Observation of proposed flux pinning sites in neutron-irradiated $YBa_2Cu_3O_{7-x}$

J.-W. Lee, H. S. Lessure, D. E. Laughlin, M. E. McHenry, and S. G. Sankar
Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

J. O. Willis, J. R. Cost, and M. P. Maley
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 20 April 1990; accepted for publication 20 August 1990)

Microstructure and magnetic hysteresis have been compared for two samples of the $YBa_2Cu_3O_{7-\delta}$ ($\delta \sim 0$) high-temperature superconductor, one unirradiated, and one irradiated with fast neutrons ($E > 0.1$ MeV) to a fluence of 3×10^{18} n/cm^2. Notable changes in the microstructure include strain-induced contrast from regions 2–7 nm in size. An intrinsic critical current density (J_c) of 4.6×10^6 A/cm^2 in zero field at 4 K has been determined from magnetic hysteresis measurements for the irradiated sample while 1.2×10^6 A/cm^2 is noted for the unirradiated sample. We propose that the observed defect structure in the irradiated material is responsible for increased pinning and consequently higher J_c's.

The recent discovery of high-temperature superconductors (HTSCs)[1,2] among oxides has led to an understandably vigorous effort to characterize and assess the potential of these materials. For many applications the bulk transport critical current density J_c can arguably be called the single most important property of these materials. In bulk HTSC materials, the influence of weak link behavior at the grain boundaries[3] and orientational relationships between anisotropic grains[4] have been identified as important factors in limiting transport J_c's. In single crystals critical current densities are several orders of magnitude larger, but are still disappointing in their field dependence and temperature dependence. J_c's at 77 K in single crystals are typically 1–2 orders of magnitude smaller than at 4 K in $YBa_2Cu_3O_{7-x}$ (Y123) single crystals.[5]

In a type II superconductor the critical current density is a nonequilibrium property determined by the volume pinning force $P_v(B,T)$. In the mixed state of a type II superconductor, magnetic flux is introduced in quantized units of flux called *fluxons* or *flux vortices*. A transport or supercurrent J can be associated with a gradient in the flux density. Further, a transport current density gives rise to a Lorentz force $\mathbf{J} \times \mathbf{B}$ which acts on fluxons or correlated volumes (bundles) of fluxons. J_c reflects the transport current density at which the Lorentz force is just supported by the pinning structure, i.e., $J_c B = P_v(B,T)$, and beyond which dissipative motion of the fluxons occurs.[6] Generally, $P_v(B,T)$ is considered a unique function of the microstructure and the thermodynamic properties of the superconductor. Simple Ginzburg–Landau free-energy considerations reveal an energy savings for fluxons which can position their normal cores in regions of depressed order parameter. Such regions, or pinning centers, can be produced by introduction of suitable defects. Size, density, and topology of the defected regions are all important in determining J_c. Conventional wisdom suggests that a uniformly dense, nonoverlapping distribution of pinning centers, of size comparable to the radius of a fluxon's normal core, represents an optimal arrangement for enhancing J_c.[7] In HTSC materials the size of the normal core (or coherence length) has been estimated as being between 0.6 and 4 nm,[8] leading some to suggest that weak pinning is an intrinsic property of the materials.[9]

Neutron irradiation has been demonstrated as a means of influencing the volume pinning force,[10–14] presumably through altering the microstructure as well as the thermodynamic properties of the superconducting phase. A previous study[14] of the fast-neutron irradiation of polycrystalline Y123 has revealed a linear decrease of T_c of approximately 2.7 K/(10^{18} n/cm^2) with fluence. Measurements of J_c at 7 K (as inferred from magnetic hysteresis loops) showed an enhancement by a factor of 3 in the zero field J_c and even more significant enhancements at high fields, for a fluence of 1×10^{18} n/cm^2. An observed eventual saturation and downturn in J_c as a function of neutron fluence (for fluences > 1–2×10^{18} n/cm^2) can alternatively be explained by the competing effects of increased pinning site density and depressed T_c or by the eventual overlap of defects with greater neutron damage to the material.

Here we examine the morphology of the defects in neutron-irradiated Y123. Comparison is made between the microstructure of a virgin control sample of polycrystalline Y123 and a similar sample irradiated to a fluence of 3×10^{18} n/cm^2. These samples were those studied in the previous study of Ref. 14. All measurements reported here were performed within a recent three month period. The fluence of 3×10^{18} n/cm^2 is substantially larger than the 1×10^{18} n/cm^2 observed as the optimum for enhancing J_c; however, J_c is still significantly larger in the irradiated sample as compared with the unirradiated sample. Preparation of the Y123 samples is detailed in Ref. 14. The microstructure was uniform with the small volume fraction of CuO impurities randomly distributed within grains of average size 10 μm. Sequential neutron irradiation of the Y123 material was performed at the Los Alamos National Laboratory Omega West Reactor. Irradiation was performed isothermally at $\sim 80°$ C using He as a cooling gas. The irradiated sample examined here accumulated a total neutron fluence of 3×10^{18} n/cm^2.

Magnetic measurements were performed on a PAR vibrating sample magnetometer (VSM) a 9 T superconducting solenoid. Low-field measurements were found to

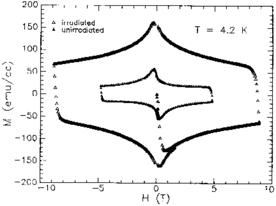

FIG. 1. Magnetic hysteresis measurements of the neutron-irradiated and the unirradiated Y123 samples in fields of up to 9 and 5 T, respectively.

correspond with those of the prior study performed on a Quantum Design superconducting quantum interference device (SQUID) magnetometer. High-field hysteresis was determined to be substantially larger on the VSM. The source of this discrepancy has been determined to be attributable to field inhomogeneity in the 6 cm sample traverse of the SQUID magnetometer.

Transmission electron microscopy (TEM) studies were performed using a Philips EM420T analytical electron microscope operating at 120 keV. Plan-view samples of the unirradiated and irradiated superconductors were mechanically ground on emery paper using lapping oil. Ion milling to electron transparency (a 50 nm foil thickness is estimated) was performed in a cold stage. The crystallographic orientation and lattice constants were determined using information derived from selected area diffraction (SAD) and microdiffraction patterns. Bright field (BF) imaging and high-resolution electron microscopy (HREM) were also employed.

Figure 1 illustrates dramatic changes in the magnetic hysteresis, as measured at 4 K, for the irradiated and the unirradiated samples of this study. Significantly larger magnetic hysteresis is apparent in the irradiated sample.

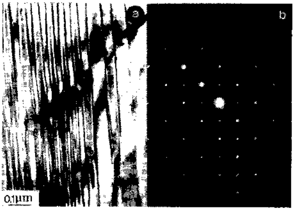

FIG. 2. (a) BF field image of unirradiated 1-2-3 sample and (b) its SAD pattern.

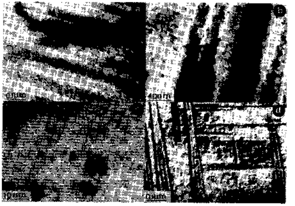

FIG. 3. Bright field images of irradiated 1-2-3 sample (a, b, and d) together with a HREM image (c).

The larger hysteresis can be attributed to larger J_c's in the irradiated sample resulting from stronger pinning in this material. These larger J_c's can be quantified using the critical state model expression:[15]

$$J_c \sim 15(M_+ - M_-)/R, \tag{1}$$

where M_+ and M_- are the magnetizations in emu/cm^3 on the decreasing and increasing field branches of the hysteresis loop, respectively, R is the average grain diameter, 10^{-3} cm, as determined from optical and scanning electron microscopy studies of the material, and J_c has units of A/cm^2. This analysis reveals an enhancement in J_c at 4 K of 3.8:1 is in zero field, increasing to 5.2:1 in an applied field of 4 T, consistent with either introduction of stronger pinning centers or an increased density of equivalent pinning sites.

In order to investigate the microstructural changes induced by neutron irradiation, we have performed TEM studies on the irradiated and unirradiated Y123 samples. Figure 2 reveals a bright field (BF) TEM image, and its SAD pattern, of an unirradiated sample. The orthorhombic superconducting phase (*Pmmm*) is clearly identified from the numerous twins that are present [Fig. 2(a)] as a consequence of the loss of symmetry which results from the tetragonal to orthorhombic phase transition which occurs in cooling the sintered material in oxygen.[16] The SAD pattern further confirms the presence of the orthorhombic phase [Fig. 2(b)].

Figure 3 shows bright field images of the irradiated Y123 sample as well as a high-resolution image of a region between twin boundaries. In the irradiated sample twins spaced at ~0.05–0.1 µm are observed as shown in Figs. 3(a), 3(b), and 3(d) consistent with the observed spacing in the unirradiated samples. Notable in the irradiated sample is the fact that a large volume fraction of homogeneously distributed defect clusters are observed which appear as dark, strain induced, contrast in circular or slightly acicular regions 2–7 nm in size [Figs. 3(a) and 3(b)]. A statistical analysis of the size of 100 defected regions yielded a mean size of 4.54 ± 1.7 nm and a mean spacing between the defected regions of 15 nm, from which an

$\sim 3\%$ volume fraction is calculated. It is possible that defect clusters arise from defect condensation from disordered regions created during neutron bombardment, though the average size of the defected regions could also be attributed to the lattice disruption for similarly excited knock-on ions as has been postulated to be the case in A15 materials.[17] The size of these defects in the Y123 samples is also comparable to those produced by neutron irradiation of A15 superconducting materials.[17] Figure 3(d) shows what appears to be a tweed-like morphology in the untwinned regions. The tweed structure, though not observed in the unirradiated sample, is seen in a very small volume fraction of the irradiated material and has been observed in Y123 materials with reduced oxygen content $(7-\delta=6.28\text{–}6.65)$.[18]

Although the structure of the defected regions resulting from the neutron irradiation has not yet been unambiguously determined, the defects observed in samples irradiated by He^+ and O^+ have been determined to be the Y123 tetragonal phase.[16] It is expected that oxygen atoms in Y123 are most easily displaced by neutron irradiation due to the presence of vacancies on the oxygen sublattice. Considering the presence of the a-axis vacancies in the small mass of oxygen, damage attributable to displaced oxygen ions is expected to have a larger spatial extent than that of other atomic species. However, displacement of other atomic species (Y, Ba, and Cu) is also probable.

A HREM image of the neutron-irradiated sample is shown in Fig. 3(c) $(z=[100])$. The lattice fringe corresponds to a ~ 1.17 nm spacing consistent with reported c-axis spacings in the orthorhombic phase. The HREM image of the defected regions indicates bending of the lattice fringes consistent with a slightly different c-axis lattice spacing. This change is consistent with that observed for the orthorhombic to tetragonal structural transition observed for Y123 but clearly at the limit of the TEM resolution. An important issue for future work will be to determine whether the defected regions are unambiguously crystalline or amorphous. At this juncture several observations point to the crystallinity of the defects; these include (1) observation of lattice fringes in defected regions (although the 50 nm foil thickness does not exclude the possibility of projection of fringes from undefected regions above or below the defect planes); (2) absence of diffuse electron diffraction rings, indicative of an amorphous phase (even in highly defected regions). The hypothesized crystallinity and observed lattice strains could be thought to result from defected regions which consist of the tetragonal Y123 phase. This would occur if the neutron irradiation served to disorder oxygen atoms in chain sites producing small microdomains of the disordered tetragonal (nonsuperconducting) phase. It is well known that transformation from the orthorhombic Y123 phase to the tetragonal phase occurs as a function of oxygen stoichiometry but can also occur without change in oxygen composition as a function of temperature.

Similarity between neutron irradiation effects in the Y123 material and the conventional A15 superconductors is striking. As discussed by Cost *et al.*,[14] the relative change of T_c $(\Delta T_c/T_c)$ with fluence is similar for the Y123 material as for that observed previously for the conventional $\mathrm{Nb_3Sn}$ superconductor. Further, in fast neutron irradiation studies of the $\mathrm{Nb_3Sn}$ superconductor Pande[17] has observed similar acicular disordered regions with sizes ranging from 2 to 6 nm for neutron fluences of $10^{17}\text{–}6\times10^{19}$ n/cm^2. At a fluence of 3×10^{18} n/cm^2 Pande observed an $\sim 4\%$ volume fraction for the disordered regions, comparable to the $\sim 3\%$ found for our Y123 sample irradiated to an identical fluence. Pande[17] has attributed the disordered regions in $\mathrm{Nb_3Sn}$ to large concentrations of antisite defects involving a local order–disorder transition whereas the mechanism here proposed for Y123 involves a similar transition between ordered oxygen and vacancy sites.

Neutron irradiation experiments were shown to yield a dense homogeneous distribution of defects with size slightly in excess of the superconducting coherence length and therefore viable candidates for effective pinning centers. The presence of this large density of defects in the irradiated sample and their absence in the unirradiated sample strongly suggest that they are responsible for the increased current carrying capacity observed with irradiation.

Helpful discussions with Dr. S. Simizu are gratefully acknowledged.

[1] J. G. Bednorz and K. A. Mueller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. A. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] R. L. Peterson and J. W. Ekin, Physica C **157**, 325 (1989); M. E. McHenry, M. P. Maley, and J. O. Willis, Phys. Rev. B **40**, 2666 (1989).

[4] J. Mannhart, P. Chaudhari, D. Dimos, C. C. Tsuei, and T. R. McGuire, Phys. Rev. Lett. **21**, 2476 (1988).

[5] J. W. Ekin, Adv. Ceram. Mater. **2**, 586 (1987).

[6] Y. B. Kim, C. F. Hempstead, and A. R. Strnad, Phys. Rev. **129**, 528 (1963).

[7] A. M. Campbell and J. E. Evetts, *Critical Currents in Superconductors* (Taylor and Francis, London, 1972).

[8] Y. Yeshurun and A. P. Malezemoff, Phys. Rev. Lett. **60**, 2202 (1988).

[9] S. Doniach, *High Temperature Superconductivity*, Los Alamos Symposium, 406 (Addison Wesley, Reading, MA, 1989).

[10] A. Umezawa, G. W. Crabtree, J. Z. Liu, H. W. Weber, W. K. Kwok, L. H. Nunez, T. J. Moran, C. H. Sowers, and H. Claus, Phys. Rev. B **36**, 7151 (1987).

[11] H. Kupfer, I. Apfelstedt, W. Schauer, R. Flukiger, R. Meier-Hirmer, H. Wuhl, and H. Scheuer, Z. Phys. B **69**, 167 (1987).

[12] S. T. Sekula, D. K. Christen, H. R. Kerchner, J. R. Thompson, L. A. Boatner, and B. C. Sales, Jpn. J. Appl. Phys. (Suppl.) **26**, 1185 (1987).

[13] R. B. van Dover, E. M. Gyorgy, L. F. Scheemeyer, J. W. Mitchell, K. V. Rao, R. Puzniak, and J. V. Waszczak, Nature **342**, 55 (1989).

[14] J. R. Cost, J. O. Willis, J. D. Thompson, and D. E. Peterson, Phys. Rev. B **37**, 1563 (1988); J. O. Willis, J. R. Cost, R. D. Brown, J. D. Thompson, and D. E. Peterson, Mater Res. Soc. Symp. Proc. **99**, 391 (1988).

[15] W. A. Feitz and W. W. Webb, Phys. Rev. **178**, 657 (1969).

[16] J. D. Jorgenson, B. W. Veal, W. K. Kwok, G. W. Carbtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas, Phys. Rev. B **36**, 5731 (1987).

[17] C. S. Pande, Phys. Status Solidi A **52**, 687 (1979).

[18] R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. P. Parkin, M. L. Ramirez, K. P. Roche, and J. E. Vazquez, Physica C **162-164**, 548 (1989).