In spite of much study, little is understood about either the normal-state excitation spectrum of the high-$T_c$ compounds,\textsuperscript{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 Pr$_{2-x}$Ce$_x$CuO$_{4-\delta}$ for $0 < x \leq 0.2$ and $\delta = 0$. At $x = 0$, Pr$_{2-x}$Ce$_x$CuO$_{4-\delta}$ is an insulator with negligible absorption below the charge-transfer gap ($\omega \sim 1.5$ eV). Our study indicates that light doping ($x \sim 0.04$) 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 ($0.04 < x \leq 0.2$) 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 La$_{2-x}$Sr$_x$CuO$_{4-\delta}$,\textsuperscript{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 Pr$_{2-x}$Ce$_x$CuO$_{4-\delta}$ grown in Pt crucibles with no after-synthesis polish. Pr$_6$O$_{11}$, CeO$_2$, and CuO powders were mixed in a concentration ratio of Pr:Ce:Cu = 1 - $x$:2.8, then heated above the peritectic melting point ($\sim 1275^\circ$C for Pr$_2$CuO$_{4-\delta}$), slowly cooled down to the eutectic point ($\sim 1030^\circ$C for Pr$_2$CuO$_{4-\delta}$), 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\textsuperscript{4} in the concentration range $x \leq 0.12$ indicated that these samples were antiferromagnetic with sharp transition widths $< 10$ K. The $x \sim 0.2$ crystal was nonmagnetic and nonsuperconducting (the superconducting phase occurs between $0.14 \leq x \leq 0.18$).\textsuperscript{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,\textsuperscript{6} and consequently no carriers are expected to arise from oxygen vacancies (i.e., $\delta \sim 0$). 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 20 000 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 \(\text{Pr}_2\text{CuO}_4-\delta\) \((x=0)\) 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 12 000 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.\(^7\) 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 (8 000 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 \(\text{Pr}_2-x\text{Ce}_x\text{CuO}_4-\delta\) 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 \(R(\omega)=fR_{\text{ins}}(\omega)+(1-f)R_{\text{met}}(\omega)\). 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 \(\text{Pr}_2-x\text{Ce}_x\text{CuO}_4-\delta\) may be further examined by considering the optical conductivity, \(\sigma\), in Fig. 2, obtained from a Kramers-Kronig transformation 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 \(\sigma_i-\sigma_f\) that occur between successive levels of doping. Here, the incremental change in conductivity,
\( \sigma_i - \sigma_j \), 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 \( \text{La}_{2-x}\text{Sr}_x\text{Cu}_4\text{O}_{4-\delta} \).

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

\[ \nu_{\text{eff}}(\omega) = \frac{2mV_{\text{cell}}}{\pi e^2} \int_{0}^{\infty} \sigma(\omega')d\omega', \]

where \( V_{\text{cell}} \) is the unit-cell volume divided by 2 (for the two 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 \( \text{La}_{2-x}\text{Sr}_x\text{Cu}_4\text{O}_{4-\delta} \) was found to be approximately independent of doping, 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 \( \text{Pr}_{2-x}\text{Ce}_x\text{Cu}_4\text{O}_{4-\delta} \) 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 \( \text{Cu}_2\text{O}_2 \) planes in \( \text{Pr}_2\text{Cu}_4 \) and \( \text{La}_2\text{Cu}_4 \) are believed to contain one hole per \( \text{Cu}_2\text{O}_2 \) 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 \( \text{Cu}_2\text{O}_2 \) planes are doped by electrons, as is indicated by room-temperature Hall effect data in \( \text{Pr}_{2-x}\text{Ce}_x\text{Cu}_4\text{O}_{4-\delta} \), 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 \( \text{Cu}_2\text{O}_2 \) planes are doped by holes, as is indicated in \( \text{La}_{2-x}\text{Sr}_x\text{Cu}_4\text{O}_{4-\delta} \) by Hall effect data, these carriers must reside on O sites. In this case, the singlet is believed 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 \( \omega_0 \sim \frac{1}{2} \varepsilon_p - \varepsilon_d < \varepsilon_p - \varepsilon_d \) 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 \( 2d \) \( \text{Cu}_2\text{O}_2 \) 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.\(^\text{11}\)

It is evident from our data that Pr\(_{2-x}\)Ce\(_x\)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 Pr\(_{2-x}\)Ce\(_x\)CuO\(_4-\delta\), and the concomitant decreease of weight above the \(-1.5\) eV gap, is unexpected. This behavior also differs from that observed in BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) (Ref. 12) and in doped semiconductors\(^\text{13}\) (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 Nd\(_{2-x}\)Ce\(_x\)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.\(^\text{14}\) 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 et al.\(^\text{15}\) 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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