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Growth of the optical conductivity in the Cu-O planes

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We have studied the development of the optical conductivity as electrons are added to the Cu-O planes in $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ by varying x ($0 \leq x \leq 0.2$). In the metallic phases, contributions to the optical conductivity below 3 eV arise from three sources: mobile carriers, mid-infrared excitations, and charge-transfer excitations. The mobile carrier spectral weight grows roughly linearly with x , while the mid-infrared band appears to evolve at low doping via a transfer of spectral weight from the charge-transfer band. Comparing these results with hole doping in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ indicates an electron-hole symmetry that is not anticipated by standard charge-transfer insulator models.

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 $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ for $0 < x < 0.2$ and $\delta \sim 0$. At $x = 0$, Pr_2CuO_4 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 (i.e., $0.1 \leq \omega \leq 0.5$ 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 $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$,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 $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ grown in Pt crucibles with no after-synthesis polish. Pr_6O_{11} , CeO_2 , and 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 ($\sim 1275^\circ\text{C}$ for $\text{Pr}_2\text{CuO}_{4-\delta}$, slowly cooled down to the eutectic point ($\sim 1030^\circ\text{C}$ for $\text{Pr}_2\text{CuO}_{4-\delta}$), and finally quenched to

room temperature. Large crystals (as large as $3 \times 3 \times 0.1$ cm³) 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°C with Ar-gas flow for 5 h and then furnace cooled to room temperature. Magnetic measurements of crystals⁴ 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 $0.14 \leq x \leq 0.18$).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., $\delta \sim 0$). 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

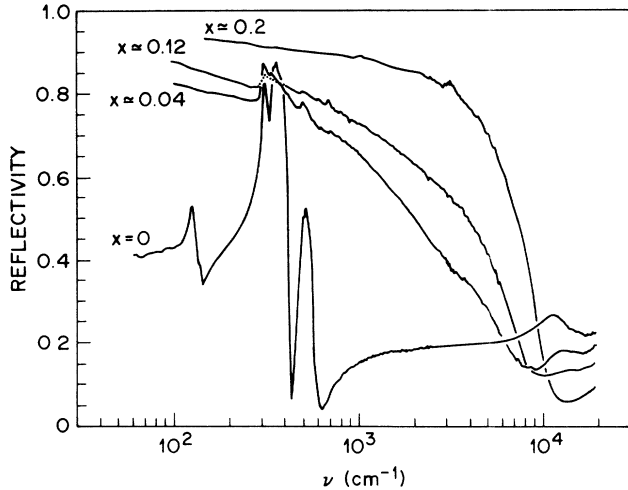


FIG. 1. Room-temperature (300 K) frequency-dependent reflectivity of $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ for a series of Ce concentrations, x . The incident light was unpolarized in the a, b plane. Note that the frequency is plotted on a logarithmic scale.

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 $\text{Pr}_2\text{CuO}_{4-\delta}$ ($x = 0$) 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 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.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 (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-Krönig 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, σ , 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, σ , in Fig. 2, obtained from a Kramers-Krönig transformation of the reflectivity data in Fig. 1. The σ 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

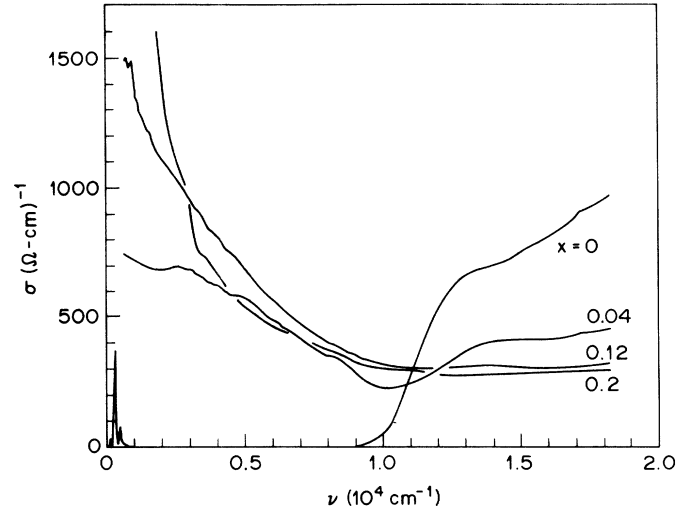


FIG. 2. Room-temperature (300 K) frequency-dependent conductivity, $\sigma(\omega)$, of $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ for a series of Ce concentrations x . These spectra were obtained from Kramers-Krönig transformations of the reflectivity spectra in Fig. 1.

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 $\sigma_i - \sigma_j$ that occur between successive levels of doping. Here, the incremental change in conductivity,

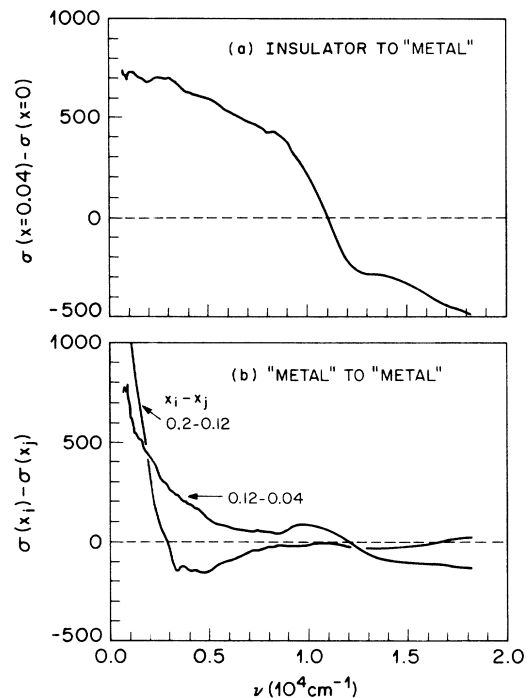


FIG. 3. (a) Incremental change in the conductivity [$\sigma_i - \sigma_j$, where $\sigma_i \equiv \sigma(x_i)$] across the metal-insulator transition, i.e., between the insulating ($x = 0$) and most lightly doped ($x = 0.04$) phases. (b) Incremental change in the conductivity ($\sigma_i - \sigma_j$)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

$\sigma_i - \sigma_j$, is defined so that $\sigma_i - \sigma_j \equiv \sigma(x_i) - \sigma(x_j)$. 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 σ 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 σ , 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 $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$.³

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

$$N_{\text{eff}}(\omega) = \frac{2mV_{\text{cell}}}{\pi e^2} \int_0^\omega \sigma(\omega') d\omega', \quad (1)$$

where V_{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

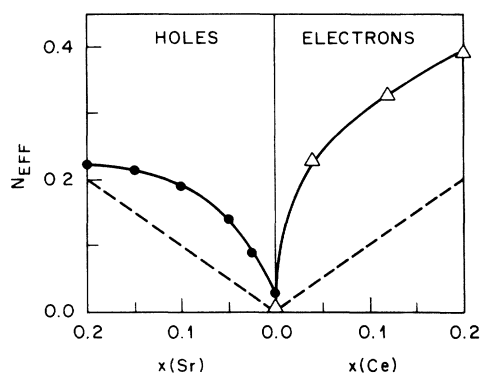


FIG. 4. The total integrated spectral weights of the optical conductivities in both $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ (triangles) and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ (solid circles) up to $\omega = 1.5$ eV, plotted as a function of concentration x . The data from $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ were taken from Ref. 3, while values for $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ were calculated from $\sigma(\omega)$ in Fig. 2 using Eq. (1) in the text. The dashed lines represent the anticipated spectral weight contributions from Ce or Sr substitution alone, assuming $m^* = m_e$ and that each Ce or Sr atom donates 1 mobile carrier/unit cell.

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 CuO_2 planes in Pr_2CuO_4 and La_2CuO_4 are believed to contain one hole per CuO_2 unit, with the holes residing primarily on the Cu site. These materials are insulating because an energy difference $\epsilon_p - \epsilon_d$ 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 CuO_2 planes are doped by electrons, as is indicated by room-temperature Hall effect data in $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$,⁵ 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 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 believed¹⁰ 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 $\omega_0 \sim t_{pd}^2/\epsilon_p - \epsilon_d < \epsilon_p - \epsilon_d$ 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 $2d$ 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.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 ~ 1.5 eV gap, is unexpected. This behavior also differs from that observed in $\text{BaPB}_{1-x}\text{Bi}_x\text{O}_3$ (Ref. 12) and in doped semiconductors¹³ (e.g., Si:P), where the low-frequency spectral weight N_{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.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.*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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