Dependence of the Infrared Properties of Single-Domain $YBa_2Cu_3O_{7-y}$ on Oxygen Content

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(Received 17 July 1991)

The first polarized infrared-reflectivity measurements of untwinned crystals of $YBa_2Cu_3O_{7-y}$ as a function of y are reported. We separate the chain and plane contributions to the infrared conductivity, and find that for crystals with $T_c \gtrsim 50$ K the prominent normal-state midinfrared feature is associated with the chains. A threshold in the plane conductivity at ~ 500 cm^{-1} has a strong temperature dependence just below T_c suggesting an association with the superconducting gap. Its temperature dependence above and below T_c is quite similar to that of relevant NMR data, and is suggestive of gap development in the normal state.

PACS numbers: 78.30.Er, 74.30.Gn, 74.70.Vy

Infrared-conductivity measurements have been established as one of the basic techniques which can be used to study the fundamental nature of the superconducting and metallic states [1–4]. For the cuprates the analysis of the infrared data has followed two divergent paths. One is based primarily on results from reduced T_c, twinned $YBa_2Cu_3O_{7-y}$ samples, in which a structure in the infrared conductivity near 2000 cm^{-1} (0.25 eV) is observed. This "two-component" approach analyzes the conductivity in terms of a midinfrared mode associated with this structure, and a conventional Drude term at low frequency [5–7]. The other approach is based primarily on results from $T_c = 93$ K $YBa_2Cu_3O_7$, in which the 2000-cm^{-1} feature is not observed. This "single-component" approach analyzes the conductivity in terms of a single, *very unconventional*, non-Drude free-carrier term [6,8–11]. The present work has allowed us to reconcile these two fundamentally different views of the normal-state dynamics. By performing the first polarized reflectivity measurements of untwinned $YBa_2Cu_3O_{7-y}$ crystals as a function of y (T_c), we are able to separate the contributions to the infrared conductivity from the CuO chains and CuO_2 planes for a sequence of samples with T_c ranging from 56 to 93 K. We confirm the existence of structure near 2000 cm^{-1}, but show that it is associated with the chains in $YBa_2Cu_3O_{7-y}$. For the CuO_2 planes the infrared conductivity drops smoothly as a function of frequency, and much more slowly than a conventional Drude term, with no evidence for a midinfrared mode, suggesting that a single-component approach is applicable for all T_c.

The two diverging approaches to the normal-state properties lead to very different views of the superconducting state as well, which revolve around very different interpretations of a $\sim$500-cm^{-1} threshold observed in the conductivity at low temperature. The single-component approach emphasizes the strong temperature dependence of the 500-cm^{-1} feature just below T_c [10–15] in the $T_c = 93$ K material, and thereby infers an essential connection with the superconducting gap, i.e., $2\Delta \sim 500$ cm^{-1} [8–15]. In the two-component approach, however, the 500-cm^{-1} feature has been associated with the low-frequency edge of the midinfrared mode. It has been argued that since this feature is observed up to room temperature in some samples [6,16], it therefore cannot be related to the superconductivity. The claim that $YBa_2Cu_3O_7$ is too clean to see the gap [7] may be subsumed within this class, since it is based on associating most of the infrared conductivity with a midinfrared mode. From the present measurements we find that the features emphasized by the two approaches are distinct. The pure CuO_2-plane conductivity has no 500-cm^{-1} feature at room temperature. The feature roughly near 500 cm^{-1} observed at room temperature in twinned samples is due to the superposition of the $\sim$2000-cm^{-1} chain related peak on the smoothly falling plane conductivity. Focusing on the conductivity of the CuO_2 planes, we find that all crystals show rapid temperature dependence just below T_c for $\omega \lesssim 500$ cm^{-1}. One finds, moreover, that a relatively modest persistence of the gap related feature above T_c in the 93-K material [10–15] becomes much more prominent as T_c is reduced. We quantitatively compare the infrared temperature dependence with that of the relevant NMR relaxation rates. Both the infrared and NMR results suggest a scenario in which pair correlations begin to develop significantly above T_c [6,17,18].

Although in the data from twinned samples [5–7] the chain and plane contributions to $\sigma(\omega)$ cannot be separated, we find that the earlier data are not inconsistent with our present results on untwinned crystals. In particular, averaging the present $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ data, while not a rigorously correct procedure, does give reflectivity and conductivity spectra that are consistent with the earlier normal-state data from twinned samples.

Twinned crystals were annealed under uniaxial stress to form single-domain crystals [19]. Crystals with values of T_c of 56, 58, 82, 92, and 93 K were studied. Each crystal has a transition width of approximately 1 K, as measured by dc susceptibility; thus these crystals are comparable to the best reduced T_c materials known.

Near-normal-incidence (12°) reflectivity was measured with polarized light using a rapid-scanning interferometer (200–5000 cm^{-1}) and a grating spectrometer (5000–25000 cm^{-1}). The interferometer data were taken at temperatures between 20 and 300 K. These were combined with the spectrometer data taken at 300 K. The combined spectra were terminated as previously described [10] and Kramers-Kronig transformed to obtain $\sigma_1(\omega)$ and $\varepsilon_1(\omega)$ for each polarization.

In Fig. 1 we show the polarized normal-state conductivity spectra for three untwinned samples with T_c of 56 K (solid curve), 82 K (dashed curve), and 93 K (dotted curve), respectively. For $\mathbf{E}\parallel\hat{\mathbf{b}}$ the real part of the conductivity exhibits a broad maximum in the vicinity of 2000 cm^{-1}. This structure is routinely observed in unpolarized studies of twinned $YBa_2Cu_3O_{7-y}$ crystals [5,6], and has been associated with a midinfrared mode. In the present work we find that this structure is present only in the $\hat{\mathbf{b}}$ polarization, which implies an association with the CuO chains, as discussed previously for the $T_c=93$ K material [11, 20]. For the $\mathbf{E}\parallel\hat{\mathbf{a}}$ polarization, which measures only the conductivity of the CuO_2 planes [11,20], the conductivity drops smoothly with frequency in the normal state [Fig. 1(b)]. The observation of significant qualitative differences between the $\mathbf{E}\parallel\hat{\mathbf{b}}$ and $\mathbf{E}\parallel\hat{\mathbf{a}}$ spectra underscores the importance of polarized studies of untwinned samples for the $YBa_2Cu_3O_{7-y}$ class.

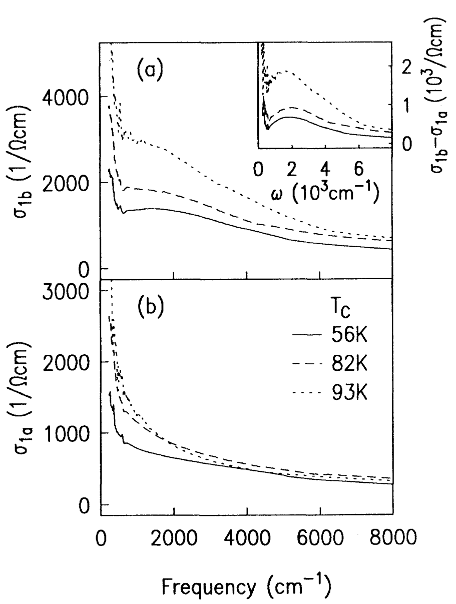

FIG. 1. Normal-state conductivity vs frequency for three untwinned crystals; $T_c=56$ K at a temperature of $T=200$ K (solid), $T_c=82$ K at $T=150$ K (dashed), and $T_c=93$ K at $T=100$ K (dotted). (a) $\mathbf{E}\parallel\hat{\mathbf{b}}$, $\sigma_{1b}(\omega)$. (b) $\mathbf{E}\parallel\hat{\mathbf{a}}$, $\sigma_{1a}(\omega)$ $=CuO_2$ plane conductivity. Inset to (a) is $\sigma_{1b}(\omega)-\sigma_{1a}(\omega)$. The chain-related conductivity features evident in $\sigma_{1b}(\omega)$ are also prominent in twinned samples (see Refs. [5] and [6]).

Two aspects of the structure of $YBa_2Cu_3O_{7-y}$ are of potential relevance to the a-b-plane anisotropy of $\sigma(\omega)$: (1) $YBa_2Cu_3O_{7-y}$ contains CuO chains oriented parallel to the $\hat{\mathbf{b}}$ axis, and (2) the lattice constant, and hence the Cu-O bond length, is about 2% larger in the $\hat{\mathbf{b}}$ direction than along $\hat{\mathbf{a}}$. In all known models of transport, a smaller lattice constant is expected to lead to a higher conductivity; hence the lattice constant difference has the wrong sign to account for the observed anisotropy (which is $\sigma_{1a}<\sigma_{1b}$ in all samples). The observation of both higher conductivity and more complexity in the $\hat{\mathbf{b}}$ spectra instead indicates that these spectra are enhanced by the presence of chains parallel to this axis, as one might expect.

To lower T_c one removes oxygen from the chain sites, and, as expected, this lowers the chain-related conductivity, $\sigma_{1b}(\omega)-\sigma_{1a}(\omega)$, shown in the inset to Fig. 1(a). $\sigma_{1b}-\sigma_{1a}$ is the conductivity of the chains plus any conductivity deriving from plane-chain interactions, assuming the anisotropy of the pure plane conductivity is relatively small. We emphasize that it is the superposition of the ~2000-cm^{-1} peak in $\sigma_{1b}-\sigma_{1a}$ on σ_{1a} which gives the broad local minimum near 500 cm^{-1} in σ_{1b}. The presence of a sharp minimum at ~550 cm^{-1} in $\sigma_{1b}-\sigma_{1a}$ does not significantly affect the shape of σ_{1b}.

Presumably both the emptying of chains and the increase in disorder on the chains contribute to the reduction in $\sigma_{1b}(\omega)-\sigma_{1a}(\omega)$. The planes, on the other hand, remain intact as T_c is reduced, and the reduction in the CuO_2-plane conductivity with decreasing T_c reflects a decrease in doping level. By integrating $\sigma_{1a}(\omega)$ up to 5000 cm^{-1}, and assuming a band mass of 1, we estimate the concentration of holes in each plane to be 0.25 hole per CuO_2 formula unit for $T_c \simeq 93$ K, 0.2 hole per CuO_2 for $T_c \simeq 82$ K, and 0.15 hole per CuO_2 for $T_c \simeq 56$ K.

Inasmuch as CuO_2 *planes* are the essential element for high-T_c superconductivity in cuprates, we will concentrate on their properties for the remainder of this Letter. This response is measured directly by $\sigma_{1a}(\omega)$. Since there is no structure in $\sigma_{1a}(\omega)$ in the normal state, and thus no clear way to divide $\sigma_{1a}(\omega)$ into separate midinfrared and Drude terms, it is natural to analyze this conductivity in terms of a frequency-dependent scattering rate and mass [3,4] at low frequency. The results of this analysis are shown in Fig. 2, where the renormalized scattering rate $1/\tau^*$ and the effective-mass enhancement m^* are plotted as a function of frequency. For each sample the scattering rate is roughly linear in ω with slopes of ~0.6, 1.0, and 1.5 for $T_c=93$, 82, and 56 K, respectively. The $T_c=93$ K data are very similar to our previously published values [11]. These data are all in agreement with our much earlier conclusion that the scattering rate is "of order $kT+\hbar\omega$, suggesting ... that $YBa_2Cu_3O_7$ is at the edge of the regime in which a Fermi-liquid theory

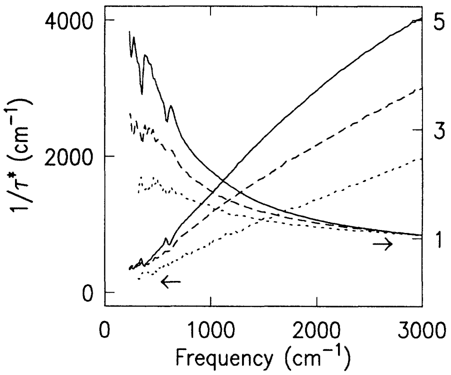

FIG. 2. The renormalized scattering rate $1/\tau^*$ and effective-mass enhancement m^* vs frequency, determined from the CuO_2-plane conductivities shown in Fig. 1(b), using the values $\varepsilon_\infty=4.0$ and $\omega_p=15500$, 16000, and 16500 cm^{-1} for $T_c=56$ K (solid), 82 K (dashed), and 93 K (dotted), respectively. For each T_c, $1/\tau^*$ is nearly linear in ω, with a slope of ~1.5, 1.0, and 0.6 for $T_c=56$, 82, and 93 K, respectively.

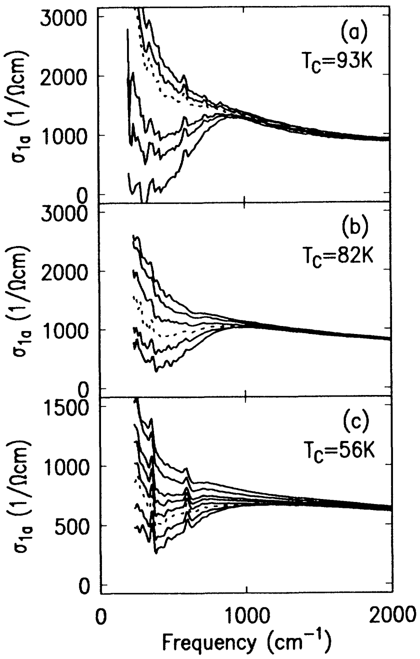

FIG. 3. CuO_2 plane conductivity $\sigma_{1a}(\omega)$ vs frequency for various temperatures T in both the normal and superconducting states. (a) $T_c=93$ K at, from top to bottom, $T=120$, 100, 90 (dashed), 80, 70, and 30 K. (b) $T_c=82$ K at $T=150$, 120, 90, 80 (dashed), 70, and 20 K. (c) $T_c=56$ K at $T=200$, 150, 120, 100, 80, 60 (dashed), 50, and 20 K. Note the persistence of the ~500-cm^{-1} threshold above T_c (above the dashed curve).

is defined" [8].

We now turn our attention to the temperature dependence of $\sigma_{1a}(\omega)$ above and below T_c. As discussed below, one finds that unusual aspects of the temperature dependence become accentuated as T_c (doping) is reduced.

For $T_c\simeq93$ K samples, the conductivity in the 200-500-cm^{-1} range has very little temperature dependence above ~110 K or below ~50 K. Between about 100 and 50 K, however, most of the conductivity in this frequency range drops out, as shown in Fig. 3(a), leaving a sharp absorption threshold at ~500 cm^{-1}. Within present experimental uncertainties, which include both measurement accuracy and sample-surface quality considerations, one can say that for $\omega\lesssim500$ cm^{-1} about (90–100)% of the normal-state conductivity is gone at low temperature for $T_c\simeq93$ K crystals. In this sense the data are consistent with an energy gap, and are certainly highly suggestive of a superconducting pair excitation threshold of 500 cm^{-1}.

For the reduced T_c samples one observes [Figs. 3(b) and 3(c)] roughly similar behavior in that a threshold at ~500 cm^{-1} forms as the temperature is reduced. One finds that considerably more conductivity remains at low temperature than for the $T_c\simeq93$ K crystal. For the $T_c\simeq82$ K sample about 70% of the normal-state conductivity is absent at low ω and T, while for the $T_c\simeq56$ K crystal about 50% is gone. It is not clear whether this finite conductivity within the gap region is intrinsic (i.e., indicative of gaplessness [21]), or if it is due to poor sample-surface quality. We observed that careful polishing increased the reflectivity of the reduced T_c samples. This suggests the latter explanation.

In Fig. 4(a) we plot the temperature dependence of $\sigma_{1a}(500\text{ cm}^{-1})$ as a function of T/T_c for three different values of T_c. For each sample, one observes that the temperature dependence is most rapid in the region just below T_c [10–15]. This observation establishes an experimental basis for relating the 500-cm^{-1} threshold to the transition to the superconducting state. One observes in addition, however, that there is also temperature dependence above T_c which becomes increasingly significant as T_c is reduced. This reflects the persistence of the ~500-cm^{-1} threshold above T_c (Fig. 3). For the $T_c\simeq56$ K crystal, we have plotted $\sigma_{1a}(\omega)$ in the gap region as a function of temperature together with the relevant NMR Korringa products from similar reduced T_c samples [23,24]. The relationship between $\sigma_1(\omega)$ and $1/T_1T$ is discussed in Ref. [2] and has been discussed by us previously for cuprate superconductors [13]. The observation that both the infrared and NMR data follow the same temperature dependence is remarkable and suggests that the observed behavior reflects an intrinsic temperature dependence associated with both charge and spin degrees of freedom. Both sets of data can be interpreted in terms of a tendency toward pair formation above T_c [6,17,18], or, in particular, the opening of a spin gap [25], which can affect the charge response, $\sigma(\omega)$, due to interactions between charge and spin excitations.

In conclusion, we have studied the infrared response of

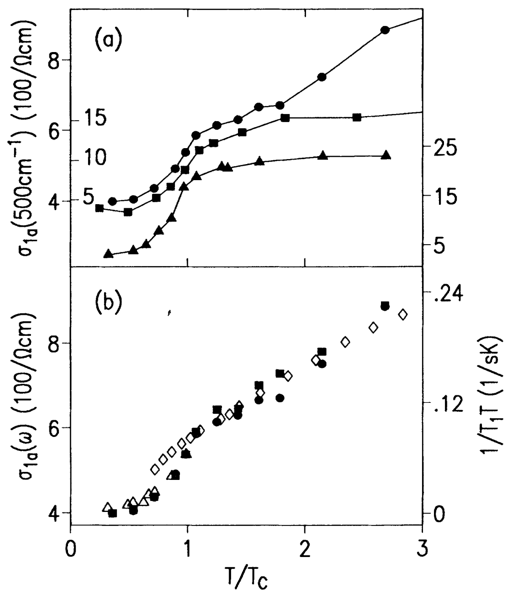

FIG. 4. (a) CuO_2-plane conductivity at 500 cm^{-1}, $\sigma_{1a}(500\,\mathrm{cm}^{-1})$, vs T/T_c for $T_c = 56$ K (circles and left outer scale), 82 K (squares and left inner scale), and 93 K (triangles and right scale, see Ref. [22]). The lines are a guide to the eye. Note the change in slope at T_c and the strong temperature dependence just below T_c. (b) Comparison between the CuO_2-plane conductivity $\sigma_{1a}(\omega)$ in the gap region [$\omega = 250$ cm^{-1} (squares) and 500 cm^{-1} (circles)] and the NMR Korringa product, $1/T_1T$, for ^{17}O in a $T_c = 62$ K sample (open diamonds, see Ref. [23]) and ^{63}Cu in a $T_c = 59$ K sample (open triangles, see Ref. [24]). $\sigma_{1a}(250\,\mathrm{cm}^{-1})$ is multiplied by 0.456 and shifted by 178 $\Omega^{-1}\mathrm{cm}^{-1}$. The ^{63}Cu data are multiplied by 4.35×10^{-3}.

a sequence of untwinned crystals $YBa_2Cu_3O_{7-y}$ with T_c varying from 93 to 56 K. For the $\mathbf{E} \parallel \hat{\mathbf{b}}$ polarization there is clear evidence for a strong midinfrared contribution to $\sigma(\omega)$ associated with the CuO chains. For the $\mathbf{E} \parallel \hat{\mathbf{a}}$ polarization, which measures just the conductivity of the CuO_2 planes, there is no midinfrared structure at room temperature. One finds instead that the conductivity decreases smoothly with frequency, and much more slowly than a conventional Drude term. In the superconducting state a threshold at ~ 500 cm^{-1} is observed for all samples. Taken together the infrared and NMR data strongly suggest a tendency toward pair formation (opening of a spin gap), in the normal state, which becomes increasingly significant as hole doping (T_c) is reduced in $YBa_2Cu_3O_{7-y}$. These results are, of course, profoundly different from expectations based on a conventional (BCS-like) picture.

The authors acknowledge valuable conversations with P. W. Anderson, H. Fukuyama, D. H. Lee, T. M. Rice, S. Sachdev, and M. Takigawa.

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