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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 $Pr_{2-x}Ce_xCuO_{4-\delta}$ 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 $La_{2-x}Sr_xCuO_{4-\delta}$ 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 $Pr_{2-x}Ce_xCuO_{4-\delta}$ for $0<x<0.2$ and $\delta \sim 0$. At $x=0$, $Pr_{2-x}Ce_xCuO_{4-\delta}$ 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 (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 $La_{2-x}Sr_xCuO_{4-\delta}$,[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 $Pr_{2-x}Ce_xCuO_{4-\delta}$ grown in Pt crucibles with no after-synthesis polish. Pr_6O_{11}, CeO_2, and CuO powders were mixed in a concentration ratio of Pr:Ce:Cu $= 1-x:x:2.8$, then heated above the peritectic melting point ($\sim 1275\,^\circ$C for $Pr_2CuO_{4-\delta}$, slowly cooled down to the eutectic point ($\sim 1030\,^\circ$C for $Pr_2CuO_{4-\delta}$), and finally quenched to room temperature. Large crystals (as large as $3\times3\times0.1$ 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 °C with Ar-gas flow for 5 h and then furnace cooled to room temperature. Magnetic measurements of crystals[4] 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 ±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

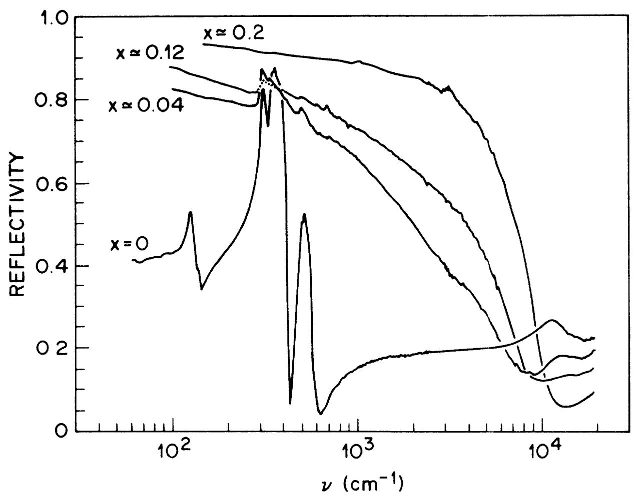

FIG. 1. Room-temperature (300 K) frequency-dependent reflectivity of $Pr_{2-x}Ce_xCuO_{4-\delta}$ for a series of Ce concentrations, x. The incident light was unpolarized in the a,b plane. Note that the frequency is plotted on a logarithmic scale.

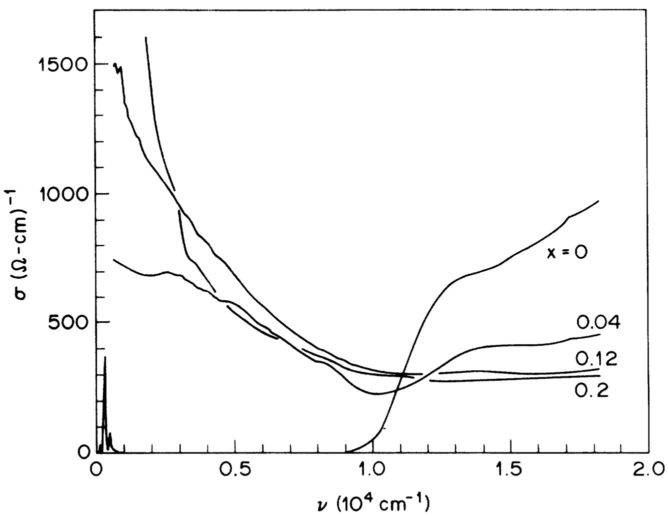

FIG. 2. Room-temperature (300 K) frequency-dependent conductivity, $\sigma(\omega)$, of $Pr_{2-x}Ce_xCuO_{4-\delta}$ for a series of Ce concentrations x. These spectra were obtained from Kramers-Krönig transformations of the reflectivity spectra in Fig. 1.

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 $Pr_2CuO_{4-\delta}$ $(x=0)$ 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 $Pr_{2-x}Ce_xCuO_{4-\delta}$ 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 $Pr_{2-x}Ce_xCuO_{4-\delta}$ 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 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,

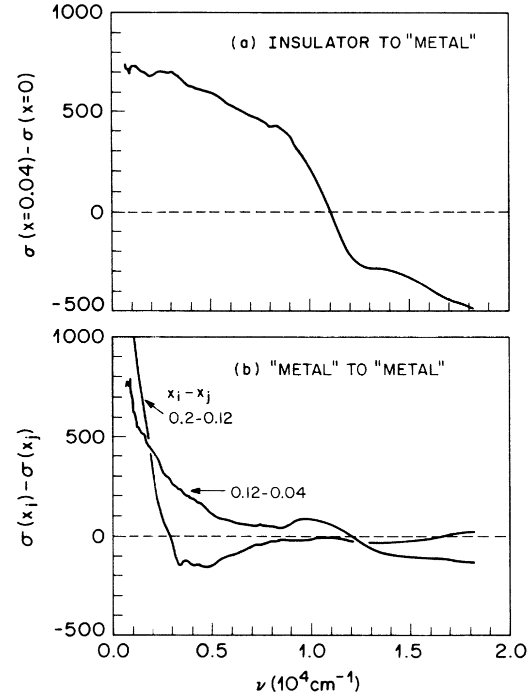

FIG. 3. (a) Incremental change in the conductivity [$\sigma_i-\sigma_j$, where $\sigma_i\equiv\sigma(x_i)$] across the metal-insulator transition, i.e., between the insulating $(x=0)$ and most lightly doped $(x=0.04)$ phases. (b) Incremental change in the conductivity $(\sigma_i-\sigma_j)$ between metallic 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 (~ 3000 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 $YBa_2Cu_3O_{6+x}$ (Ref. 8) and $La_{2-x}Sr_xCuO_{4-\delta}$.[3]

The doping dependence of the total integrated spectral weight below the charge-transfer band edge at 1.5 eV is shown for both $Pr_{2-x}Ce_xCuO_{4-\delta}$ (triangles) and $La_{2-x}Sr_xCuO_{4-\delta}$ (solid circles) in Fig. 4. The integrated spectral weight, or normalized effective carrier density $N_{\mathrm{eff}}(\omega)$, is defined by

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

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 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 $La_{2-x}Sr_x$-$CuO_{4-\delta}$ 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 $Pr_{2-x}Ce_xCuO_{4-\delta}$ 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.

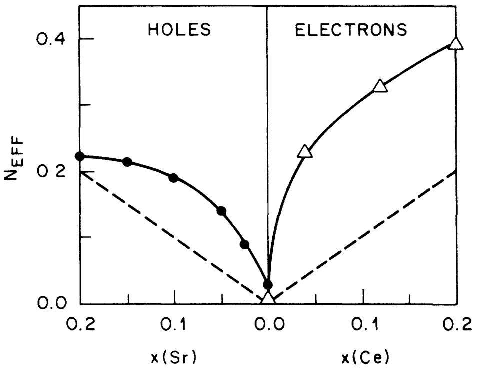

FIG. 4. The total integrated spectral weights of the optical conductivities in both $Pr_{2-x}Ce_xCuO_{4-\delta}$ (triangles) and $La_{2-x}Sr_xCuO_{4-\delta}$ (solid circles) up to $\omega = 1.5$ eV, plotted as a function of concentration x. The data from $La_{2-x}Sr_xCuO_{4-\delta}$ were taken from Ref. 3, while values for $Pr_{2-x}Ce_xCuO_{4-\delta}$ 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.

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 $\varepsilon_p - \varepsilon_d$ 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 CuO_2 planes are doped by electrons, as is indicated by room-temperature Hall effect data in $Pr_{2-x}Ce_xCuO_{4-\delta}$,[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 $La_{2-x}Sr_xCuO_{4-\delta}$ 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 $\omega_0 \sim t_{pd}^2/\varepsilon_p - \varepsilon_d < \varepsilon_p - \varepsilon_d$ 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 $2d$ 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 computation 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 $\mathrm{Pr_{2-x}Ce_xCuO_{4-\delta}}$ 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 $\mathrm{Pr_{2-x}Ce_xCuO_{4-\delta}}$, and the concomitant decrease of weight above the ~1.5 eV gap, is unexpected. This behavior also differs from that observed in $\mathrm{BaPB_{1-x}Bi_xO_3}$ (Ref. 12) and in doped semiconductors[13] (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 $\mathrm{Nd_{2-x}Ce_xCuO_{4-\delta}}$ 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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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] S. Tajima, S. Tanaka, T. Ido, and S. Uchida (unpublished).

[4] H. Mook, G. Aeppli, S-W. Cheong, and Z. Fisk (private communication).

[5] H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).

[6] G. H. Kwei, S-W. Cheong, Z. Fisk, F. H. Garzon, J. A. Goldstone, and J. D. Thompson, Phys. Rev. B **40**, 9370 (1989).

[7] S. Tajima, H. Ishii, T. Nakahashi, T. Takagi, S. Uchida, M. Seki, S. Suga, Y. Hidaka, M. Suzuki, T. Murakami, K. Oka, and H. Unoki, J. Opt Soc. Am. B **6**, 475 (1989).

[8] S. L. Cooper, G. A. Thomas, J. Orenstein, D. H. Rapkine, M. Capizzi, T. Timusk, A. J. Millis, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. B **40**, 11 358 (1989); J. Orenstein, G. A. Thomas, A. J. Millis, S. L. Cooper, D. H. Rapkine, T. Timusk, L. F. Schneemeyer, and J. V. Waszczak Phys. Rev. B (to be published).

[9] N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Green, and W. R. McKinnon, Phys. Rev. B **35**, 8807 (1987).

[10] T. M. Rice and F. C. Zhang, Phys. Rev. B **37**, 815 (1989).

[11] M. Grill, B. G. Kotliar, and A. J. Millis (private communication).

[12] S. Tajima, S. Uchida, A. Masaki, H. Takagi, K. Kitazawa, S. Tanaka, and A. Katsui, Phys. Rev. B **32**, 6302 (1985).

[13] G. A. Thomas, M. Capizzi, F. De Rosa, R. N. Bhatt, and T. M. Rice, Phys. Rev. B **23**, 5472 (1981).

[14] J. W. Allen, C. G. Olson, M. B. Maple, J.-S. Kang, L. Z Liu, J.-H. Park, R. O. Anderson, W. P. Ellis, J. T. Markert, Y. Dalichaouch, and R. Liu, Phys. Rev. Lett. **64**, 595 (1990).

[15] Mark S. Hybertsen, E. B. Stechel, M. Schluter, and D. R. Jennison, Phys. Rev. B (to be published).