

Optical excitations in CuO_2 sheets and their strong dependence on Cu-O coordination and bond length

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The charge-transfer (CT)-type optical excitations from O $2p$ to Cu $3d$ and to Cu $4s$ states have been observed around 1.5 and 5.0 eV, respectively, in undoped T' -phase $L_2\text{CuO}_4$ single crystals, where $L = \text{Pr, Nd, Sm, Eu, or Gd}$. The spectral shapes of these CT excitations are greatly modified upon electron doping by Ce substitution for the L sites. The CT excitation energies in a series of $L_2\text{CuO}_4$ compounds with the T , T^* , and T' structures strongly depend on the L species, indicating the crucial effect of the in-plane Cu-O bond-length variation as well as of the Cu-O coordination on the electronic states in the CuO_2 sheets.

Among the many experimental investigations for the clarification of the mechanism of high- T_c superconductivity, pressure effects on T_c (Refs. 1 and 2) would be one of the most noteworthy results. The observed strong dependence of T_c on pressure suggests that the change of lattice parameters, or more specifically of some Cu-O bond lengths, in high- T_c compounds should be sensitive to their electronic parameters which are relevant to the occurrence of high- T_c superconductivity. Spectroscopic investigations may be useful to reveal variation of the electronic structures in CuO_2 sheets with the bond lengths. The parent CuO_2 -layered compounds without carriers show optical transitions at 1.4–2.0 eV. This transition energy corresponds to the charge-transfer (CT)-type energy gap between the O $2p$ -like valence state of the Cu $3d$ -like empty state. The gap value Δ has been reported to show a strong dependence on the pattern of the Cu-O network.³

In this paper, we report an additionally important variation of the CT gap excitations: the critical dependence of the CT gap Δ on the in-plane Cu-O bond length d_s in the so-called T' -phase compounds $L_2\text{CuO}_4$ (2:1:4) ($L = \text{Pr, Nd, Sm, Eu, or Gd}$). The T' phase is of great advantage to spectroscopic studies of the variation of electronic parameters in the CuO_2 sheets with the value of d_s because there are a variety of rare-earth substitutions with different lattice parameters and also because there is no apical oxygen which would otherwise affect the electronic parameters in a complicated way.⁴ We also report the finding of the Cu $4s$ related optical transition in parent T' -phase compounds. It was observed to be polarized parallel to the Cu-O sheets and to show large variations of the spectral shape and position with the d_s value as well as upon electron doping.

Single crystals of $L_2\text{CuO}_4$ and $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ were grown by a conventional CuO flux method. Powders of lanthanide oxide and CuO were mixed, heated above peritectic temperature⁵ (1250–1300°C), and then slowly cooled down at a rate of 5–10°C/h in a Pt crucible. A typical size of the obtained crystals was $3 \times 3 \times 0.05 \text{ mm}^3$.

In addition, a bulky single crystal of Pr_2CuO_4 with a thickness of 3 mm was grown by the traveling solvent floating-zone method for the measurement of optical anisotropy on (100) surface. For Ce-doped single crystals, the Ce concentration x was estimated from the c -axis length determined by x-ray diffraction measurements. Uncertainty of x was estimated to be within 0.02 from a cross-check by electron-probe microanalyses on some of the samples.

Optical reflectivity spectra in the photon-energy region of 0.05–15 eV were measured mostly on specularly polished (001) surfaces of single-crystal samples in the configuration of near-normal incidence at room temperature. The spectra were measured also on as-grown surfaces for some single crystals, which ensured that the procedure of polishing surface affects neither the spectral shape nor the magnitude within the accuracy of our optical measurements. The absolute value of reflectivity was checked using microscopic optical systems in the energy region of 0.25–3 eV. The relative experimental error of the reflectivity was estimated to be less than 5% (typically $\Delta R < 0.02$) up to 6 eV and 10% even in the vacuum-ultraviolet region by checking the reproducibility and consistency in several runs of measurements. We also measured reflectivity spectra on (100) surface of Pr_2CuO_4 single crystal with the light polarizations of $\mathbf{E} \parallel c$ and $\mathbf{E} \perp c$ in the photon-energy region of 2–35 eV. Dielectric function and optical conductivity spectra in an energy range of up to 10 eV were calculated by a Kramers-Kronig analysis of the reflectivity using the data at least up to 15 eV.

Figure 1 shows spectra of the optical reflectivity (top panel) and the transformed conductivity (bottom panel) in Pr_2CuO_4 single crystal with the polarization parallel ($\mathbf{E} \perp c$, solid lines) and perpendicular ($\mathbf{E} \parallel c$, dashed lines) to the CuO_2 sheet. [We omit the lower-lying (< 0.1 eV) phonon structures to avoid complexity.] In the $\mathbf{E} \perp c$ spectra, intense transitions are observed around 1.5 and 5.0 eV, while no prominent structure is discernible in the $\mathbf{E} \parallel c$ spectrum in this energy region. These in-plane polarized transitions seem to carry fairly large oscillator strengths

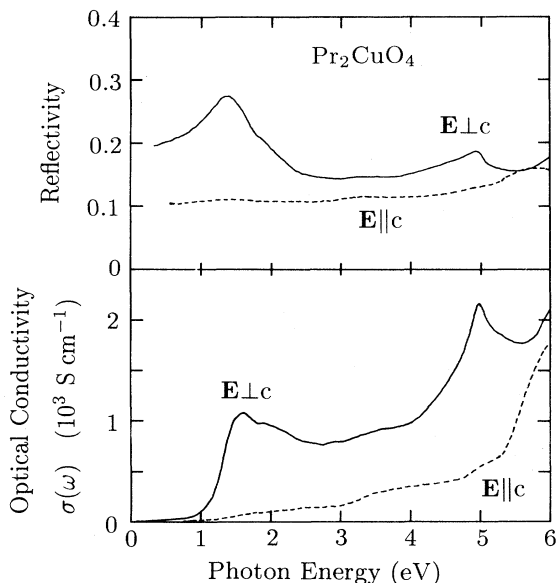


FIG. 1. Optical reflectivity (top panel) and conductivity (bottom panel) spectra of Pr_2CuO_4 with the polarization parallel (solid lines) and perpendicular (dashed lines) to the CuO_2 sheet.

(f 's); crudely, $f \sim 0.5$ for the 1.5 eV band and $f \sim 0.2$ for the 5.0 eV band, if we subtract an overlapping broad continuum.

These transitions were observed to show a noticeable change with Ce doping which can introduce electrons in the CuO_2 sheets. Figure 2 shows the ϵ_2 spectra of Pr_2CuO_4 and the $\text{Pr}_{1.88}\text{Ce}_{0.12}\text{CuO}_4$ with the $E \perp c$ light polarization. The structure around 1.5 eV in the spectrum of undoped Pr_2CuO_4 is much reduced with Ce doping. Instead, Drude-like absorption appears in the low-energy range below 1 eV. The 5.0-eV peak also disappears with Ce doping and seems to change into lower-lying broad absorptions. Concerning the spectral change below 3 eV, it has already been reported on the $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (Ref. 6) system and also on the relevant system $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (Ref. 7) that the spectral weight of the 1.5-eV excitation is transferred to the lower-energy region. The result of

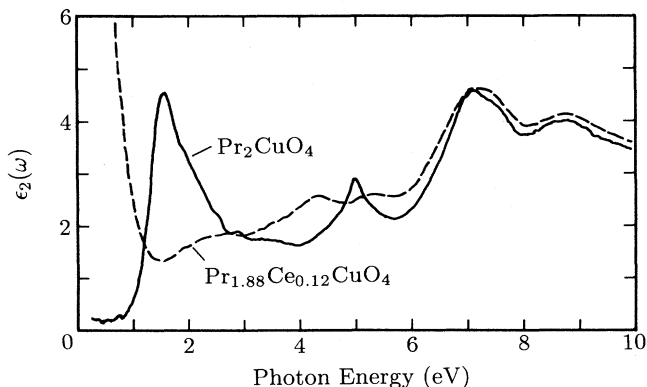


FIG. 2. Calculated ϵ_2 spectra ($E \perp c$) of $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ single crystals for $x=0$ and $x=0.12$.

this study is also consistent with this, although the lower limit of the photon energy in this study is not enough for quantitative analysis.

The strong dependences of the two optical transitions around 1.5 and 5.0 eV in Pr_2CuO_4 on the light polarization and Ce doping indicate that they should be ascribed to the electronic excitations inherent to the CuO_2 sheets. The similar two optical transitions are also observed in a $(\text{Ca},\text{Sr})\text{CuO}_2$ crystal (or the so-called infinite-layer compound), which does not include fluoritelike $L_2\text{O}_2$ blocks, but similar CuO_2 sheets with no apical oxygen.⁸

Now we discuss the origins of the two transitions based on a local picture, which is thought to be suitable at least in the insulator region. Possible candidates for the in-plane polarized optical transitions with fairly strong intensities in such a relatively low-photon-energy region are of the following three types of charge-transfer excitations in the CuO_2 sheets for the CT transitions: (1) from O $2p$ to Cu $3d$ state, (2) from O $2p$ to Cu $4s$ state, and (3) from Cu $3d$ to neighbor-site Cu $3d$ state. The initial state for the former two transitions, which is located at the topmost portion of the valence states, is dominantly of the O $2p_\sigma$ character, which is strongly hybridized with the Cu $3d_{x^2-y^2}$. The interatomic Cu $3d$ - $3d$ transition, i.e., from the lower Hubbard band to the upper Hubbard one, would be the lowest optical gap excitation if the compound were a simple Mott insulator. The observed two transitions around 1.5 and 5.0 eV should be assigned to two of these excitations. Among these, the lower-lying transition can be assigned to the CT gap excitation (1) between the O $2p_\sigma$ and Cu $3d_{x^2-y^2}$, which has been well evidenced also by other spectroscopic studies.^{9,10} As for the 5.0-eV transition, we assign this band to transition (2) mainly from O $2p_\sigma$ to Cu $4s$ states rather than the interatomic d - d transition (3) because of the strong dependence of its energy position on the Cu-O bond lengths, as well as on the oxygen coordination around Cu, as described later.

The remarkable changes of these CT excitations on carrier doping may be ascribed to the change of the electronic states near the Fermi level. It has been suggested by previous photoemission studies¹¹ that the electron doping in the T' -phase compound gives rise to the new state within the O $2p$ -Cu $3d$ CT gap where the Fermi level is pinned. Such a gap-filling state is likely to be composed of hybridized O $2p$ and Cu $3d_{x^2-y^2}$ states, which may be a new initial state in the optical excitation process. With Ce doping, however, the local CT picture will be inappropriate and rather transformed to the band picture with Ce doping.¹²

Shown in Fig. 3 are the calculated ϵ_2 spectra for the T' -phase insulators with various L substitutions. One may notice systematic shifts of the transition energies of both the CT excitations at issue. Plotted in Fig. 4 are the d_s dependences of the optical excitation energies estimated from the peak positions of ϵ_2 spectra for these $L_2\text{CuO}_4$ compounds. For comparison, we include the data for La_2CuO_4 (T phase), $(\text{La},\text{Gd},\text{Sr})_2\text{CuO}_{4-\delta}$ (T^* phase), $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, and $(\text{Ca},\text{Sr})\text{CuO}_2$ single crystals, which are also members of single- CuO_2 -layered insulating cuprates.³ No prominent structure corresponding to the 5.0-eV band of the T' -phase compounds could be detected

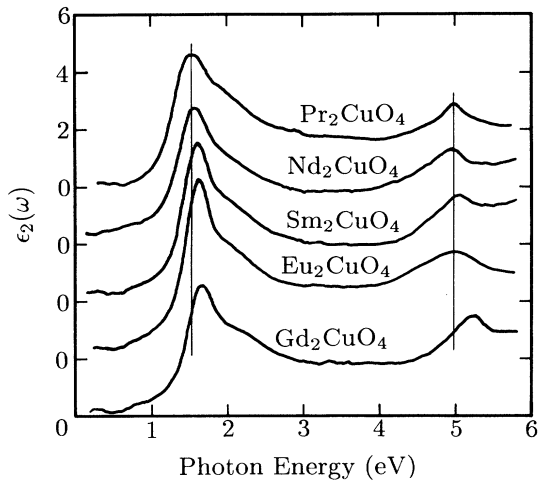


FIG. 3. Calculated ϵ_2 spectra ($\mathbf{E} \perp c$) of T' -phase $L_2\text{CuO}_4$ single crystals where $L = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu},$ and Gd .

in the optical spectra of the T and T^* phases below 6 eV, which may probably be located at a higher energy and be masked by overlapping strong lanthanide-related transitions of 6–10 eV.

As shown in the bottom panel of Fig. 4, the CT gap value Δ is mostly governed by the anion coordination around Cu sites.³ The Δ increases with the total negative valence Q of anions surrounding Cu, such as 1.5–1.7 eV for the T' -phase compounds and $(\text{Ca}, \text{Sr})_2\text{CuO}_2$ ($Q=8$), 1.7–1.9 eV for the T^* phase and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ($Q=10$), and 2.0–2.1 eV for the T phase ($Q=12$). This empirical law possibly indicates the importance of Madelung-type interaction for electronic parameter in the Cu–O sheets.¹³ Besides the coordination around Cu, the in-plane Cu–O bond length d_s may be another important factor to modify the Madelung energy, and hence Δ . In fact, the present study for the T' -phase family has proved that Δ depends also on d_s . The tendency observed in the T' phase seems to be reasonable because the compound with the shorter d_s must have the more intense ligand field around Cu, resulting in the higher Cu 3d level.

Recently, Cooper *et al.* pointed out a simple scaling between Δ and d_s for the 2:1:4 systems.¹⁴ However, their scaling law seems to fail in compounds with crystal structures other than the T' phase; for example, the so-called infinite-layer compound $(\text{Ca}, \text{Sr})\text{CuO}_2$ shows a rather small Δ value (ca. 1.56 eV), while the compound $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ shows a rather large one (ca. 1.88 eV). This is also the case even for the T and T^* phases, as shown in the bottom panel of Fig. 4. The value of Δ is shown to be still sensitive to the presence of the apex(es), which leadingly affects the Cu 3d energy level. The contradiction between their data and ours for the 2:1:4 systems might be caused by the difference of the upper photon-energy limit of the measured reflectivity spectrum, which has a great influence on the accuracy of a Kramers-Kronig transformation, according to our experience.

The top panel of Fig. 4 shows that the energy position

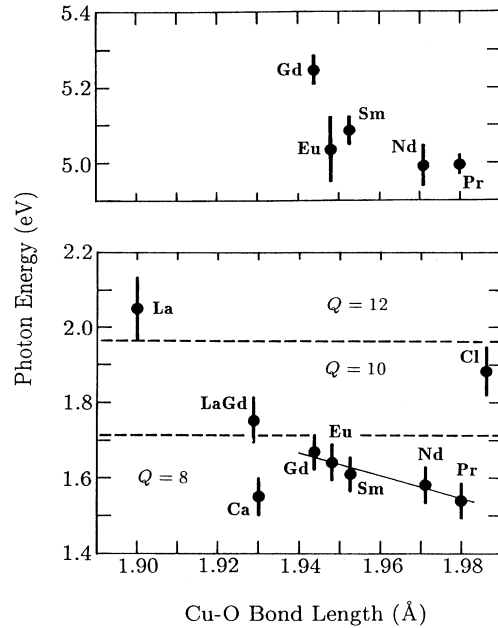


FIG. 4. The relation between the in-plane Cu–O bond length and the optical transition energy for the O 2p–Cu 3d (bottom panel) and O 2p–Cu 4s (top panel) transitions in various insulating cuprates (from this work and Ref. 3); La_2CuO_4 (La), $(\text{La}, \text{Gd}, \text{Sr})_2\text{CuO}_{4-s}$ (LaGd), $(\text{Ca}, \text{Sr})\text{CuO}_2$ (Ca), Gd_2CuO_4 (Gd), Eu_2CuO_4 (Eu), Sm_2CuO_4 (Sm), Nd_2CuO_4 (Nd), Pr_2CuO_4 (Pr), and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (SrCl). The straight line is drawn for five T' -phase insulators using a least-squares method. The parameter Q is defined as the sum of the formal negative valence of anions surrounding Cu (see text).

of the optical transition around 5.0 eV also depends on d_s systematically as for the T' phase. It is noteworthy that the corresponding transition is missing below 6 eV in the T and T^* phases. If the transition energy were dependent mainly on d_s , it should be observed below 6 eV also in the T and T^* -phase compounds (see the dashed line in the top panel of Fig. 4). Otherwise, if it were the Cu 3d–3d CT excitation, the energy would be even less dependent on the Cu–O bond length. Interpreting this excitation as the O 2p to Cu 4s transition, such a critical Cu–O network dependence of the transition energy may be explained by reasoning that the energy level of the Cu 4s state with the isotropic wave function strongly depends not only on the in-plane Cu–O bond length, but also on the presence of the apex(es).¹⁵

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