for $H \parallel$ ab-plane for all the measurements for crystal V15 a) 10K and b) 40K.
- Figure 12. a) The recovery of the critical current density in crystal V15 with annealing temperature for the two orientations of the magnetic field in a field of 2T.
- b) The recoveries of the critical current density in the three crystals with annealing temperature for $H \parallel$ c-axis in a field of 2 T at a) 10 K.

Fig. 1

Fig. 2

100 NM

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12