Normal-state gap transition in Cu-O superconductors

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The reflectivity spectra of $La_{2-x}Sr_xCuO_4$ for $x=0$ and 0.175, and $Ba_2YCu_3O_{9-\delta}$ ($\delta\sim 2.1$) were measured over a broad frequency range, from 0.005 to 3 eV. In the normal state of these compounds the reflectivity is temperature independent and significantly smaller than expected from the Drude model. We describe a dielectric function which reproduces the main features of the spectra by supplementing the Drude contribution with a strong transition across a gap.

The discovery of superconductivity at high temperatures in the La-Ba-Cu-O chemical system[1] has led to an intense search for the underlying mechanism. To shed light on possible mechanisms we have studied the optical reflectivity over a broad range of frequency in the normal state of $La_{2-x}Sr_xCuO_4$ for $x=0$ and 0.175, and $Ba_2YCu_3O_{9-\delta}$ (for $\delta\sim 2.1$). We have found that optical transitions appear in the $La_{2-x}Sr_xCuO_4$ compounds upon Sr doping which cannot be described by the nearly-free-electron model. Instead, most of the electronic oscillator strength resides in a transition across a gap of frequency ~ 0.5 eV. The results for $Ba_2YCu_3O_{9-\delta}$ are analogous to the metallic phase of the $La_{2-x}Sr_xCuO_4$ compounds, except that the scale of frequency is shifted upwards by a factor ~ 1.5.

The samples for reflectivity measurements were ceramic powders pressed into pellet form. The technique for preparation of these samples is described elsewhere.[2,3] The pellets were polished using oil or alcohol as lubricants in order to minimize exposure of the surface to water. Spectra from 0.005–3.0 eV were obtained by assembling data from three instruments: a Michelson interferometer ($\omega < 0.05$ eV), a Perkin-Elmer Fourier-transform infrared spectrometer (0.05–0.5 eV), and a grating spectrometer ($\omega > 0.5$ eV). Composite reflectivity spectra for La_2CuO_4 and $La_{1.825}Sr_{0.125}CuO_4$ are plotted in Fig. 1, and for $Ba_2YCu_3O_{9-\delta}$ in Fig. 3. The spectra show reflectivity R as a function of photon energy $\hbar\omega$, and were recorded with the samples at room temperature for $\omega > 0.05$ eV, and at 100 K for $\omega < 0.05$ eV.

The starting point for analyzing R of $La_{1.825}Sr_{0.175}CuO_4$ is the Drude model for the dielectric function:

$$\tilde{\epsilon}(\omega)=\epsilon_\infty-\frac{\omega_p^2}{\omega(\omega+i\gamma)}\ , \tag{1}$$

where ω_p is the plasma frequency, γ is the reciprocal of the transport relaxation time, and ϵ_∞ is the background dielectric constant associated with interband transitions at $\omega \gg \omega_p$. Assuming that γ is frequency independent its value can be determined from the relation $\gamma=\omega_p^2/4\pi\sigma_0$, where σ_0 is the conductivity at $\omega=0$, measured to be $\sim 10^3\ \Omega^{-1}\text{cm}^{-1}$ at room temperature.[4] The best fit obtainable by varying the three parameters in Eq. (1), and assuming that γ is independent of frequency, is compared with the experimentally determined reflectivity in Fig. 2(a). The theoretical curve corresponds to Drude parameters $\omega_p=2.0$ eV, $\gamma=0.50$ eV, and $\epsilon_\infty=4.5$. The reflectivity rise, or plasma edge, occurs near 0.9 eV, which is the screened plasma frequency, $\omega_{ps}\equiv\omega_p/\sqrt{\epsilon_\infty}$.

As the comparison in Fig. 2(a) makes clear, R for $\omega < \omega_{ps}$ is much smaller than expected. Another problem is that, if γ were directly related to σ_0, a strongly temperature dependent R would be required since $\sigma_0(T_c)/\sigma(300\ \text{K})$ is ~ 3.[4] Our measurements show less than a few percent variation in R as T was varied above T_c. There are several possible explanations for this low R, two of which concern experimental difficulties. One factor is the granularity of the pressed pellet samples. We believe that this morphology is unimportant because an optical study of a pressed pellet and a single-crystal sample of $BaPb_{1-x}Bi_xO_3$ showed the same spectra for frequencies below $\sim 10^4\ \text{cm}^{-1}$ (1.2 eV).[5] A more serious difficulty is the high degree of anisotropy predicted for $La_{2-x}Sr_xCuO_4$ by band-structure calculations,[6,7] a complication not encountered in the optical studies of cubic

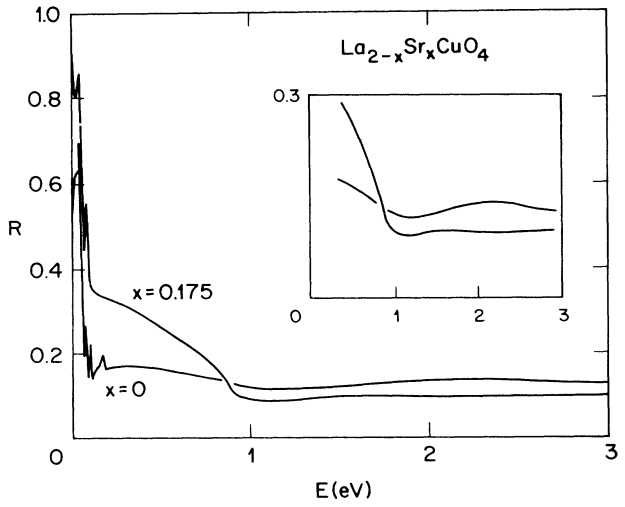

FIG. 1. Reflectivity spectrum of $La_{2-x}Sr_xCuO_4$ for $x=0$ and 0.175, from 0.005 to 3.0 eV. The inset shows the dip and subsequent rise in reflectivity at ~ 0.9 eV.

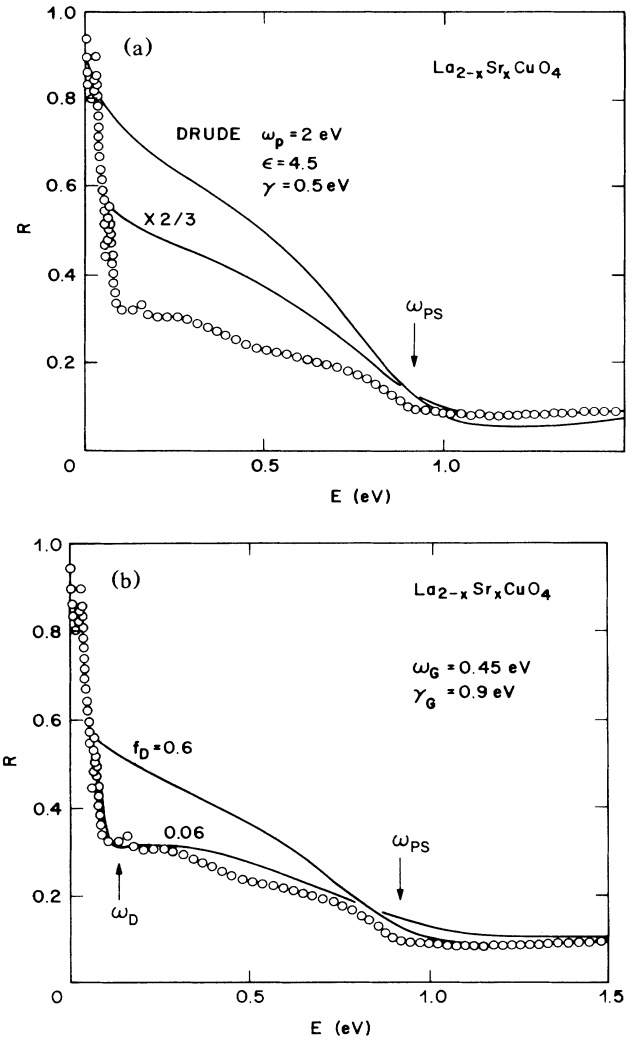

FIG. 2. (a) Open circles show the spectrum of $La_{1.825}Sr_{0.175}CuO_4$ from 0.005 to 1.5 eV, solid lines show theoretical curves obtained from the Drude model, Eq. (1). The lower spectrum was scaled by $\frac{2}{3}$ to simulate the effect of optical anisotropy. (b) The reflectivity of $La_{1.825}Sr_{0.175}CuO_4$ is shown again as open circles. Solid lines are reflectivity spectra obtained by supplementing the Drude contribution to $\tilde{\epsilon}(\omega)$ with a transition across a gap of energy 0.45 and width 0.9 eV. The two curves show reflectivity for different oscillator strengths of the Drude term.

$BaPb_{1-x}Bi_xO_3$. Optical anisotropy will certainly lead to differences between the reflectivity of single and polycrystalline samples.

To estimate the effect of anisotropy on R we assume a dielectric tensor for $La_{2-x}Sr_xCuO_4$ of the form appropriate for a uniaxial crystal, with the c-axis component $\epsilon_{\parallel}$ equal to ϵ_∞, and $\epsilon_\perp$ given by Eq. (1). We find that the dependence of R on grain orientation is described approximately by the relation $R = R_{\parallel} + (R_\perp - R_{\parallel})\sin^2\theta$ where θ is the angle between the electric field vector $\mathbf{E}$ and the c axis, and $R_{\parallel}$ and $R_\perp$ are the normal incidence reflectivities for $\theta = 0$ and $\pi/2$, respectively. If the wavelength λ is less than the typical dimension of a crystallite d, then the effective R can be approximated by averaging over orientation. In this limit $R \simeq R_{\parallel} + (R_\perp - R_{\parallel})\langle\sin^2\theta\rangle$ and $\langle\sin^2\theta\rangle = \frac{2}{3}$. For $\lambda > d$ the effective medium approximation becomes appropriate and one may think of regions with $\mathbf{E}\|\hat{\mathbf{c}}$ being shunted by grains with $\mathbf{E}$ more nearly parallel to the conducting plane. In this regime the effect of anisotropy is diminished compared to the short wavelength limit. We therefore regard the factor $\frac{2}{3}$ as an upper bound on the reduction in R due to polycrystallinity. In Fig. 2(a) we have plotted the reflectivity spectrum of the model uniaxial crystal described above, scaled by $\frac{2}{3}$ to simulate the effect of anisotropy. It is apparent that the deviation from free-electron behavior is still quite large. We have not carried out a Kramers-Kronig analysis of R because such a determination of $\tilde{\epsilon}$ would be substantially in error without an inclusion of the complicated effects of anisotropy. Instead we have fit R by a phenomenological form for $\tilde{\epsilon}(\omega)$ similar to that suggested by Tajima *et al.*[5] in their study of $BaPb_{1-x}Bi_xO_3$.

We assume that a fraction f_G of the total electronic oscillator strength is consumed in an optically allowed transition across a gap. The dielectric function then has the form

$$\tilde{\epsilon}(\omega) = \epsilon_\infty + \omega_p^2 \left(\frac{f_G}{\omega_G^2 - \omega^2 - i\omega\gamma_G} - \frac{1 - f_G}{\omega(\omega + i\gamma_D)} \right), \quad (2)$$

where ω_G is the gap frequency and γ_G is the linewidth of the transition. In Fig. 2(b) R derived from Eq. (2) is plotted for two values of $f_D \equiv 1 - f_G$, with $\omega_p = 2$ eV as before, and ω_G and γ_G fixed at 0.45 and 0.90 eV, respectively. The theoretical curves have been multiplied by $\frac{2}{3}$ as an approximate anisotropy correction. As the spectra illustrate, shifting oscillator strength to the gap transition reduces R for $\omega < \omega_{ps}$ while the position of the edge remains fixed. In addition, as f_D decreases the true plasma edge in R, due to the Drude resonance at $\omega = 0$, shifts downwards in frequency to

$$\omega_D \sim \omega_p \left(\frac{f_D}{\epsilon_\infty + f_G\omega_p^2/\omega_G^2} \right)^{1/2}.$$

The best fit to R of $La_{1.825}Sr_{1.75}CuO_4$ corresponds to $f_D \equiv 0.06$, and $\omega_D \sim 0.1$ eV. Since this ω_D is in the energy regime of lattice vibrations, it may be additionally screened by the polarizability due to optic phonons. While the spectrum obtained from Eq. (2) reproduces the main features of the data, there remains some deviation. Particularly noticeable is that the large γ_G required to fit R for $\omega < \omega_{ps}$ damps the abrupt rise seen near ω_{ps}. This suggests that the absorption associated with the gap transition is not well described by a single Lorentzian.

Most of the electronic oscillator strength which appears with the addition of Sr is in the gap transition. We can estimate the number of electrons which contribute to the change in R due to Sr from the sum rule on ϵ_2. An ω_p of 2 eV implies that $n = 2.5\times10^{21}$ cm$^{-3}(m^*/m)$, which is equal to the Sr concentration of $\sim 2\times10^{21}$ cm^{-3} if $m^*/m = 0.8$. Finally, we suggest that the gap transition should be directly observable in transmission experiments on thin films. Using our fitting parameters we predict a

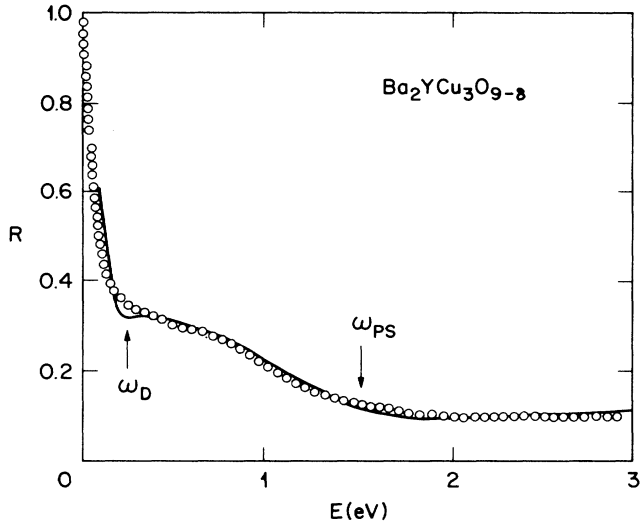

FIG. 3. The reflectivity spectrum of $Ba_2YCu_3O_{9-\delta}$, for $\delta \sim 2.1$, from 0.005 to 3.0 eV, is plotted as open circles. The solid line shows the reflectivity calculated from Eq. (2) of the text, with parameters $\omega_p = 3.0$ eV, $\epsilon_\infty = 4.5$, $\omega_G = 0.65$ eV, $\gamma_G = 1.3$ eV, $f_D = 0.08$, and $\gamma_D = 0.04$ eV.

(T-independent) absorption band centered near 0.5 eV with peak absorption coefficient of $\sim 10^5$ cm^{-1}.

The spectrum of $Ba_2YCu_3O_{9-\delta}$ is plotted in Fig. 3, together with the fit obtained from Eq. (2), again corrected for anisotropy. The optical properties of this compound are similar to $La_{2-x}Sr_xCuO_4$ in that R for $\omega < 1.5$ eV is much lower than expected from the Drude model, and essentially independent of temperature above T_c. Taking into account the optical properties of $BaPb_{1-x}Bi_xO_3$ it appears that this behavior is a general property of superconducting oxides. The curve generated from Eq. (2) yields a good fit for parameters $\omega_p = 3$ eV, $\epsilon_\infty = 4.5$, $f_G = 0.08$, $\omega_G = 0.65$ eV, and $\gamma_G = 1.3$ eV. The change in parameters, compared with $La_{1.825}Sr_{0.175}CuO_4$ corresponds to an increase in energy scale by a factor ~ 1.5.

We offer the following speculations concerning the reflectivity anomaly in the high-T_c oxides. Although the band structure of La_2CuO_4 suggests that it should be a metal,[6,7] there is a gap at E_F due to the short-range Coulomb interaction. It has been predicted that excitations across this gap, associated with charge transfer between Cu and O neighbors, dominate $\sigma(\omega)$ for $\omega \sim 1$ eV and contribute to the attractive interaction between electrons in the metallic phase.[8] The transition we have observed is consistent with this prediction. It has also been conjectured[9] that the Coulomb interaction correlates electrons into singlet pairs, and that the correlation persists

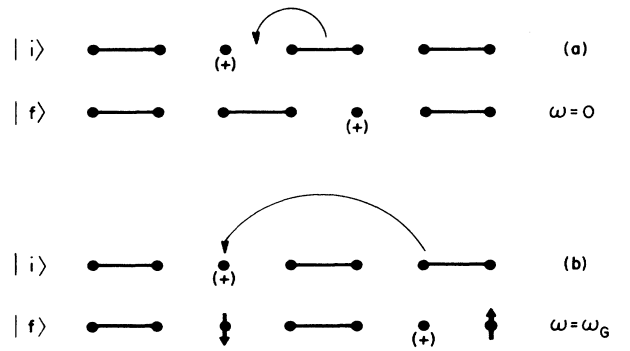

FIG. 4. Dynamical processes which could contribute to $\sigma(\omega)$ in a highly correlated band. The illustration is one-dimensional for the sake of simplicity. Electrons are coupled into singlet pairs or (bonds), represented by lines. At slightly less than half-filling, there are a few unoccupied sites, indicated by (+). Charge fluctuations may occur near $\omega = 0$ by (a) bond hopping, or at $\omega = \omega_G$ by (b) bond breaking.

when carriers are introduced by doping. If this is correct, the ground state for $x > 0$ consists of unoccupied sites in a sea of "bonds." The analogy[10] of these unoccupied sites to charged solitons in polyacetylene[11,12] suggests two types of dynamical processes. Charge motion at $\omega = 0$ might take place by hopping of bonds, as illustrated in Fig. 4(a). At higher frequency, displacement of charge could occur by bond breaking, as shown in Fig. 4(b). In this picture the Drude and gap terms in Eq. (2) correspond to the processes shown in Figs. 4(a) and 4(b), respectively. The ratio of oscillator strengths, which is ~ 15, would then reflect the ratio of effective masses for conduction versus optical processes. The model also predicts that the two types of absorption vary as x, since both processes require unoccupied sites.

In conclusion, we have modeled $\tilde{\epsilon}(\omega)$ of two high-T_c superconductors by shifting most of the oscillator strength from the Drude contribution to a gap transition. We can reproduce the main features of the spectra with parameters which increase by the factor ~ 1.5 from $La_{1.825}Sr_{0.175}CuO_4$ to $Ba_2YCu_3O_{9-\delta}$. Finally, we have discussed a physical picture of charge fluctuations in these compounds in terms of recent theoretical models.

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