In-Plane Anisotropy of the Penetration Depth in $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$ Superconductors

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The superfluid response of single-crystal $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$ shows a strong anisotropy in the a-b plane as revealed by far infrared spectroscopy. The value of the London penetration depth in both systems is considerably smaller in the direction along the Cu-O chains, suggesting that a substantial portion of the superconducting condensate is on the chains.

It is generally agreed that the most important element of the copper-oxide high-temperature superconductors is the two-dimensional copper-oxygen plane. These materials contain several other structural elements in their complex unit cells. The one-dimensional copper-oxygen chains in $YBa_2Cu_3O_{7-x}$ (123) or the double chains in $YBa_2Cu_4O_8$ (124) are examples of such elements. These chains are believed to be carrier reservoirs, providing holes to the CuO_2 planes. In this sense their function is analogous to that of the Bi-O layers or Tl-O layers in other high-T_c compounds. The possibility that these elements can contribute to the superconducting behavior of the cuprates, if established experimentally, may be of fundamental importance for the understanding of the electronic structure of the cuprates. Because the chains have a well defined direction in the crystal, their influence can be investigated by a study of the anisotropy of the in-plane transport properties, such as the conductivity and the superconducting penetration depth.

In this Letter we report measurements of the a-b plane anisotropy of the London penetration depth in high quality, untwinned single crystals of 123 and 124. We used infrared spectroscopy to obtain two of the diagonal components of the λ_L tensor (λ_a and λ_b) from the reflectance measured with polarization along the corresponding principal axes of the crystal (R_a and R_b). Methods commonly used to probe the superfluid, such as muon spin resonance (μSR), dc magnetization, or microwave techniques, yield values of λ_L which average at least two of the components of the penetration depth tensor. In contrast, infrared spectroscopy can be used to obtain the absolute values of each of the diagonal components of λ_L, λ_a, λ_b, λ_c, by measurement of the reflectances R_a, R_b, R_c with polarization along the a, b, and c axes.

We find that the superconducting penetration depth in untwinned single crystals of 123 and 124 is smaller in the chain direction than it is normal to the chains; therefore, a

large portion of the spectral weight that can be attributed to the chains in the normal state condenses below T_c. These results indicate that superconductivity, at least in the 123 and 124 compounds, is not confined to the planes but extends to the chains as well.

The superconducting penetration depth can be found from the reflectance in two ways. Kramers-Kronig (KK) analysis of $R(\omega)$ allows one to obtain the real and imaginary parts of the complex conductivity, $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$. The imaginary part of the conductivity, $\sigma_2(\omega)$, is directly related to λ_L:

$$c^2/\lambda_L^2 = \omega_{ps}^2 = 4\pi\omega\sigma_2(\omega), \qquad (1)$$

where ω_{ps} is plasma frequency of the condensate given by $4\pi n_s e^2/m^*$. In this expression n_s is the density of the condensate and m^* the effective mass of the carriers. Equation (1) is a direct consequence of the delta function peak in the real part of the conductivity at $\omega = 0$. Alternatively, the strength of the delta function peak can be obtained from the oscillator strength sum rule:

$$c^2/\lambda_L^2 = 8\int_0^\infty (\sigma_n - \sigma_s)\,d\omega, \qquad (2)$$

where σ_n and σ_s are the real parts of the complex conductivity in normal and superconducting states. Equation (2) states that spectral weight lost at low frequencies in the superconducting state has been transferred to the zero frequency delta function response of the superconducting condensate [1].

The experiments described here have been done on two samples of 123 and one of 124. The first 123 sample, designated as sample 1, was grown and detwinned at the University of British Columbia with the far infrared (FIR) measurements being done at McMaster University. The second, designated as sample 2, was grown at the University of Illinois and measured at the University of Florida. Sample 1 was produced by a flux-growth technique described elsewhere [2] and was detwinned

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under uniaxial stress. The oxygen content was set at $O_{6.95}$. The critical temperature of this sample was 93.5 K with a transition width of less than 0.2 K. Above T_c the anisotropy of the resistivity, determined from the microwave surface resistance in the a-b plane, was as high as 2.3 [3]. Reference [4] describes the preparation and characterization of sample 2. This crystal had zero resistance at 92 K and a dc resistivity anisotropy greater than 2.1. The single crystals of 124 were grown under high oxygen pressure [5]. The critical temperature of these samples was 80 K with $\Delta T_c < 0.5$ K. Crystals of 124 are naturally untwinned as well as underdoped. The optical conductivity of this material was obtained at McMaster; the normal state results are in accord with the normal state results of Refs. [6,7].

In Fig. 1 we show the polarized reflectance of 123 and 124 crystals at $T = 10$ K (at 20 K for 123 sample 2) measured over a broad spectral range. The major difference between R_a and R_b occurs at high frequencies. The positions of the plasma edges are significantly different in the a and b directions, in agreement with other studies [8–11]. Also consistent with earlier experiments, the near infrared anisotropy is more pronounced for the double chain 124 material [6]. However, in contrast to earlier work on untwinned 123 [10–12], which showed a reduced reflectance in the chain direction at low frequencies, we find a b-axis reflectance that is nearly equal to the a-axis reflectance below 500 cm^{-1}.

KK analysis gives the frequency dependent penetration depth, defined as $\lambda(\omega) = c/[4\pi\omega\sigma_2(\omega)]^{1/2}$, and optical conductivity, $\sigma_1(\omega)$. To extrapolate the reflectance mea-

surements for the KK analysis, we used the data in Ref. [13] up to 45 eV. At low frequencies the particular extrapolation chosen does not have much influence on the conductivity in the region where actual measurements exist. The results are plotted in Fig. 2. It is clear that $\lambda(\omega)$ is almost frequency independent at low temperatures because the superfluid response dominates the other contributions to the conductivity, demonstrating that the FIR measurements give the static limit of the penetration depth. The values of λ obtained directly from σ_2 or through the sum rule [Eq. (2)] are close within (5–7)% accuracy. The data presented in Fig. 2 differ from previous work in the strong a-b anisotropy of λ. The penetration depth is *strongly reduced* in all samples in the b polarization (along the Cu-O chains). The penetration depths obtained are $\lambda_b = 800$ Å, $\lambda_a = 2000$ Å for the 124 material; $\lambda_b = 1000$ Å, $\lambda_a = 1600$ Å for sample 1 of 123; and $\lambda_b = 1200$ Å, $\lambda_a = 1600$ Å for sample 2.

The strong anisotropy in the London penetration depth reported here is consistent with the transport anisotropy in the normal state. In the single-chain 123 materials the dc resistivity anisotropy in the a-b plane, ρ_a/ρ_b, is 2–2.3 [4,14] and in the double-chain 124 as high as 3.3 [15]. In sample 1 the anisotropy of the low frequency limit of $\sigma_1(\omega)$ at 95 K is $\sigma_b/\sigma_a = 2$. Using the classical skin effect in the normal state, the surface resistance measurements on a similar crystal gave a slightly higher anisotropy of $\sigma_b/\sigma_a = 2.3$. Using a two-component

FIG. 2. Left panels: Frequency dependent London penetration depth $c/\lambda_L = [4\pi\omega\sigma_2(\omega)]^{1/2}$ for 124 sample (upper panel), 123 sample 1 (middle panel), and 123 sample 2 (lower panel). Right panels: the real part of the complex conductivity. All curves shown are at 10 K except for sample 1 where the b-axis conductivity is also shown at 95 K by the thick line and 124 sample where the a-axis conductivity is also shown at 85 K by a thick line.
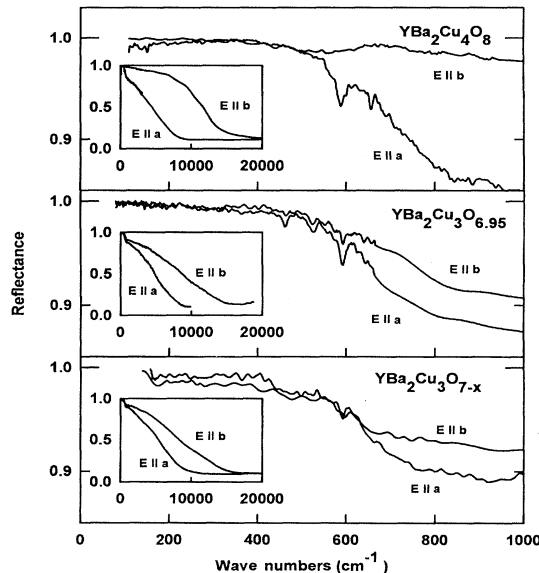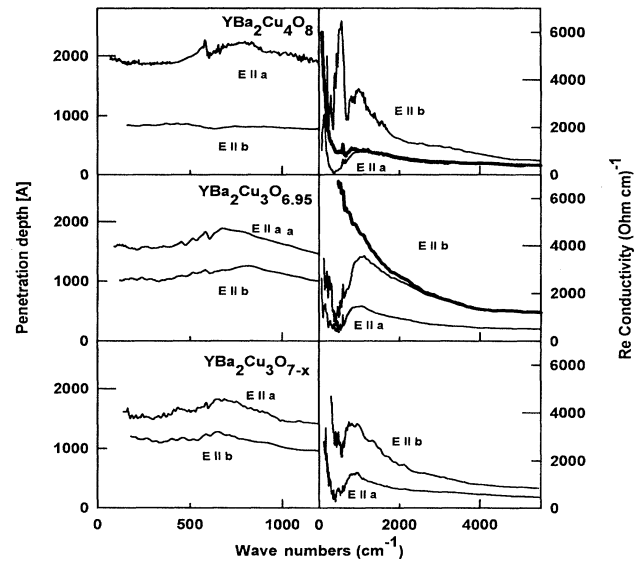
FIG. 1. Polarized FIR reflectance of 124 sample (upper panel), 123 sample 1 (middle panel), and 123 sample 2 (bottom panel) in the superconducting state. The insets show the reflectances over a broader frequency range.

analysis of the normal state optical conductivity [16], we also find a similar anisotropy in the normal state Drude plasma frequency $\omega_D^2 = 4\pi ne^2/m^*$: $\omega_{Db}^2/\omega_{Da}^2 \simeq [(2.0 \text{ eV})/(1.3 \text{ eV})]^2 = 2.2 \pm 0.2$. Because the dc conductivity may be written as $4\pi\sigma(0) = \omega_{pD}^2\tau$, we conclude that the scattering time τ is nearly isotropic in the a-b plane, making the anisotropy of the conductivity arise mainly from the anisotropy in the plasma frequency. These normal state results are in good agreement with local density approximation band structure calculations [17] which have predicted an anisotropy close to 2.3 for the plasma frequency of 123. This anisotropy is a consequence of three bands that cross the Fermi surface, one of which is principally chainlike and has a highly anisotropic effective mass. The anisotropy of the penetration depth $\lambda_a/\lambda_b = 2.3$ is remarkably close to the anisotropy of the normal state conductivity or the Drude plasma frequency. Thus, the value of $(n/m^*)_b/(n/m^*)_a$ taken from *any* of these experiments on 123 is 2.2 ± 0.2. The chains not only increase the spectral weight in the normal state but also enhance the superfluid density by the same factor. This suggests that the condensate resides on both *the chains and the planes*. In qualitative agreement with this picture, the anisotropy of both the normal state properties and of λ_L is even more pronounced in the double-chain 124 system.

The superconducting condensate uses only about half of the total spectral weight available in the infrared, as revealed by the conductivity in both the a and b polarizations. A residual conductivity remains in the superconducting state, where a finite $\sigma_1(\omega)$ can be observed down to the low frequency limit of our data in both polarizations. This aspect of the $\sigma_1(\omega)$ spectra, seen in both 123 samples, is in general agreement with the earlier data [11,12]. In particular, in the a direction, normal to the chains, the conductivity at the minimum at 400 cm^{-1} is remarkably consistent and is equal to 350 ± 50 (Ω cm)$^{-1}$ for our samples as well as for the samples used in the earlier work [11,12]. The conductivity in the chain direction is much more variable, and we think that a large part of the sample-to-sample variability of both *twinned* and untwinned 123 may be traced to the variability of the chain contribution.

It is quite remarkable that the frequency dependence of the real part of the conductivity of sample 1 is essentially the same along chain direction and perpendicular to the chains. The qualitative similarity between a- and b-axis response of the similar sample has also been revealed by the microwave experiments which have demonstrated almost identical temperature dependences of the penetration depth and of the microwave conductivity when probed along two directions in the crystal [3]. In all these cases the dependences of $\sigma(\omega)$, $\lambda(T)$, and $\sigma(T)$ are the same as those found earlier in the twinned crystals from the same batch [18–20], and the difference is only in the anisotropy of the absolute value which is the same for the resistiv-

ity, plasma frequency, or penetration depth as discussed above.

Where the new data presented here differ most from previous work is in the strong anisotropy of the condensate density measured in the chain direction. In the earlier crystals, the anisotropy of the FIR conductivity was as low as 1.1–1.3, and no anisotropy in λ_L was observed [10]. We suggest that this difference results mainly from significant disorder in the chains in the earlier samples. That disorder may dominate the chain response is shown by the report of hopping conductivity in certain samples [11]; in contrast, highly ordered chains are expected to exhibit metallic properties [21]. In samples with disorder, the contribution of chains to the conductivity resembles the response of a one-dimensional metal with localized electronic states with a clear *peak* near 3000 cm^{-1} [10,11], the so-called "chain peak." This peak is completely absent from the normal state conductivity of sample 1; the spectral weight associated with the "chain" band in disordered samples seems to be shifted to the Drude component in the case of our sample 1. Recent calculations on disordered chains bear out these ideas [22]. The enhancement of the Drude component in the b direction shows up in the increased dc resistivity anisotropy of the newer crystals [4,14] and suggests that the newer samples have more perfect chains.

Some of the differences among samples might be caused by a difference in crystal growth procedures. All three of our samples were grown in yttria stabilized zirconia crucibles, whereas gold or Al$_2$O$_3$ crucibles were used in the preparation of the earlier samples. It is known that Au and Al atoms have a tendency to occupy chain Cu sites [23,24], leading to a greater degree of disorder on the chains.

The superconducting behavior of the chains is also consistent with NMR experiments. The Knight shift and the NMR relaxation time T_1, on both chain and plane copper sites, have similar temperature dependences below T_c indicative of strong hybridization of plane and chain states leading to closely coupled superconducting behavior of carriers associated with the chains and planes [25,26].

Below we briefly outline some of the implications of superconducting chains in 123 and 124 as suggested by the anisotropy of the penetration depth.

The strong anisotropy of λ_L caused by the presence of the superconducting chain layer may explain some of the deviations from the universal correlation between T_c and the superfluid density $n_s/m^* = 1/\lambda_L^2$ suggested by Uemura *et al.* [27], at least in materials with Cu-O chains, such as 123, 124, (Pr/Y)Ba$_2$Cu$_3$O$_7$, etc. A comparison of the values for the penetration depth by μSR and those inferred from our FIR measurements finds that $1/\lambda_{\mu SR}^2$ falls between $1/\lambda_a^2$ and $1/\lambda_b^2$ [27,28]. The comparison suggests that μSR yields an averaged value of n_s/m_{ab}^*. If T_c is determined strictly by the carrier density in the CuO$_2$ planes, then it is not the ab-

averaged value but the in-plane density n_s/m_a^* determined from our FIR measurements that ought to be related to the critical temperature in the above compounds. As we have discussed above, the anisotropy of λ_L is important only if the chains are highly ordered. Then the doping dependence of averaged λ_{ab} for the system with chains may deviate from the universal behavior reflecting ordering in the chains in the materials close to the stoichiometric composition. This chain-related behavior may lead to the so-called plateau regions in the Uemura correlation, where the dependence of T_c from n_s/m_{ab}^* shows a saturation.

With coupled chains and planes, the interpretation of c-axis transport in 123 and 124 should be reexamined. The anisotropy of the penetration depth between the a-b plane and the c axis is suggestive of Josephson coupling of superconducting elements *inside* the bulk of a crystal [29,30], implying the presence of a nonsuperconducting barrier in the c direction. In order to reconcile the c-axis Josephson tunneling with strong coupling of chains and planes one has to assume that it is Y layer that serves as a barrier in 123 and 124. This conclusion is unexpected since, at least in underdoped compounds, the coupling has been found to lead to interplane magnetic coherence across the Y layers as seen by magnetic neutron scattering [31].

If the superconducting behavior of the chains is due to the proximity effect between electronic states on the superconducting planes coupled to intrinsically nonsuperconducting chains, we note that proximity coupling seems to have little effect on T_c in the 123 system. For example, gold doping renders the chains insulating and therefore presumably destroys the proximity coupling between the planes and chains. However, the T_c changes by only 1.5 K as the result of gold doping up to the 10% level [23].

Finally, we note that the anisotropy of the penetration depth found in the a-b plane response of 123 and 124 should not be confused with an anisotropic energy gap. The a-b plane conductivity is consistent with the clean limit [32], where the magnitude of the penetration depth and the gap are not related to each other.

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