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Field-dependent microwave absorption in high-T_c superconductors

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Substantial field-dependent microwave absorption is found in superconducting materials of the $YBa_2Cu_3O_7$ class. Abrupt changes occur over a 20-G range at zero field which are qualitatively different for polycrystalline and single-crystal materials. A strong hysteresis in polycrystalline samples is quenched by modulation fields of 0.2 G_{pp}. Formally the dissipative processes observed may be described in terms of flux relaxation, but the underlying physical mechanisms remain unresolved. As measurements on 100-μg specimens can be performed in a few seconds, this property may prove useful for material characterization.

Amidst the welter of information concerning the new high-temperature superconducting materials are several reports of anomalous microwave behavior.[1,2] Electron-spin-resonance experiments, intended to probe $g=2$ Cu^{2+} levels, show a marked base-line shift and strong zero-field absorption changes as one enters the superconducting regime. While many samples do exhibit a $g=2$ resonance, its intensity has markedly decreased as the caliber of materials has improved and this signal appears indicative of the "wrong" phase.

The unanticipated $H=0$ behavior, however, persists in the best of materials. In a ESR spectrometer, which senses field-dependent microwave absorption, this absorption is too large to be easily dismissed. Spectra for 100-μg samples can be measured within seconds and, for samples < 1 g, absorption changes are apparent even in klystron mode-sweep patterns. This paper summarizes our own observations concerning low-field microwave absorption. Field and temperature dependences prove to be highly sample dependent and significant anisotropies occur with single crystals. In all instances, we find a decrease in absorption at $H=0$. Because of the sensitivity of this experiment to sample variations, it bears promise of becoming a useful technique for material characterization. The physical basis of these absorption changes, however, remains speculative.

EXPERIMENT

A conventional ESR spectrometer was used in this study (Varian V-4500), the only relevant modification being buckout coils to permit sweeps through zero field. Because of the uncertain origins of the effects observed, we summarize certain saliencies of the apparatus. The sample is centered in an X-band TE_{102} cavity (9.5 GHz). The external magnetic field H_0 defines the z axis. This field is modulated, $\omega_m=100$ kHz, with peak-to-peak amplitudes H_m of 6 mG to 12 G. The microwave magnetic field H_1 lies parallel to the x axis and has a maximum at the sample position. Its amplitude may be varied from < 1 mG to 1 G and, at higher power levels, microwave heating may be used to force transitions to the normal state. The microwave electric field E_1 is parallel to H_0 but has a node at the sample position. The cavity is matched to the exciting waveguide for zero reflected power and automatic frequency control circuitry adjusts the klystron frequency so that changes in reflected power are due to energy absorbed within the cavity. The detector senses the component of reflected power modulated at ω_m. In all experiments to date, no quadrature component has been found, i.e., detected modulations are in phase with the H_0 modulation.

Single crystals were grown from a eutectic flux as described elsewhere.[3] Following mechanical separation from the flux, the crystals were annealed in flowing oxygen at 500 °C to maximize the oxygen content of the lattice. Crystal A was grown in zirconia crucible and crystal B in an alumina crucible. The actual composition of the latter was $YBa_2Cu_{3-x}Al_xO_7$, $x=0.1$, with aluminum substituted for copper in the CuO chains.[4]

Samples were held in 1-mm Pyrex capillaries with rectangular constrictions in the case of oriented specimens. The capillaries were inserted in 5-mm quartz tubes containing glass-forming iso-pentane to improve thermal contact. These tubes were then placed in a Dewar insert coaxial with the x axis. Samples could be rotated about this axis, thereby varying their orientation with respect to H_0, but not H_1.

Several tests were made to establish that the microwave-sample interaction was via H_1 and not E_1. As the sample lies at a node of the E_1 field, coupling with this field should be position sensitive. The cavity was asymmetrically loaded with lossless dielectric (Teflon) shifting the cavity frequency by an amount equivalent to a 1-mm nodal displacement. Alternatively, the sample position was jiggled ± 1 mm after omitting the surrounding quartz tube. In neither circumstance was the low-field absorption affected.

It should be noted that Pyrex, but not quartz, also exhibits an absorption minimum at zero field, width ~ 10 G, although its strength is magnitudes less than that of the materials investigated. This dip decreases markedly with temperature, particularly in the vicinity of 100 K, but can be still be observed at room temperature. In none of the materials examined has any response been detected above 93 K.

RESULTS

We shall discuss experimental results characteristic of several materials of nominal composition $YBa_2Cu_3O_7$, noting only that analogous behavior has been found for other rare-earth variations. Figure 1 shows a spectrum taken at 88 K for a 500-μg specimen of sintered material ($0.9\times0.5\times0.2$ mm). The field was swept from -25 to $+250$ G and back in 30 s. At $H=0$, a strong "absorption" is found with a slight anisotropy and a 10-G peak-to-peak width. The phase-detected signal is proportional to the derivative of absorption with respect to magnetic field, but the sign of this function must be inferred. Comparison with resonance absorptions, the $g=4$ Pyrex line or the $g=2$ Cu^{2+} resonance, shows the $H=0$ feature to be an absorption minimum. Klystron mode-sweep displays with larger samples evince a similar conclusion. Above T_c, substantial eddy current losses of the normal phase lead to a weak cavity dip. On passing to the superconducting phase, this dip drops nearly to the base line, indicating a substantial decrease in cavity loss. A discernible (10%) variation can then be seen as the field is swept through $H=0$, corresponding to minimum loss at this field. Although qualitative, such behavior demonstrates that field-dependent microwave absorption processes contribute significantly to cavity loss mechanisms.

Figure 2 plots integrals for the data in Fig. 1, more clearly revealing the shape of the absorption minimum. Minor differences on the forward and reverse scans lie within uncertainties in setting the base-line offset and we have refrained from postexperimental corrections. The long tails reflect the fact that the plots in Fig. 1 approach a nonzero or slowly varying limit as the field increases. Line shapes have not been consistently analyzed. For the spectra in Fig. 1, the tail drops off as $H^{-1.45\pm0.05}$, implying absorption increases as $1/\sqrt{H}$.

Figure 3 shows the amplitude and width of the $H=0$ signal as a function of temperature. A sharp amplitude change occurs at 87 K. Below 85 K, response appears to level off and above 91 K no signal was detected. Peak-to-peak widths varied from 12 G at the lower temperatures to a 7 G minimum at 87 K. Above 90 K, just before disappearing, the spectrum's shape changes to a step function (Fig. 4) with a height comparable to the magnitude of the high-field response at lower temperatures (Fig. 1).

Experiments with single crystals gave markedly different results. Figure 5 plots the magnetic response for one 100-μg crystal ($0.9\times0.4\times0.05$ mm). A step from negative to positive values occurs at $H=0$, integration giving a linear dependence of absorption versus field magnitude. The step size is similar to the high-field response for polycrystalline material (Fig. 1). Response is decidedly orientation dependent. Greatest changes occur with the static field perpendicular to the flat crystal face, i.e., parallel to the crystal's c axis. All single crystals examined to date have shown this step, although in some cases

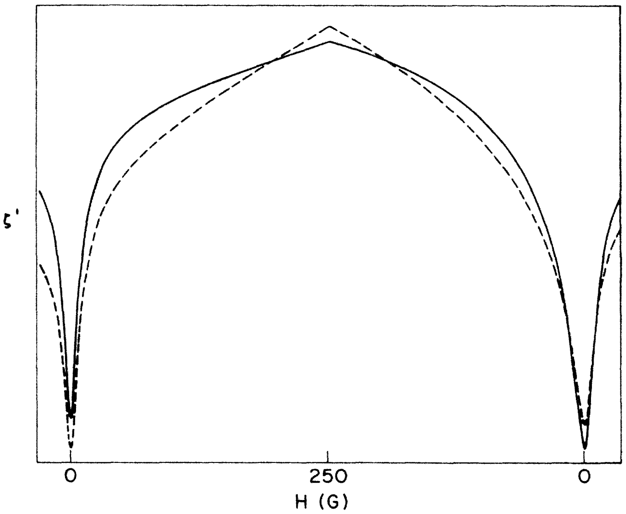

FIG. 2. Integrated plots for Fig. 1 showing the shape of the zero-field absorption region.

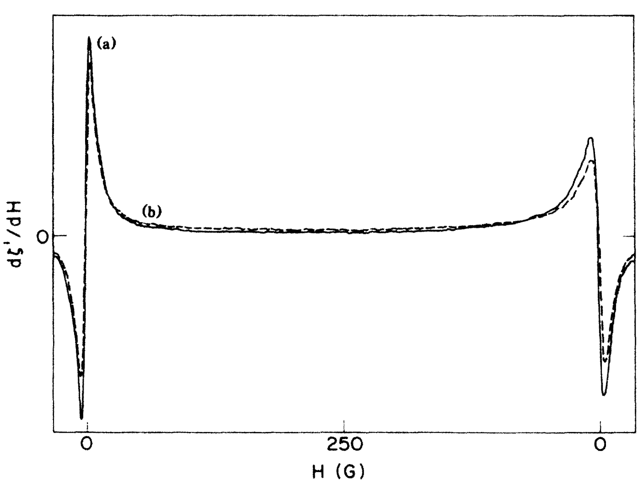

FIG. 1. Derivative microwave absorption spectra for a planar, polycrystalline $YBa_2Cu_3O_7$ sample. The magnetic field was swept from -25 to $+250$ G and back. For curves a and b, respectively, the field was normal and parallel to the plane of the sample.

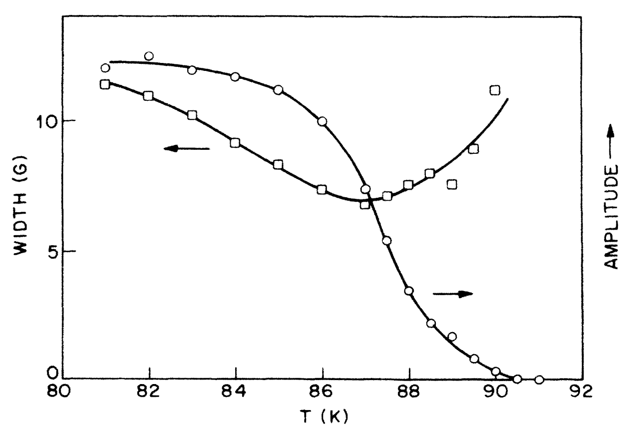

FIG. 3. Temperature dependence of the peak-to-peak height and width for the zero-field features of the sample described in Fig. 1.

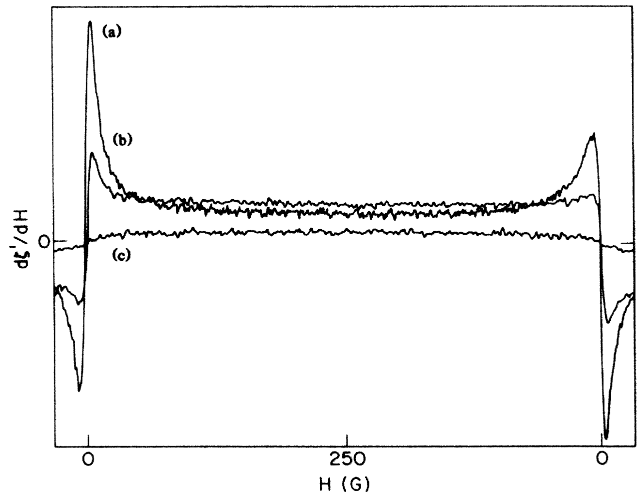

FIG. 4. Derivative absorption spectra near T_c for the sample described in Fig. 1: (a) 89.5 K, (b) 90 K, and (c) 90.5 K.

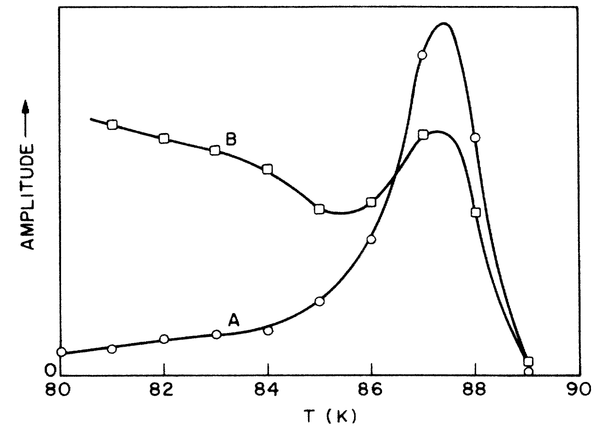

FIG. 6. Temperature dependence of the step height for two single crystals. Crystal A has the lower impurity content.

additional cusps may be superimposed. The temperature variation of the step height for two crystals is shown in Fig. 6. Both reveal an 87 K maximum. For the higher quality crystal A, a significant signal appears only over a 1–2 degree range. Crystal B, in contrast, gives a strong response at temperatures below 87 K.

An exceptional hysteresis occurs in all polycrystalline samples, whether single sintered fragments or powdered material. This effect is wholly a function of field-modulation amplitude. Figure 7 shows absorption behavior for several field sweeps between ± 50 G at 5 G/s. Figure 8 plots the symmetry and amplitude of the zero-field signal as a function of modulation amplitude. The symmetry coefficient is defined as the ratio of the heights of the derivative extrema. For sweeps symmetric about $H=0$, response is independent of sweep direction and rate. Symmetry changes occur over a narrow modulation range near 0.2 G_{pp}. At low modulations, the phase of the signal indicates an increase in absorption as one scans through zero field. Further, superimposing a larger, incoherent, low-frequency modulation, 20 Hz to 1 kHz, on a small 100-kHz modulation field shifts the 100-kHz response from hysteretic to normal.

Hysteresis is not an overmodulation artifact. Absorption changes take place over a 10 G range and larger modulations will broaden the response, but not alter its symmetry or dependence on sweep direction. The noise in Fig. 7 is inherent in the sample and well above instrumentation levels. Response is quite sensitive to nonuniform field changes. Normally, the field is swept with a 1000-step digital to analog staircase. Under hysteretic conditions, narrow spikes can be seen superimposed at each step. For the data in Figs. 7 and 8, the sweep voltage was a true linear ramp derived from RC integrator circuitry (PAR model 175 Universal Programmer).

Ephemeral observations have been noted of "fine structure" in the rapidly changing portions of plots similar to Fig. 7, with 1–3 ripples comparable to the noise but repetitive in position. No definitive changes have been

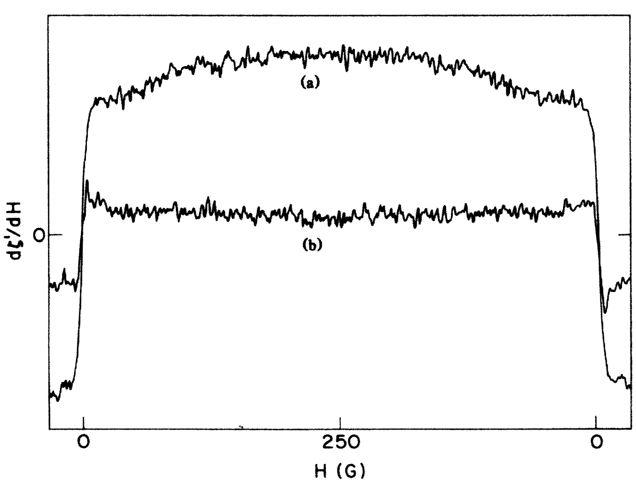

FIG. 5. Derivative absorption spectra for a single crystal at 86 K with the c axis (a) parallel, and (b) perpendicular to the static field.

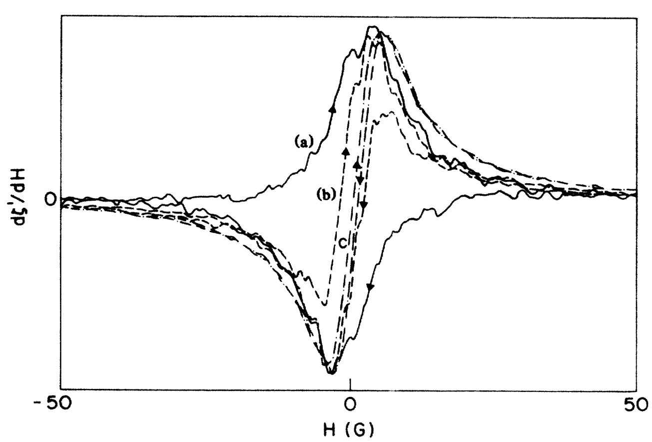

FIG. 7. Derivative absorption spectra for a polycrystalline sample (Fig. 1) showing hysteresis as a function of modulation. Peak-to-peak modulation amplitudes are (a) 0.012 G, (b) 0.24 G, and (c) 2.4 G.

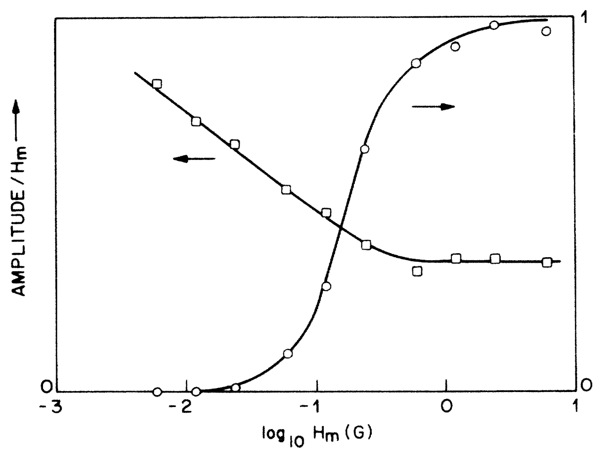

FIG. 8. Variation of the amplitude and symmetry of the zero-field absorption of a polycrystalline sample with field modulation. The symmetry is the ratio of the negative and positive extrema amplitudes. The amplitude is normalized with respect to the modulation level.

found in the response of single crystals at low modulation amplitudes, possibly because of smaller samples and weaker changes. In one experiment using 0.12 G_{pp} modulation, an apparently noisy response was obtained between 0 and 500 G after averaging 16 sweeps. Repeating the experiment yielded an identical plot of "noise" versus field. Raising the temperature to 93 K dropped the noise level an order of magnitude and eliminated its recurrent aspects. Powders, but not single fragments of sintered material, show an additional hysteretic feature at high fields. In sweeps to 500 G and back, an immediate, discontinuous step occurs when the sweep direction is reversed. This characteristic can also be overridden by large modulations (>2 G). While we shall not discuss these effects further, we believe they are indicative of the questionable behavior of these superconducting materials and suggestive of avenues for future exploration.

DISCUSSION

The experiments of interest involve microwave absorption. Provided the penetration of microwave fields is small compared with both the free-space wavelength and sample dimensions, the energy passing into the sample is proportional to the surface impedance, ζ.[5] For metals,

$$\zeta = i\omega\delta/c = (i\omega/4\pi\sigma)^{1/2} , \quad (1)$$

where the complex distance δ determines field penetration, e.g., $H = H_0\exp(-z/\delta)$. The real part of $1/\delta$ is the skin depth, 5 μm for the conductivity, approximately 10^4 mho/cm characterizing these materials in their normal state at low temperatures.[6]

Similar expressions for the superconducting state follow from London equations for harmonic fields in terms of magnetic induction **B**, and current density **J**,

$$\nabla\times\mathbf{B} = 4\pi\mathbf{J}/c ,$$
$$\nabla\times\mathbf{J} = -(ne^2/mc + i\omega\sigma/c)\mathbf{B} = -\Gamma\mathbf{B} \quad (2)$$

when displacement currents are neglected.[7] The surface impedance and field penetration parameters are

$$\zeta = i\omega\lambda/c ,$$
$$1/\lambda^2 = (4\pi/c^2)(ne^2/m + i\omega\sigma) = 1/\lambda_L^2 + 1/\delta^2 , \quad (3)$$

where λ_L is a real number, the London penetration length, and δ is a complex number akin to a normal metallic value. Results for high-T_c materials suggest $\lambda_L \sim 0.1$ μm.[8] This distance is less than the microwave skin depth so superconducting behavior is anticipated at 9.5 GHz.

The explicit form for Γ in Eq. (2) presumes the total current to be the sum of a supercurrent and a normal current $\sigma\mathbf{E}$. More generally we shall consider Γ to be a frequency-dependent material parameter. This dependence implies flux relaxation, i.e., the supercurrent distribution requires a finite time to adjust to a magnetic-field change. The imaginary part of Γ leads to dissipation at nonzero frequencies. In an idealized superconductor, the relaxation time would be related to gap frequencies lying well above the microwave region. A more realistic appreciation of the new materials may suggest alternative rate-limiting processes.

Detection of only field-modulated microwave absorption implies the signal observed is proportional to $\mathrm{Re}(d\zeta/dH)$. We presume that, in some sense, ζ reflects the state of the sample. If the sample is in thermodynamic equilibrium then ζ will be a function of H^2 and $d\zeta/dH$ should be antisymmetric about $H=0$. This is the case for single crystals, but for polycrystalline samples such behavior is only observed when a sufficiently large modulation is superimposed. Otherwise, the state of polycrystalline material as $H\rightarrow 0$ is indeterminate.

Polycrystalline materials show a narrow dip in absorption within ± 5 G of zero field. Supposing this range reflects a flux quantization limitation $HS^2 \simeq \Phi_0$ with Φ_0 being the flux quantum, and the corresponding area S^2 is 4 μm^2. This area is commensurate with grain size and requires supercurrent loops crossing grain boundaries. Thus, a quantization limit is consistent with the dependence on granularity of the $H=0$ behavior in polycrystalline material.

Ebner and Stroud have analyzed the magnetic susceptibility for random arrays of weakly coupled, superconducting particles sized less than the penetration depth.[8] At low fields, the flux distribution for minimum-energy configurations is strongly field dependent due to quantized loop interferences. They find that the equilibrium susceptibility changes from its normal of high-frequency value to a superconductor value over the range $H < \frac{1}{2}\Phi_0 S^2$. Thus, at low fields their model predicts a field-dependent relaxation for flux patterns, provided kinetically allowed paths exist.

Several groups have made ac susceptibility measurements at $H=0$ on high-T_c materials.[9-11] The report χ' and χ'' values insensitive to frequency (10–1000 kHz, but strongly dependent on modulation amplitude. At low modulations, χ' indicates nearly complete shielding and χ'' exhibits a narrow peak near T_c. With modulations >1 G, however, these features shift to much lower temperatures. The strongly nonthermodynamic behavior manifested by microwave absorption at low modulations near $H=0$ appear related. Similar ac susceptibility behavior is encountered with traditional superconductors and its interpretation appears fraught with pitfalls.[12] It is moot whether the time-dependent processes complicating low-frequency measurements are those directly responsible for microwave absorption because of considerable frequency differences. The absence of a significant 100-kHz quadrature signal indicates that the low-frequency processes do not respond to 100-kHz fields. Qualitatively, time-dependent magnetic behavior may be rationalized in terms of flux trapping and relaxation. The indeterminate state of high-T_c materials at $H=0$ can be due to trapped flux which alters those properties determining ζ. Low modulations, approximately 0.2 G_{pp}, suffice to release trapped flux and bring the material to a state independent of its history.

For the single crystal examined $d\zeta/dH$ shows only a step change at $H=0$. As $T\rightarrow T_c$ with polycrystalline material, sharp features vanish first, leaving a similar response and suggesting that grains have been disconnected and exhibit the response of a superposition of individual crystallites. The width of the single-crystal steps, given by the width at half-height of $d^2\zeta/dH^2$ is also 5–10 G. At higher fields, $d\zeta/dH$ is nearly constant, implying $\zeta\propto H$. For type-II behavior, the vortex state should arise when $H>H_{c1}$ and the vortex density should increase approximately linearly with field until H_{c2} is reached. In the best crystals, microwave loss is only observed near T_c and one may postulate that vortex migration in a "soft" lattice leads to flux relaxation. In less perfect crystals, relaxation is observed at temperatures well below T_c.

The 5–10 G field range near T_c characteristic of both polycrystalline material and single crystals is comparable with H_{c1} estimates deduced from magnetization measurements.[6] $M(H)$ plots in this temperature range develop nonlinearities over this range.[13] Under idealized conditions, the gap energy should decrease rapidly near T_c and changes in microwave response might be anticipated because of the proximity of microwave and gap frequencies. This does not appear to be significant. Resistance measurements generally give T_c values near 93 K for these materials. Microwave absorption is greatest at or below 87 K. As thermocouple readings were correct to <1 K in boiling N_2, we believe this difference is real.

Finally, we note the difference in the anisotropic behavior of similarly shaped polycrystalline and single-crystal specimens. For the former, orientation effects are minor. In the latter case, significantly stronger absorption changes are found with the static field normal to the flat sample face. In this orientation, induced currents lie in the *a-b* crystal plane favored for electron conductivity in the normal state.[14] The static field may be expected to exert a greater influence on the superconducting state when applied normal to these planes.

CONCLUSIONS

Microwave absorption offers a sensitive and expeditious technique for characterizing high-T_c superconductors. Samples of only 100 μg are required. The material property probed is not well understood but appears related to magnetic flux relaxation. Major differences are found in the behavior of polycrystalline and single-crystal materials. Flux relaxation is an important limitation for possible magnetic applications and microwave studies may prove useful in understanding macroscopic behavior. The nature of the relaxation processes is still speculative and further work in the time or frequency domain correlated with other properties and controlled materials will be needed for a definitive picture to emerge.

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