Enhancement of the Critical Current Density of YBa$_2$Cu$_3$O$_x$ Superconductors under Hydrostatic Pressure

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Abstract

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$_2$Cu$_3$O$_x$. $J_c$ is found to increase rapidly under pressure at +20 %/GPa. A new diagnostic method is introduced (pressure-induced $J_c$ relaxation) which reveals a sizeable concentration of vacant oxygen sites in the grain boundary region. Completely filling such sites with oxygen anions should lead to significant enhancements in $J_c$. 

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 (\(J_c \approx 10^6 - 10^7\) 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\(^\circ\) through suitable grain alignment (texturing) procedures \([2]\) and by properly preparing the GB region \([1]\), for example, through Ca doping \([3]\). Very recent detailed TEM and EELS studies have attributed the success of Ca doping both to strong Ca segregation near the dislocation cores \([4]\) 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 \([5]\). 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\(_2\)Cu\(_3\)O\(_x\) (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 \(x = 6.98\) \([6]\), even though \(T_c\) passes through a maximum at optimal doping \((x \approx 6.95)\). This behavior was also observed in thin film GBs \([7]\). The determination of the concentration of vacant oxygen sites in the GB is, however, a difficult problem \([5]\). Even when the bulk material is fully oxygenated, the GBs are likely oxygen deficient.

In this paper 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\(^\circ\) GB is found to be clearly oxygen deficient.

Early experiments on YBa\(_2\)Cu\(_4\)O\(_8\) and Tl\(_2\)CaBa\(_2\)Cu\(_2\)O\(_8+\delta\) ceramics \([8]\) and polycrystalline YBCO thin films \([9]\) 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 \(\theta\) and oxygen content \(x\) \([10]\).

For a single 25\(^\circ\) GB in a YBCO bicrystal, we find that \(J_c\) increases rapidly with hydrostatic pressure. The rate of increase (+20 %/GPa) is much more rapid than that expected from a simple GB model which takes into account the compression of the tunnel barrier width \(W\)
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. To avoid heating effects at high field amplitudes (∼ 300 G), the field coil is placed outside the tailpiece of the cryostat and the ac frequency is reduced to 1 Hz to ensure full field penetration to the sample. Standard ac susceptibility techniques are used with a SR830 digital lock-in amplifier. Further details of the high pressure and sample preparation procedures for the melt-textured YBCO bicrystalline rings 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. Here we utilize ac susceptibility measurements to obtain similar information. In Fig 1 (left) an ac field $H(t) = H_{ac}\sin\omega t$ with amplitude $H_{ac} = 10$ G at 1 Hz is applied by the primary coil to the ring sample inducing ring currents $I(t) = I_{ac}\cos\omega t$. In the single-turn solenoid approximation, we have $I_{ac} = DH_{ac}$, $D$ being the average of the inner and outer ring diameters. 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 temperature is increased above 67 K, however, the ring current $I_{ac}$ 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 $\chi'$ versus temperature, therefore, two important properties of the nearly optimally doped YBCO ring are determined: (1) the value of the critical current density $J_c(T_{kink}) \simeq DH_{ac}(T_{kink})/A$ through the GB at the temperature of the kink in $\chi'$ and (2) the value of the transition temperature $T_c \simeq 91.84$ K (midpoint of $\chi'$) in bulk YBCO. If the oscillatory field amplitude $H_{ac}$ is increased, $T_{kink}$ shifts to lower temperatures, yielding the temperature dependence of $H_{ac}(T)$ 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, as pointed out earlier by Herzog et al.

Fig 1 (left) also displays $\chi'(T)$ data obtained after the application of 0.6 GPa hydrostatic He-gas pressure at ambient temperature. $T_{kink}$ 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 both ambient and 0.6 GPa pressure; these data are fit using the expression

$$J_c(T) = J_c(0) \left[1 - T/T_c \right]^\beta,$$

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. This value increases to +0.26 GPa$^{-1}$ if a dc magnetic field of 120 G is applied above 92 K before cooling. Note that the superconducting transition temperature decreases slightly under pressure ($d\ln T_c/dP \simeq -25 \times 10^{-4}$ GPa$^{-1}$), a rate $\sim 80\times$ 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.

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 $d\ln J_c/d\ln W = \kappa_{GB}^{-1}(d\ln J_c/dP)$, where the compressibility of the GB is defined by $\kappa_{GB} \equiv -d\ln W/dP$. If we assume to a first approximation that $\kappa_{GB}$ is roughly comparable with the average linear compressibility $\kappa_a \equiv -d\ln a/dP$ of YBCO in the CuO$_2$ plane, where $\kappa_a \approx 2 \times 10^{-3}$ GPa$^{-1}$ 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 $100\times$ 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 % can be readily achieved through epitaxial growth techniques.

We now examine the question of the mechanism behind 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 $\phi$, (2) promotion of oxygen ordering in the GB, in analogy with the well
studied pressure-induced oxygen ordering effects in the bulk \[16, 17, 18, 19\].

Considering the first possibility, the WKB approximation applied to a potential barrier gives the following simple expression: 
\[ J_c = J_{co} \exp(-2KW) \]
where \( W \) is the barrier width, \( J_{co} \) 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 \( \phi \) \[20\]. Since parallel studies on melt-textured YBCO rings with no GB reveal that \( d\ln J_{co}/dP \approx 0 \) \[11\], one obtains for the relative pressure dependence of \( J_c \)
\[ \frac{d\ln J_c}{dP} \approx - \left[ \left( \frac{d\ln W}{dP} \right) \ln \left( \frac{J_{co}}{J_c} \right) \right] - \frac{1}{2} \left[ \left( \frac{d\ln \phi}{dP} \right) \ln \left( \frac{J_{co}}{J_c} \right) \right]. \]  
(2)

Does the strong enhancement in \( J_c \) under pressure arise primarily from the first term on the right in Eq. (2), i.e. from the decrease in the barrier width \( W \)? To address this question, we assume \[14\], as above, that to a first approximation \(-d\ln W/dP \equiv \kappa_{GB} \approx \kappa_a \approx 2 \times 10^{-3} \) GPa\(^{-1}\). From Fig 1 we see that for the \( \theta = 25^\circ \) ring \( J_c \approx 1,400 \text{ A/cm}^2 \) at low temperatures and ambient pressure. Setting \( J_{co} \approx 250,000 \text{ A/cm}^2 \) for a melt-textured YBCO ring with no GB \[11\], we find \(( -d\ln W/dP ) \ln(J_{co}/J_c) \approx +0.01 \) GPa\(^{-1}\), a value 20\( \times \) less than the above experimental value \( d\ln J_c/dP \approx +0.20 \) 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 \( \phi \) at the GB. From Eq. (2) a pressure derivative of only \( d\ln \phi/dP \approx -0.073 \) GPa\(^{-1}\) would be sufficient to yield the experimental value \( d\ln J_c/dP \approx +0.20 \) 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. It is well established that pressure-induced oxygen ordering effects in high-\( T_c \) oxides can have a dominant influence on the pressure dependence of bulk properties, such as the value of \( T_c \) \[16, 17, 18, 19\]. In an overdoped \( \text{Tl}_2\text{Ba}_2\text{CuO}_{6+x} \) sample, for example, the hydrostatic pressure dependence even changes sign from \( dT_c/dP \approx -8.9 \) K/GPa to \( +0.35 \) K/GPa depending on whether, respectively, oxygen-ordering effects occur or not \[16\]. Significant oxygen ordering effects in \( dT_c/dP \) have also been observed in YBCO \[17, 18\].

Oxygen ordering effects in many cuprate oxides have their origin in the appreciable mobility of oxygen anions in certain regions of the oxygen sublattice, even at ambient temperatures. In YBCO at ambient temperatures and below, oxygen anions in the CuO chains possess considerable mobility, in contrast to oxygen anions in the 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 CuO\(_2\) planes by changing the average valence of the ambivalent cations (in YBCO these are the Cu cations in the CuO chains \[21\], in Tl\(_2\)Ba\(_2\)CuO\(_{6+x}\) the Tl cations in the Tl\(_2\)O\(_2\) double layer \[16\]). Since \( T_c \) is a sensitive function of \( n \), the degree of oxygen ordering may have a sizeable effect on \( T_c \), as pointed out above for Tl\(_2\)Ba\(_2\)CuO\(_{6+x}\).

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 \( \tau \) 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

\[ J_c(t) = J_c(\infty) - [J_c(\infty) - J_c(0)] \exp \left\{ -\frac{t}{\tau^\alpha} \right\}, \tag{3} \]

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 \( \alpha \approx 0.34 \). Using the Arrhenius law \( \tau = \tau_o \exp\left[\frac{E_a}{k_B T}\right] \), 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 \(^{21}\). 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 \(^{17, 18, 19}\), and (2), in agreement with the relaxation of \( T_c \) in the bulk \(^{14, 18, 19}\), the magnitude of the relaxation effects in \( J_c \) increases substantially in underdoped (underoxygenated) YBCO bicrystals \(^{11}\) where the concentration of empty oxygen sites is much higher, thus opening up many more relaxation channels.

We now examine the relaxation data in Fig 2 in detail and address the question whether or not pressure-induced oxygen ordering effects in the GB region are 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 non-relaxation (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÷0.156 or 80% of the large initial increase of \( J_c \) with pressure is due to non-relaxation effects. We thus find that \( (d \ln J_c/dP)_{\text{relax}} \approx (0.031 \div 1.291) \div (0.6 \text{ GPa}) = +0.04 \text{ GPa}^{-1} \) and \( (d \ln J_c/dP)_{\text{intr}} \approx (0.125 \div 1.291) \div (0.6 \text{ GPa}) = +0.16 \text{ GPa}^{-1} \). Oxygen ordering effects thus contribute 20% to the large increase in \( J_c \) under pressure; non-relaxation (intrinsic) phenomena, such as the reduction in the barrier height \( \phi \), 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 sizeable implies that there must be a significant number of vacant oxygen sites available in the GB region. As will be discussed elsewhere, 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 over-doped 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 $\phi$ may be the dominant effect.

Sizeable 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 $T_c = T_c(T, P, t)$. 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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In view of the fact that GBs contain vacancies and other structural defects, $\kappa_{GB}$ is likely somewhat greater than $\kappa_a$. In YBCO, for example, the average linear compressibility in the CuO$_2$ plane increases by 17% if the oxygen concentration in the chains is reduced by 35% (see Ref. 15).
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Figure Captions

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

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).
