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Possible twin-boundary effect upon the properties of high-T_c superconductors

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We have studied the field at which superconductivity nucleates in grain-aligned samples of $Y_1Ba_2Cu_3O_{7-\delta}$ very close to the transition temperature T_c. For the field parallel to the c axis and for temperatures within 2 K of T_c, the nucleation field is found to vary as $(1-T/T_c)^{1/2}$. The data suggest that superconductivity localized near twin boundaries may exist at temperatures close to T_c.

Two of the many unusual features of the high-T_c superconductor $Y_1Ba_2Cu_3O_{7-\delta}$ are that the material is highly anisotropic and heavily twinned. At about 750 °C, it undergoes a transition from the tetragonal to the orthorhombic phase in which the a and b dimensions of the primitive cell are no longer equal.[1] To accommodate the orthorhombic distortion, a system of twinning planes (TP's) appears in {110} planes parallel to both the c axis and the diagonal of the ab rectangular basis of the cell. A typical transmission-electron-microscope (TEM) picture of a grain is given in Fig. 1. The TEM samples were prepared by mechanically thinning 3-mm disks to less than 150 μm in thickness, followed by ion milling. Observation of these samples revealed large, angular grains which were faulted heavily on {110} planes. This is in agreement with investigations that have described these faults as twin boundaries.[2,3] Measurements of the distance L between TP's carried out on a number of grains in two separate samples, yield L's in the range 1270–1400 Å (Ref. 2 reports L close to 600 Å). The twins were absent in thin regions near the foil edge, while in thicker domains the parent/twin interface was observed to have a definite width of about 30 Å, which may simply be due to the imagining conditions.

In a series of experimental and theoretical papers, the *critical-temperature enhancement* in single-crystal materials (Sn and Nb, for instance) that arises when the TP's are introduced, has been discussed. The pioneering work has been done by Khaikin and Khlustikov;[4] one can find further references in a recent review.[5] Although the microscopic mechanism of this effect is not yet understood, the T_c enhancement is attributed to the possibility of soft phonons along the TP or to distinct two-dimensional electronic states (for a recent discussion of the TP dynamics see Ref. 6). The domain of enhanced electron-electron interaction is localized within a few interatomic distances of the TP; a phenomenological description of the superconductivity localized around TP's is achieved by introducing a term $\gamma\delta(x)|\psi|^2$ in the Ginzburg-Landau (GL) free-energy expansion for a TP located at $x=0$.[7] The parameter γ is proportional to the relative enhancement

$$\tau_0=(T_c-T_{c0})/T_{c0}\ , \qquad (1)$$

where T_c is the critical temperature and T_{c0} is the bulk critical temperature in the absence of TP's. Observed values of τ_0 in Sn and Nb are about 1% (for well-separated TP's). The order parameter ψ at temperatures $T_{c0}<T<T_c$ is nonzero in a layer centered at the TP; if T is close to T_c, ψ decreases exponentially with distance x from the TP with a decay length $\xi(T)$, ξ being the GL coherence length of the bulk material (note that ξ is finite at T_c and diverges at T_{c0}). The attenuation is due to the proximity to the rest of the bulk metal, which is still normal for $T>T_{c0}$.

The situation is reminiscent of a superconducting film of thickness $2\xi(T)$ embedded in a bulk metal with critical temperature $T_{c0}<T_c$. As is well known, the nucleation field parallel to the film of a thickness on the order of ξ varies near T_c as $(1-T/T_c)^{1/2}$. The calculation of Ref. 7 results in

$$H_{c2}=0.42\frac{\phi_0}{\xi_0^2}\left[\left(\frac{T_c}{T_{c0}}-1\right)\frac{T_c}{T_{c0}}\right]^{1/2}\left(1-\frac{T}{T_c}\right)^{1/2}, \qquad (2)$$

where ξ_0 is the Bardeen-Cooper-Schrieffer coherence length and ϕ_0 is the flux quantum.[8] The domain of validity of this result is $(T_c-T)/(T_c-T_{c0})\ll 1$, i.e., the square-root T dependence of H is expected in a region narrow with respect to the enhancement T_c-T_{c0}, not to T_c.

Two conditions are required for an experiment to check

FIG. 1. Transmission electron micrograph of $Y_1Ba_2Cu_3O_{7-\delta}$ showing twin boundaries imaged using $(2\bar{1}3)$ planes. Upper portion of the figure is nearest to the foil edge.

the model described. First, since there must be a well-defined H_{c2}, it is critical to use grain-aligned samples or single crystals. With randomly oriented grains in polycrystalline samples, the anisotropy of H_{c2} will prevent a clear definition of the phase transition. Second, the entire sample must have the same T_c. Any variation in T_c will tend to give tailing of the magnetization M vs H curves near H_{c2}. Both conditions now are achievable in grain-aligned samples. A simple method recently has been found to orient the c axes of fine-grained single-crystal powders of $Y_1Ba_2Cu_3O_7$ in a magnetic field and freeze them in place with an epoxy resin.[9] Random orientation of grains in the a and b directions is of no importance in our experiment because all TP's are parallel to the c axes and the latter are parallel to each other and to the applied field.

For the determination of H_{c2} it is important to have a clear signature specifying the place where the sample becomes normal. Above T_c, the susceptibility varies rather slowly with T compared to the changes in the superconducting state. Indeed, the magnetization M at 93 K is essentially the same as that at 95 K on this scale. The M versus H data of Fig. 2(a) show that a plot of $M(93)-M(T)$ vs H is linear in H, and there is a sharp kink which is identified as H_{c2}. Data were taken both by sweeping H at constant T and by sweeping T at constant H [Fig. 2(b)]. In both cases H_{c2} is easily identified. The zero-field $T_c = 91.7 \pm 0.1$ K has been obtained from the data on $M(T)$ in a small field (both perpendicular and parallel to $\hat{c}$) as well as from a sharp transition observed in the ac susceptibility.

A plot of H_{c2} vs T is shown in Fig. 3. Between T_c and 89 K the data obey a $(1-T/T_c)^{1/2}$ behavior rather well. The dashed line, in fact, represents the equation

$$H_{c2} = 30.8(1-T/T_c)^{1/2}\ \mathrm{T}\ . \tag{3}$$

Thus, our data are compatible with the idea of superconductivity localized near TP's and having the critical temperature enhanced with respect to the bulk T_{c0}. One may wonder why in other measurements of $H_{c2}(T)$ on single crystals (see, e.g., Ref. 10) the $(1-T/T_c)^{1/2}$ dependence was not seen. A possible cause may lie in an ambiguity of the H_{c2} definition based upon the temperature dependence of resistance (see also Ref. 11); also note that Eq. (3) represents the data only within a narrow domain (~ 2 K) near T_c.

In comparing the T-independent factors in Eqs. (2) and (3) one should bear in mind that T_{c0} is an unknown quantity. For the critical temperature enhancement (1) the comparison yields $\tau_0(\tau_0+2) = 1.34 \times 10^{-7}\ \xi_0^4$, where ξ_0 is in Å. The estimate of T_{c0} is, therefore, very sensitive to the value of the coherence length: For $\xi_0 = 15$ Å one obtains $\tau_0 = 6.8 \times 10^{-3}$ which corresponds to $T_{c0} = 90$ K, whereas for $\xi_0 = 34$ Å one estimates $\tau_0 = 0.16$ and $T_{c0} = 79$ K. The last estimate is based on the value of ξ_0 obtained from the data on the slope of the bulk H_{c2} parallel to the c direction of a single crystal of $Y_1Ba_2Cu_3O_7$.[10] It is interesting that our estimate of T_{c0} is close to the break in slope of H_{c2} observed in this experiment. Although possibly a coincidence, this change in slope may be due to a crossover from bulk behavior below T_{c0} to bulklike behavior influenced by TP's above T_{c0}, which eventually turns into the thin-film-like square-root T dependence near T_c.

The enhanced superconductivity near TP's may well be responsible for the high observed values of the critical-current density J_c in fields parallel to the c axis, as well as for its anisotropy (Refs. 9, 12–15). To estimate the TP contribution to J_c, let us assume that all the vortices and TP's have the most favorable alignment for pinning: vor-

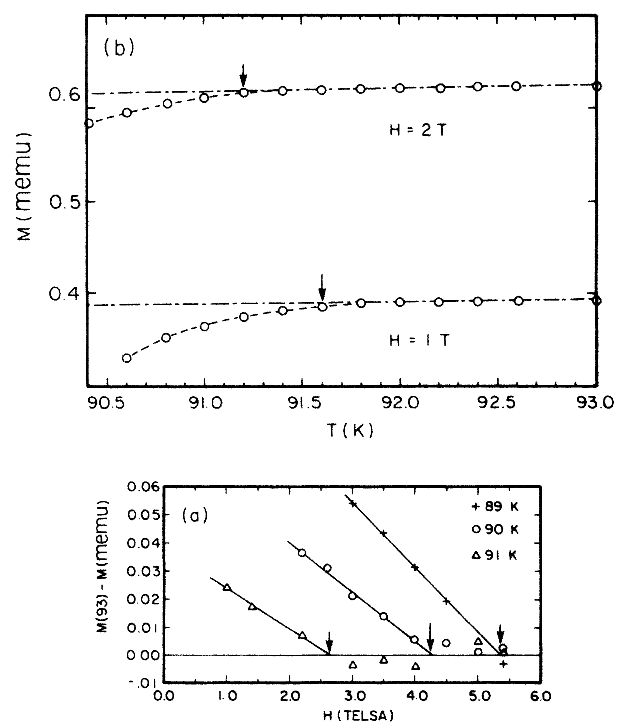

FIG. 2. (a) The difference between the magnetizations at 93 K (normal state) and at a constant temperature vs magnetic field. The straight lines are the least-squares fits to the data. (b) M vs T at a constant field. The arrows indicate the phase boundary $H_{c2}(T)$ in both (a) and (b).

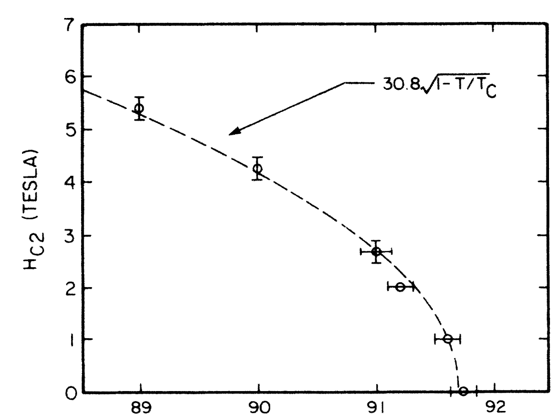

FIG. 3. The nucleation field as a function of temperature. The curve corresponds to Eq. (3).

tices parallel to the TP's (and to the c axis) and the current parallel to the TP's and normal to the vortices. This assumption leads to an upper limit for J_c, since the effect of pinning is strongly reduced for other TP and vortex orientations.[14] Let us compare the vortex core energy per unit length $\varepsilon = \pi\xi^2 H_c^2/8\pi = \phi_0^2/64\pi^2\lambda^2$ (H_c is the thermodynamic critical field) at the TP and in the bulk, far from the TP at low T's when the whole sample is superconducting. The energy difference, $\Delta\varepsilon = \varepsilon_b(\lambda_b^2/\lambda_{TP}^2 - 1)$, where the λ's are the penetration depths and the subscript b denotes bulk values. At low temperatures λ^{-2} is proportional to $\Delta(0)$ (in the dirty case), with $\Delta(0)$ being the zero-temperature pair potential,[16] which is proportional to the corresponding critical temperature. We then obtain $\Delta\varepsilon = \varepsilon_b \tau_0$. The energy $\Delta\varepsilon$ is associated with the relocation of a vortex from the TP to a distance of the order of ξ from the TP; the corresponding pinning force per unit length is $f \sim \Delta\varepsilon/\xi$. If the magnetic flux density B is sufficiently low and the interactions among vortices are sufficiently weak, the direct summation method yields $J_c \sim c\Delta\varepsilon/\phi_0\xi$.[17] We expect this approximation to be valid, however, only when $B < \phi_0/L^2$ and L is the average TP spacing. Using $\Delta\varepsilon = 0.16\varepsilon_b$ ($T_{c0} = 79$ K, $T_c = 91.7$ K) with the values $\lambda = 260$ Å and $\xi = 34$ Å from Ref. 13, we obtain $J_c = 2.3 \times 10^8$ A/cm^2 as an upper-limit estimate for J_c at low T's and in low fields. This result is about an order of magnitude less than the depairing current density $cH_c/3\sqrt{6}\pi\lambda$ we estimate from the Ginzburg-Landau theory. The measured value of J_c at 4.2 K with the same sample as in this work is 2×10^7 A/cm^2.[9] For $B > \phi_0\xi/L^2$, the intervortex spacing $a_0 \sim (\phi_0/B)^{1/2}$ becomes smaller than L, and only vortices near TP's can take full advantage of the TP pinning. Following the approach of Ref. 17 for grain-boundary pinning, we obtain $J_c \sim (c\Delta\varepsilon/\phi_0\xi)(a_0/L)$. When $B = 4$ T and $L = 1400$ Å ($\phi_0/L^2 = 0.1$ T), we obtain the upper-limit estimate, $J_c \sim 3.7 \times 10^7$ A/cm^2. The predicted weak dependence upon B appears to be consistent with experimental observations at low T's,[13] although the above estimate of J_c exceeds the value obtained in this experiment.

At temperatures above the bulk T_{c0}, twinned specimens should behave as systems of alternating normal and superconducting layers. The J_c's of weakly proximity-coupled superconducting-normal-superconducting (SNS) systems are known to sometimes exhibit exponential dependences on H and T.[18] In this way, one might be able to understand the dependence $J_c \propto \exp(-H/H_0)$ with a constant H_0 observed in bulk sintered specimens at high temperatures and fields.[19] Moreover, one might also expect an exponential decrease in J_c with T at high fields, as in weakly coupled SNS proximity systems with clean and thick normal layers.

Although we have presented here the case for superconductivity *enhancement* at the TP's, one can offer another explanation (which we believe to be less likely, however) in terms of superconductivity *weakening* at the TP's.[20] If the local atomic composition at the TP's were so strongly altered from that in the bulk that the TP's behave as tunnel barriers and if the barriers were thick enough to nearly decouple adjacent twins, then each twin would behave essentially as an independent slab or film (of thickness L and bulk transition temperature T_{c0}). The parallel nucleation field versus temperature would have a thin-film-like square-root temperature dependence for T sufficiently close to T_{c0} so that $L < 1.8\xi(T)$, but a linear temperature dependence at lower temperatures, when $L > 1.8\xi(T)$.[21] With $\xi_0 = 34$ Å and $L = 1400$ Å, however, the expected square-root-like temperature regime would be limited to within 0.2 K of T_{c0}, in disagreement with the results shown in Fig. 3, although if L were so small as 600 Å,[2] the square-root regime would lie within 1.0 K of T_{c0}, in better agreement with our experiments. To explain the J_c anisotropy by TP superconductivity weakening, either a calculation similar to that for grain-boundary pinning[17] or one based on pinning by surface-barrier effects (see, e.g., Refs. 17 and 22) could be used. The change in slope of H_{c2} versus temperature reported in Ref. 10, on the other hand, apparently could not be understood in terms of TP superconductivity weakening.

There is yet another indication in favor of superconductivity with enhanced T_c localized along TP's: Zero-field J_c measurements on bulk polycrystals[23] and on films[24] show that $J_c \propto (T_c - T)^{3/2}$ near T_c. This two-dimensional behavior is well known in thin films[21] and is expected for TP-enhanced superconductivity,[7] while the model of Ref. 20, where TP's are assigned to play a role of Josephson barriers, predicts $J_c \propto (T_c - T)^2$. Finally, the experimental observation of T_c increases in Sn, Re, Tl, and Nb with increased density of twin boundaries,[5] favors a description of TP superconductivity enhancement, rather than weakening.

According to Ref. 7, although the T_c enhancement might be small when $L/\xi \gg 1$ and the TP's are decoupled, T_c/T_{c0} should increase substantially if L is on the order of ξ and the TP's are strongly coupled via the proximity effect. Experimental studies of T_c versus twin density for specimens with otherwise identical bulk composition are needed, because they would provide a stringent test of the validity of the TP superconductivity enhancement mechanism.

Other plane defects different from (110) TP's have been observed in crystals of $Y_1Ba_2Cu_3O_7$.[25,26] The question of whether or not these defects contribute to the T_c enhancement[27] remains open until the microscopic mechanism of the enhancement is established.

In conclusion, we have found experimentally that the upper critical field varies as $(1 - T/T_c)^{1/2}$ near T_c in a grain-aligned sample of $YBa_2Cu_3O_{7-\delta}$. We suggest that T_c enhancement at the twin boundaries explains this dependence, as well as the observed strong anisotropy of J_c and its $(T_c - T)^{3/2}$ behavior.

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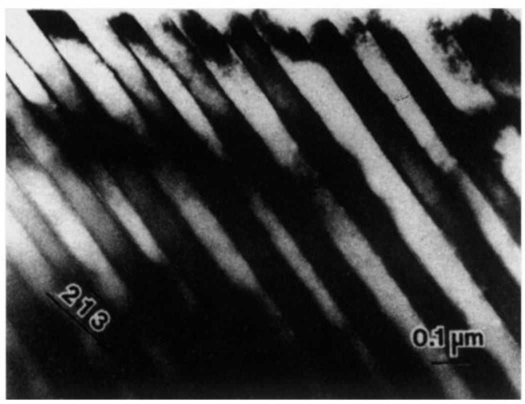

FIG. 1. Transmission electron micrograph of $Y_1Ba_2Cu_3O_{7-\delta}$ showing twin boundaries imaged using $(2\bar{1}3)$ planes. Upper portion of the figure is nearest to the foil edge.