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Enhancement of the Critical Current Density of $YBa_2Cu_3O_x$ Superconductors under Hydrostatic Pressure

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The dependence of the critical current density J_c on hydrostatic pressure to 0.6 GPa is determined for a single 25° [001]-tilt grain boundary in a bicrystalline ring of nearly optimally doped melt-textured $YBa_2Cu_3O_x$. J_c is found to increase rapidly under pressure at $+20\%/\mathrm{GPa}$. A new diagnostic method is introduced (pressure-induced J_c relaxation) which reveals a sizable concentration of vacant oxygen sites in the grain boundary region. Completely filling such sites with oxygen anions should lead to significant enhancements in J_c.

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One of the primary factors limiting applications using ceramic high-T_c superconductors has been the inability of grain boundaries (GBs) to tolerate large critical current densities ($J_c \simeq 10^6$–10^7 $\mathrm{A/cm^2}$), particularly at high magnetic field levels [1]. The value of J_c in polycrystals can be dramatically enhanced by reducing GB mismatch angles to values less than 4° through suitable grain alignment (texturing) procedures and by properly preparing the GB region, for example, through Ca doping [1]. Very recent detailed TEM and EELS studies have attributed the success of Ca doping both to strong Ca segregation near the dislocation cores [2] and to reduction in strains in the GB region which reduces the depletion of oxygen anions, thus enhancing the (hole) carrier concentration in the GB [3]. In either scenario, oxygen depletion in the GB leads to serious reductions in J_c.

The oxygen concentration in the GB region is evidently a parameter of vital importance in the optimization of J_c, even as the oxygen content within a grain plays a major role in the optimization of T_c. In melt-textured $YBa_2Cu_3O_x$ (YBCO) bicrystals we have observed that the GB J_c increases monotonically as the oxygen content in the bulk is increased from the underdoped condition to nearly full oxygenation at $x = 6.98$ [4], even though T_c passes through a maximum at optimal doping ($x \approx 6.95$). The determination of the concentration of vacant oxygen sites in the GB is, however, a difficult problem [3]. Even when the bulk material is fully oxygenated, the GBs are likely oxygen deficient.

In this Letter we introduce an experimental procedure, pressure-induced J_c relaxation, which provides a sensitive test for the presence of oxygen vacancies in the GB region. In the slightly overdoped YBCO bicrystal studied, the single 25° GB is found to be clearly oxygen deficient.

Early experiments on $YBa_2Cu_4O_8$ and $Tl_2CaBa_2Cu_2O_{8+\delta}$ ceramics [5] and polycrystalline YBCO thin films [6] indicated that the bulk J_c increases with pressure, but relaxation behavior was not studied. Samples containing a single well-defined grain boundary are clearly needed for quantitative tests of GB models. Such experiments have recently become possible through the availability of YBCO bicrystalline melt-textured rings with single [001]-tilt GBs with varying misorientation angle θ and oxygen content x [7].

For a single 25° GB in a YBCO bicrystal, we find that J_c increases rapidly with hydrostatic pressure. The rate of increase ($+20\%/\mathrm{GPa}$) is much more rapid than that expected from a simple GB model which takes into account the compression of the tunnel barrier width W alone.

The Vespel sample holder containing the YBCO bicrystalline ring (4 mm OD × 2 mm ID × 0.5 mm) is placed in the 7 mm dia bore of a He-gas pressure cell (Unipress). Two counterwound Cu pickup coils are positioned on the outside of the sample holder for the ac susceptibility measurement. Standard ac susceptibility techniques are used with a SR830 digital lock-in amplifier. Further details of the high pressure [8,9] and sample preparation procedures [7] are given elsewhere.

In previous studies the GB J_c was determined from the change in magnetization of YBCO bicrystalline rings as a function of temperature and dc magnetic field using a SQUID magnetometer [7]. Here we utilize ac susceptibility measurements to obtain similar information. In Fig. 1 (left) an ac field $H(t) = H_{\mathrm{ac}} \sin\omega t$ with amplitude $H_{\mathrm{ac}} = 10$ G at 1 Hz is applied by the primary coil to the ring sample inducing ring currents $I(t) = I_{\mathrm{ac}} \cos\omega t$. In the single-turn solenoid approximation, we have $I_{\mathrm{ac}} = DH_{\mathrm{ac}}$, D being the average of the inner and outer ring diameters [7]. As seen in Fig. 1 (left), for temperatures below 67 K at ambient pressure, the oscillatory magnetic field generated by these ring currents is equal and opposite to the oscillatory applied field, thus preventing flux from entering. As the

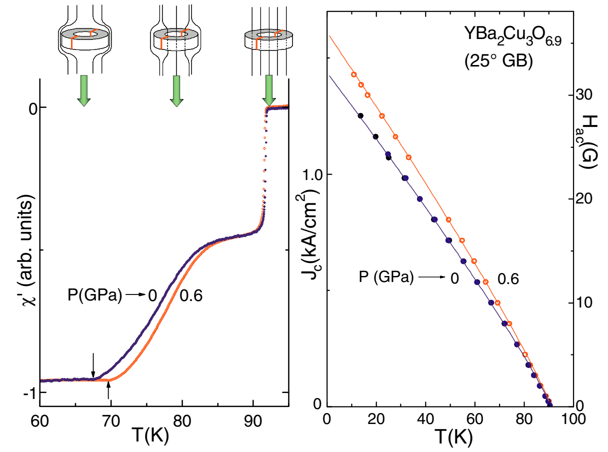

FIG. 1 (color online). (left) Real part of ac susceptibility χ' versus temperature at $H_{\rm ac} = 10$ G (1 Hz) for nearly optimally doped YBCO bicrystalline ring with 25° GB at 0 GPa (●) and 0.6 GPa (○) pressure. Arrows mark the temperature of kink $T_{\rm kink}$ in $\chi'(T)$ where flux begins to enter ring (see illustration at top). (right) ac field amplitude $H_{\rm ac}$ and calculated critical current density $J_c(T)$ versus temperature at 0 and 0.6 GPa. Solid lines are fits using Eq. (1).

temperature is increased above 67 K, however, the ring current $I_{\rm ac}$ exceeds the critical current I_c and magnetic flux begins to flow in and out of the ring through the weaker of the two grain boundaries. Knowing the cross-sectional area A of the ring, one can estimate the critical current density $J_c = I_c/A$. For temperatures in the region 85–91 K, $\chi'(T)$ reaches a plateau where the applied flux is only excluded from the superconducting material in the ring itself. Finally, above $T_c \simeq 92$ K the ring is in the normal state and magnetic flux penetrates uniformly through the entire ring.

From this measurement of χ' versus temperature, therefore, two important properties of the nearly optimally doped YBCO ring are determined: (1) the value of the critical current density $J_c(T_{\rm kink}) \simeq DH_{\rm ac}(T_{\rm kink})/A$ through the GB at the temperature of the kink in χ' and (2) the value of the transition temperature $T_c \simeq 91.84$ K (midpoint of χ') in bulk YBCO. If the oscillatory field amplitude $H_{\rm ac}$ is increased, $T_{\rm kink}$ shifts to lower temperatures, yielding the temperature dependence of $H_{\rm ac}(T)$ or $J_c(T)$ shown in Fig. 1 (right). The $J_c(T)$ dependences obtained in these ac susceptibility studies are in good agreement with the results of magnetization measurements in dc fields using a SQUID magnetometer [4], as pointed out earlier by Herzog *et al* [10].

Figure 1 (left) also displays $\chi'(T)$ data obtained after the application of 0.6 GPa hydrostatic pressure at ambient temperature. $T_{\rm kink}$ is seen to shift to higher temperatures, indicating that J_c increases under pressure. This result is brought out clearly by the $J_c(T)$ data in Fig. 1 (right) at 0 and 0.6 GPa pressure; these data are fit using the expression

$$J_c(T) = J_c(0)[1 - T/T_c]^{\beta}, \tag{1}$$

where $\beta = 0.89$ and $J_c(0) = 1.44$ and 1.61 kA/cm^2 for $P = 0$ and 0.6 GPa, respectively. For temperatures below T_c, the relative pressure dependence $J_c^{-1}(dJ_c/dP) = d\ln J_c/dP \simeq +0.20$ GPa^{-1} (+20%/GPa) is obtained. Note that the superconducting transition temperature decreases slightly under pressure ($d\ln T_c/dP \simeq -25 \times 10^{-4}$ GPa^{-1}), a rate ~80× less than that of J_c. Strong pressure-induced J_c enhancements are also found for nearly optimally doped and underdoped YBCO bicrystals with mismatch angles 4° to 31°, as discussed elsewhere [8,9].

The rapid increase in J_c under pressure suggests that J_c can be further increased in applications at ambient pressure by compressing textured YBCO material through suitable processing procedures. The relative change in J_c with GB width W is given by $d\ln J_c/d\ln W = \kappa_{\rm GB}^{-1}(d\ln J_c/dP)$, where the compressibility of the GB is defined by $\kappa_{\rm GB} \equiv -d\ln W/dP$. If we assume to a first approximation that $\kappa_{\rm GB}$ is roughly comparable with the average linear compressibility $\kappa_a \equiv -d\ln a/dP$ of YBCO in the CuO$_2$ plane [11], where $\kappa_a \approx 2 \times 10^{-3}$ GPa^{-1} [12] and a is an in-plane lattice parameter, it follows that $d\ln J_c/d\ln W \approx -100$. This implies that J_c increases under pressure at a rate which is 100× more rapid than the decrease in GB width. Compressing the GB by 10% should, therefore, lead to a tenfold enhancement in J_c. Lattice compression by a few percentage points can be readily achieved through epitaxial growth techniques.

What causes the strong enhancement in J_c as the GB is compressed? High pressures may modify the GB in a number of different ways, including: (1) reduction of the tunneling barrier width W and change in the tunneling barrier height ϕ, (2) promotion of oxygen ordering in the GB, in analogy with the well studied pressure-induced oxygen-ordering effects in the bulk [13–15].

Considering the first possibility, the WKB approximation applied to a potential barrier gives the following simple expression: $J_c = J_{\rm co}\exp(-2KW)$, where W is the barrier width, $J_{\rm co}$ is the critical current density for zero barrier width, i.e., no grain boundary, and $K = \sqrt{2m\phi}/\hbar$ is the decay constant which increases with the barrier height ϕ [16]. Since parallel studies on melt-textured YBCO rings with no GB reveal that $d\ln J_{\rm co}/dP \simeq 0$ [8], one obtains for the relative pressure dependence of J_c

$$\frac{d\ln J_c}{dP} \simeq -\left[\left(\frac{d\ln W}{dP}\right)\ln\left(\frac{J_{\rm co}}{J_c}\right)\right] - \frac{1}{2}\left[\left(\frac{d\ln\phi}{dP}\right)\ln\left(\frac{J_{\rm co}}{J_c}\right)\right]. \tag{2}$$

Does the strong enhancement in J_c under pressure arise primarily from the first term on the right in Eq. (2)? To address this question, we assume [11], as above, that to a first approximation $-d\ln W/dP \equiv \kappa_{\rm GB} \approx \kappa_a \approx 2 \times 10^{-3}$ GPa^{-1}. From Fig. 1 we see that for the $\theta = 25°$ ring

$J_c \simeq 1400\ \mathrm{A/cm^2}$ at low temperatures and ambient pressure. Setting $J_{co} \approx 250\,000\ \mathrm{A/cm^2}$ for a YBCO ring with no GB [8], we find $(-d\ln W/dP)\ln(J_{co}/J_c) \approx +0.01\ \mathrm{GPa^{-1}}$, a value 20× less than the above experimental value $d\ln J_c/dP \simeq +0.20\ \mathrm{GPa^{-1}}$. Within the simple tunneling barrier model, therefore, the strong enhancement in J_c under pressure does not arise from the compression of the GB width W, but may be the result of a strong reduction in the barrier height ϕ at the GB. From Eq. (2) a pressure derivative of only $d\ln\phi/dP \simeq -0.073\ \mathrm{GPa^{-1}}$ would be sufficient to yield the experimental value $d\ln J_c/dP \simeq +0.20\ \mathrm{GPa^{-1}}$.

The second potential mechanism proposed above for the rapid increase of J_c with pressure is through oxygen-ordering effects in the GB. Such effects in high-T_c oxides can have a dominant influence on the pressure dependence of bulk properties, such as the value of T_c [13–15]. In an overdoped $\mathrm{Tl_2Ba_2CuO_{6+x}}$ sample, for example, the pressure dependence even changes sign from $dT_c/dP \simeq -8.9\ \mathrm{K/GPa}$ to $+0.35\ \mathrm{K/GPa}$ depending on whether, respectively, oxygen-ordering effects occur or not [13]. Significant oxygen-ordering effects in dT_c/dP have also been observed in YBCO [14,15].

Oxygen-ordering effects in YBCO arise from the considerable mobility of oxygen anions in the CuO chains at ambient temperature, in contrast to oxygen anions in the $\mathrm{CuO_2}$ planes. The degree of local order assumed by the mobile oxygen anions changes as a function of pressure or temperature: raising the temperature above ambient reduces the order in an equilibrated system, applying pressure at ambient temperatures enhances the order. The existence of pressure-induced oxygen-ordering effects can be readily demonstrated by applying pressure at ambient temperature to enhance local order, but releasing it at temperatures sufficiently low (<200 K for YBCO) to prevent the oxygen anions from diffusing back, thus effectively freezing in the higher degree of order.

The degree of local oxygen ordering influences indirectly the charge carrier concentration n in the $\mathrm{CuO_2}$ planes by changing the average valence of the ambivalent cations (in YBCO these are the Cu cations in the CuO chains [17], in $\mathrm{Tl_2Ba_2CuO_{6+x}}$ the Tl cations in the $\mathrm{Tl_2O_2}$ double layer [13]). Since T_c is a sensitive function of n, the degree of oxygen ordering may have a sizable effect on T_c, as pointed out above for $\mathrm{Tl_2Ba_2CuO_{6+x}}$.

There are two special cases where no pressure-induced oxygen-ordering effects are expected: (1) no mobile oxygen anions are present in the oxygen sublattice, (2) the oxygen sublattice is completely filled up with oxygen anions, so that no change in the degree of local ordering is possible. If oxygen-ordering effects are observed, therefore, this very fact implies that the oxygen sublattice is only partially filled; i.e., empty oxygen sites are available. The presence or absence of relaxation effects in T_c can thus be used as a diagnostic tool to test whether or not the lattice is able to accommodate further oxygen anions.

We now apply this same procedure to test for oxygen-ordering effects in the GB region of a YBCO bicrystal. In Fig. 2 (upper) one sees that the application of 0.6 GPa pressure at 290 K prompts J_c at 9 K to increase from point 1 to point 2. If the pressure is then released at temperatures below 50 K, J_c is seen to *not* decrease completely back to its initial value at point 1, but rather to remain at a higher value (point 3). Remeasuring J_c after annealing the sample for $\frac{1}{2}h$ at successively higher temperatures results in no change in J_c (points 3 through 9) until the annealing temperature T_a reaches values above 250 K; at point 11 J_c is seen to have fully relaxed back to its initial value (point 1).

In a subsequent experiment [see Fig. 2 (lower)] the relaxation time τ for the GB relaxation process is estimated by annealing for different lengths of time at a *fixed* temperature (270 K) following pressure release at low temperatures. The value of J_c at 9 K is seen to show an exponential time-dependent relaxation behavior which obeys the equation

$$J_c(t) = J_c(\infty) - [J_c(\infty) - J_c(0)]\exp\{-(t/\tau)^\alpha\}, \qquad (3)$$

where $J_c(0)$ and $J_c(\infty)$ are the initial and fully relaxed values of the critical current density, respectively. From the best fit to the data, the estimated GB relaxation time is $\tau = 5.9$ h for $\alpha \simeq 0.34$. Using the Arrhenius law

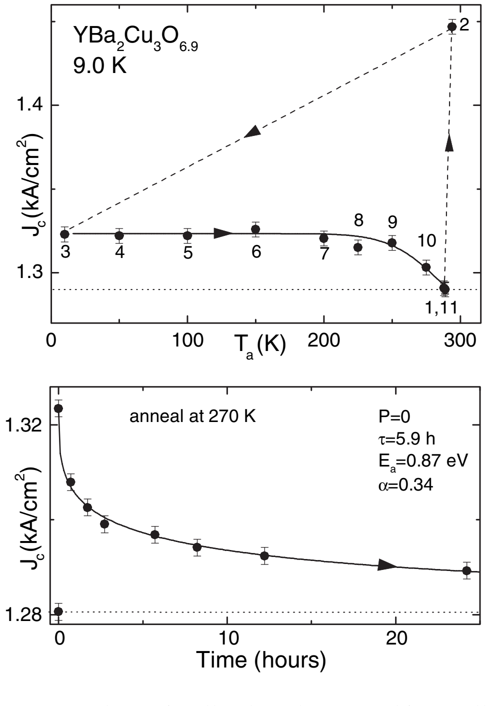

FIG. 2. For nearly optimally doped YBCO bicrystalline ring with 25° GB: (top) dependence of critical current density J_c at 9 K on annealing temperature T_a. Numbers give order of measurement. Solid and dashed lines are guides to the eye. Horizontal dotted line marks initial value of J_c(9 K) at point 1. (bottom) Dependence of J_c on time for fixed annealing temperature $T_a = 270$ K. Solid line is fit to data using Eq. (3).

$\tau = \tau_o \exp[E_a/k_B T]$, the activation energy is estimated to be $E_a = 0.87$ eV, where we set $\tau_o = 1.4 \times 10^{-12}$ s from previous studies [17]. That this relaxation in J_c indeed results from the motion of oxygen anions in the GB region is supported by two experimental findings: (1) the relaxation in J_c takes place in the same temperature range (250–290 K) where oxygen-ordering phenomena in bulk YBCO are known to occur [14,15], and (2), in agreement with the relaxation of T_c in the bulk [14,15], the magnitude of the relaxation effects in J_c increases substantially in underdoped (underoxygenated) YBCO bicrystals [8] where the concentration of empty oxygen sites is much higher, thus opening up many more relaxation channels.

Are pressure-induced oxygen-ordering effects in the GB region primarily responsible for the large enhancement of J_c under pressure? In Fig. 2 (upper) the initial application of 0.6 GPa pressure at 290 K is seen to increase J_c by 0.156 kA/cm^2 from 1.291 kA/cm^2 (point 1) to 1.447 kA/cm^2 (point 2), a 12% increase, thus implying $d\ln J_c/dP = +0.12 \div (0.6\text{ GPa}) = +0.20\text{ GPa}^{-1}$, as cited above. This pressure-induced increase in J_c can be divided up into a relaxation and a nonrelaxation (intrinsic) contribution, i.e., $d\ln J_c/dP = (d\ln J_c/dP)_{\text{relax}} + (d\ln J_c/dP)_{\text{intr}}$. The relative importance of these two contributions can be determined by releasing the pressure at a temperature sufficiently low (<250 K) to freeze out the relaxation contribution. If the relaxation contribution strongly dominates, then the release of pressure at low temperatures should cause little or no change in J_c. The fact that J_c decreases by 0.125 kA/cm^2 upon release of pressure at temperatures below 50 K implies that $0.125 \div 0.156$ or 80% of the large initial increase of J_c with pressure is due to nonrelaxation effects. We find that $(d\ln J_c/dP)_{\text{relax}} \simeq (+0.031 \div 1.291) \div (0.6\text{ GPa}) = +0.04\text{ GPa}^{-1}$ and $(d\ln J_c/dP)_{\text{intr}} \simeq (+0.125 \div 1.291) \div (0.6\text{ GPa}) = +0.16\text{ GPa}^{-1}$. Oxygen-ordering effects thus contribute 20% to the large increase in J_c under pressure; nonrelaxation (intrinsic) phenomena, such as the reduction in the barrier height ϕ, contribute 80%.

Although the principal mechanism for the pressure-induced enhancement in J_c does not originate from oxygen-ordering effects, the fact that this relaxation component is sizable implies that there must be a significant number of vacant oxygen sites available in the GB region. As will be discussed elsewhere [8], a similar result is obtained for other nearly optimally doped and underdoped YBCO rings with varying mismatch angles.

In summary, the critical current density J_c across a 25° [001]-tilt GB in a slightly overdoped YBCO bicrystal is found to increase strongly with hydrostatic pressure at the rate +20%/GPa. This suggests a new procedure to enhance J_c at ambient pressure: compress the GB as much as possible through epitaxial growth or other chemical means. The rate of increase of J_c is far too large to be caused by the decrease in width W of a tunnel barrier alone; a decrease in the barrier height ϕ may be the dominant effect.

Sizable pressure-induced oxygen-ordering effects are found to occur in the GB, revealing that the value of J_c is a complicated function of the pressure/temperature history of the sample, i.e., $J_c = J_c(T, P, t)$, in analogy with the well studied relaxation processes in the bulk where $T_c = T_c(T, P, t)$ [13,14]. These J_c relaxation effects are responsible for only 20% of the total increase in J_c with pressure. However, the fact that these relaxation effects in J_c occur at all indicates that a significant concentration of oxygen vacancies must be present in the GB. Filling these vacancies by annealing the sample under high oxygen pressure at high temperature or through electro-chemical oxidation should lead to further enhancements in J_c.

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