Title
Growth of the optical conductivity in the Cu-O planes

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In spite of much study, little is understood about either the normal-state excitation spectrum of the high-$T_c$ compounds,1,2 or the manner in which this spectrum develops from the insulating phase as a function of doping. We address these issues here in an optical-reflectivity study of $n$-type $\text{Pr}_{2-x}\text{Ce}_x\text{Cu}_4\text{O}_{4-x}$ for $0 < x < 0.2$ and $\delta = 0$. At $x = 0$, $\text{Pr}_{2-x}\text{Ce}_x\text{Cu}_4\text{O}_{4-x}$ is an insulator with negligible absorption below the charge-transfer gap ($\omega \approx 1.5$ eV). Our study indicates that light doping ($x \approx 0.04$) gives rise to an unexpectedly large growth of spectral weight in the mid-infrared frequency range ($0.1 \leq \omega \leq 0.5$ eV), and an accompanying decrease in the charge-transfer band. Further doping ($0.04 < x < 0.2$) leads to an $x$-dependent increase in absorption at low frequencies ($\omega < 0.1$ eV), but causes little change in the mid-infrared or charge-transfer contributions. Notably, similar behavior has also been observed recently in $p$-type $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-x}$,3 indicating a qualitative particle-hole symmetry associated with the doping process in high-$T_c$ cuprates. These optical results appear to be inconsistent with standard charge-transfer insulator models.

The optical measurements reported in this paper were performed on single crystals of $T'$-phase $\text{Pr}_{2-x}\text{Ce}_x\text{Cu}_4\text{O}_{4-x}$ grown in Pt crucibles with no after-synthesis polish. $\text{Pr}_6\text{O}_{11}$, $\text{CeO}_2$, and $\text{CuO}$ powders were mixed in a concentration ratio of $\text{Pr}:\text{Ce}:\text{Cu} = 1-x:x:2.8$, then heated above the peritectic melting point ($\sim 1275^\circ$C for $\text{Pr}_2\text{Cu}_3\text{O}_{4-x}$, slowly cooled down to the eutectic point ($\sim 1030^\circ$C for $\text{Pr}_2\text{Cu}_3\text{O}_{4-x}$), and finally quenched to room temperature. Large crystals (as large as $3 \times 3 \times 0.1$ cm$^3$) with flat and shiny surfaces were grown on the surface of the flux. After they were mechanically removed from the flux, the crystals were annealed at $875^\circ$C with Ar-gas flow for 5 h and then furnace cooled to room temperature. Magnetic measurements of crystals$^5$ in the concentration range $x \leq 0.12$ indicated that these samples were antiferromagnetic with sharp transition widths $< 10$ K. The $x = 0.2$ crystal was nonmagnetic and nonsuperconducting (the superconducting phase occurs between $0.14 < x < 0.18$).$^5$ The Ce concentrations in these crystals were determined from lattice-parameter measurements by x-ray diffraction, and are accurate to $\pm 5\%$. Furthermore, the nominal O concentration was determined from neutron-scattering studies to be 4 oxygen atoms/unit cell,$^6$ and consequently no carriers are expected to arise from oxygen vacancies (i.e., $\delta = 0$). Pt doping from the crucible is believed to be negligible because impurity contributions are not apparent in the insulating ($x = 0$) crystals. In-plane thermoelectric power in all crystals were measured to be negative at room temperature, indicating electronic carriers. Reflectivity spectra from 100 to 20000 cm$^{-1}$ (12.5 meV to 2.5 eV) were performed close to a normal-incidence configuration using a rapid scanning interferometer. Mirror optics were used to focus the modulated, collimated light beam from the spectrometer onto the sample, and then onto a variety of detectors covering the above frequency range.

Figure 1 shows the frequency-dependent reflectivity $R$...
between 100 and 20000 cm$^{-1}$ for a series of Ce concentrations $x$. The most notable feature of these reflectivity spectra is the transition between insulating and metallic behavior that occurs with increased Ce substitution. The frequency-dependent $R$ of undoped $Pr_2CuO_4-x$ ($x = 0$) is characteristic of an insulator, exhibiting a response dominated at low frequencies by phonon peaks, and at high frequencies by a peak in reflectivity near 12000 cm$^{-1}$ (1.5 eV). The latter peak, observed in the insulating phases of all high-$T_c$ cuprates, has been attributed to the onset of Cu-O charge-transfer excitations. Upon substituting Ce$^{4+}$ for Pr$^{3+}$ ($x > 0$), the appearance of metallic behavior is betrayed by two changes: a rapid increase in the low-frequency reflectivity due to absorption by electronic process, and the development of a plasma edge near 1 eV (8000 cm$^{-1}$). Notably, the changes in $R$ shown in Fig. 1 are consistent with samples that are homogeneously doped on a macroscopic length scale. For example, a Kramers-Kronig analysis of these data demonstrates that the phonons in $Pr_{2-x}Ce_xCuO_4-y$ maintain roughly constant oscillator strengths with doping. By contrast, in samples composed of mixed insulating (with fraction $f$) and metallic (with fraction $1-f$) phases, the $R$ would be given, within the effective-medium approximation, by $R(\omega) = f R_{ins}(\omega) + (1-f) R_{met}(\omega)$. In conductivity, $\sigma$, this mixed-phase response would give rise to an anomalous variation in phonon intensities with doping.

The influence of doping on the spectral response of $Pr_{2-x}Ce_xCuO_4-y$ may be further examined by considering the optical conductivity, $\sigma$, by Kramers-Kronig transformations of the reflectivity data in Fig. 1. The $\sigma$ of the insulating phase ($x = 0$) exhibits phonons at low frequencies, a broad gap to electronic excitations, and an absorption edge near 1.5 eV. The absence of electronic absorption below this gap edge indicates negligible doping from O vacancies or other electrically active impurities. Light doping ($x = 0.04$ electrons/unit cell) produces a large increase in low-frequency spectral weight, as well as a substantial decrease in spectral weight above the charge-transfer gap ($\omega > 1.5$ eV). The change in the optical conductivity is more clearly illustrated in Fig. 3, which shows the incremental changes in conductivity $\sigma_x - \sigma_{x-}$ that occur between successive levels of doping. Here, the incremental change in conductivity,

FIG. 1. Room-temperature (300 K) frequency-dependent reflectivity of $Pr_{2-x}Ce_xCuO_4-y$ for a series of Ce concentrations, $x$. The incident light was unpolarized in the $a,b$ plane. Note that the frequency is plotted on a logarithmic scale.

FIG. 2. Room-temperature (300 K) frequency-dependent conductivity, $\sigma(\omega)$, of $Pr_{2-x}Ce_xCuO_4-y$ for a series of Ce concentrations $x$. These spectra were obtained from Kramers-Kronig transformations of the reflectivity spectra in Fig. 1.

FIG. 3. (a) Incremental change in the conductivity $[\sigma_x - \sigma_{x-}]$, where $\sigma_x = \sigma(x)$, across the metal-insulator transition, i.e., between the insulating ($x = 0$) and most lightly doped ($x = 0.04$) phases. (b) Incremental change in the conductivity $[\sigma_x - \sigma_{x-}$] between metallic phases, including $\sigma(x = 0.12) - \sigma(x = 0.04)$ and $\sigma(x = 0.2) - \sigma(x = 0.12)$. 

FIG. 4. (a) INSULATOR TO "METAL"

(b) "METAL" TO "METAL"
\( \sigma_i - \sigma_j \), is defined so that \( \sigma_i - \sigma_j = \sigma(x_i) - \sigma(x_j) \). The transfer of spectral weight as \( x \) changes across the metal-insulator transition is evident in Fig. 3(a), which plots the optical conductivity difference, \( \sigma_i - \sigma_j \), between crystals with \( x = 0.04 \) and \( x = 0 \). Notably, increases in \( \sigma \) below 1.5 eV consist of two parts: a contribution centered at \( \omega = 0 \), presumably arising from mobile carriers, and a broad mid-infrared absorption band centered near 0.4 eV (\( \sim 3000 \text{ cm}^{-1} \)). Further doping (\( x \geq 0.04 \)), as shown in Figs. 2 and 3(b), leads to a continued increase in the low-frequency mobile carrier contribution, but to little additional change in the mid-infrared and charge-transfer bands. These differences in growth rate distinguish between the mobile carriers and the mid-infrared absorption even when the two bands are not spectroscopically resolved. The presence of this two-component \( \sigma \), and its behavior with doping, is similar to that observed in \( p \)-type high-\( T_c \) compounds \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) (Ref. 8) and \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-\delta \). \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-\delta \). \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-\delta \)

The doping dependence of the total integrated spectral weight below the charge-transfer band edge at 1.5 eV is shown for both \( \text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4-\delta \) (triangles) and \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-\delta \) (solid circles) in Fig. 4. The integrated spectral weight, or normalized effective carrier density \( N_{\text{eff}}(\omega) \), is defined by

\[
N_{\text{eff}}(\omega) = \frac{2mV_{\text{cell}}}{\pi \varepsilon^2} \int_0^\infty \sigma(\omega')d\omega',
\]

where \( V_{\text{cell}} \) is the unit-cell volume divided by 2 (for the two \( \text{Cu} \) atoms per unit cell), \( m \) is the free electron mass, and \( e \) is the electron charge. The dashed lines are the weight calculated by assuming that each acceptor or donor contributes one carrier with an effective mass \( m^* \) equal to the free electron mass \( m_e \). It is clear from Fig. 4 that the spectral weight below 1.5 eV is larger than that expected from the carrier concentration alone, suggesting that some charge-transfer spectral weight has shifted to low frequencies as a function of doping. Significantly, the integrated spectral weight below 4 eV in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-\delta \) was found to be approximately independent of doping,\(^3\) also indicating that spectral weight is redistributed to low frequencies from the charge-transfer band with doping. As illustrated in both Figs. 3(a) and 4, the redistribution of weight in \( \text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4-\delta \) occurs at very low doping (\( x \leq 0.04 \)), while additional increases in spectral weight for \( x > 0.04 \) are consistent with increases in the donor concentration alone [Fig. 3(b)]. Therefore, these data suggest two consequences of doping: first, the addition of \( x \) mobile carriers into a Drude-like band centered at \( \omega = 0 \), and second, an abrupt shifting of spectral weight from the charge-transfer gap to a mid-infrared band near the metal-insulator transition. Furthermore, a comparison of the two sides of Fig. 4 illustrates the qualitative symmetry between electron and hole doping.

The above experimental results are difficult to reconcile with simple models of doping in a charge-transfer insulator, in which one expects a weak dependence of spectral weight in the charge-transfer gap on doping, a spectral weight below the fundamental gap that scales with \( x \), and a prominent particle-hole asymmetry that leads to more low-frequency spectral weight in the hole-doped than in the electron-doped materials. These simple expectations may be understood by first recalling that the \( \text{CuO}_2 \) planes in \( \text{Pr}_2\text{CuO}_4 \) and \( \text{La}_2\text{CuO}_4 \) are believed to contain one hole per \( \text{CuO}_2 \) unit, with the holes residing primarily on the Cu site. These materials are insulating because an energy difference \( \varepsilon_p - \varepsilon_d \) inhibits promotion of a hole from Cu to O orbitals (i.e., charge transfer), and a larger correlation energy \( U \) inhibits double occupancy of a Cu site by holes.

When the \( \text{CuO}_2 \) planes are doped by electrons, as is indicated by room-temperature Hall effect data in \( \text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4-\delta \), the electrons eliminate holes by principally residing on Cu sites. Doping with \( x \) electrons/unit cell is expected to result in two optical processes: (1) The itinerant motion of holes, having relative spectral weight \( x \) (allowed because some Cu sites are now unoccupied); (2) charge-transfer absorption processes, having spectral weight \( (1 - x) \) (reduced from that in the insulator because \( x \) Cu sites no longer contain holes). In contrast, if the \( \text{CuO}_2 \) planes are doped by holes, as is indicated in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-\delta \) by Hall effect data,\(^9\) these carriers must reside on O sites. In this case, it is believed\(^10\) that each hole binds to a Cu spin, forming a local singlet. This binding should give rise to three allowed optical processes: (1) itinerant motion of singlets, having a spectral distribution centered at \( \omega = 0 \) with spectral weight \( x \); (2) unbinding of the O hole from the Cu spin, giving a contribution centered at finite frequency \( \omega_0 - t_d^2/\varepsilon_p - \varepsilon_d < \varepsilon_p - \varepsilon_d \) and also having relative weight \( x \); (3) Cu-O charge-transfer processes, having spectral weight that is only weakly doping dependent (since the number of occupied Cu sites is not changed by hole doping). Quantitative calculations of these effects for a 2\( d \) \( \text{CuO}_2 \) lattice with realistic parameters have not yet been performed. However, a particle-hole asymmetry in the optical properties is expected within the above picture, as may be illustrated by compu-
tation of the optical conductivity for simple Cu-O clusters and by approximate auxiliary boson calculations for infinite lattices.\textsuperscript{11}

It is evident from our data that \(\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4-\delta\) does not evolve with doping in a manner expected of a doped charge-transfer insulator, suggesting that such a simple picture is not adequate for describing these materials. In particular, the anomalously large growth of mid-infrared spectral weight near the metal-insulator transition of \(\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4-\delta\), and the concomitant decrease of weight above the $\sim$1.5 eV gap, is unexpected. This behavior also differs from that observed in \(\text{BaPb}_1-\delta\text{Bi}_2\text{O}_3\) (Ref. 12) and in doped semiconductors\textsuperscript{13} (e.g., Si:P), where the low-frequency spectral weight \(N_{\text{eff}}\) scales linearly with the number of donors. Notably, a recent photoemission study on \(\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4-\delta\) has also concluded that electronic states near the Fermi level in the metallic phases evolve from higher-frequency states found in the insulating phase.\textsuperscript{14} Our results illustrate not only that low-frequency weight in the metallic phases derive specifically from the charge-transfer band in the insulating phase, but also that this transferred weight goes principally into a mid-infrared band as the system is lightly doped.

Note added in proof. Using a first-principles density functional description of the Cu-O plane electronic structure, Hybertsen \textit{et al.}\textsuperscript{15} find that the low-frequency carrier dynamics of the high-$T_c$ cuprates exhibit a remarkable symmetry between electron and holes, in qualitative agreement with the data presented here.

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