

Optical excitations in $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$: Evidence for localized (excitonic) and delocalized charge-transfer gaps

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The optical properties of $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (2:2:0:1) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2:2:1:2) have been investigated by transmission electron-energy-loss spectroscopy. At low energy, $E_{\text{loss}} \leq 10.0$ eV, common features are observed in the spectra of these two materials at $E_{\text{loss}} = 0.0, \sim 2.7, 3.6,$ and 4.6 eV. The effective number of charges associated with these excitations has been estimated using the optical sum rule, and from the ratio of effective charges in the two materials, the origin of this feature has been inferred based on the relative number of Cu-O₂ and Bi-O layers per formula unit. The effective-charge ratio for the free carriers at zero energy loss, $N_{2:2:1:2}/N_{2:2:0:1} = 5.0$, could not be used to determine whether the carriers were in the Cu-O₂ or Bi-O planes because the oxygen doping in the two materials was not known. But at $E_{\text{loss}} = 2.7$ and 3.6 eV, the effective-charge ratio is 2.6 indicating that these transitions are associated with the Cu-O₂ planes since the ratio is close to 2/1. The effective-charge ratio is 0.9 for $E_{\text{loss}} = 4.6$ eV suggesting that this excitation is localized in the Bi-O planes. If the two excitations in the Cu-O₂ layers of 2:2:0:1 and 2:2:1:2 are identified with the delocalized and localized charge-transfer reactions [Mark S. Hybertsen, Michael Schlüter, and Niels E. Christensen, *Phys. Rev. B* **39**, 9028 (1989)], then the three-band Hubbard parameters $\epsilon = \epsilon_p - \epsilon_d$ and U_{pd} (ϵ is the energy difference between the Cu $3d$ and O $2p$ levels and U_{pd} is the Coulomb repulsion between two holes occupying adjacent Cu and O sites) are 1.8 and 0.9 eV, respectively, with an uncertainty of ± 0.5 eV.

The electronic structure of high-temperature superconductors in the normal state cannot be understood in terms of the independent-particle model, but many properties of these materials are consistent with the Mott-Hubbard model. The insulating gap in the undoped phase of high- T_c compounds is thought to arise from the charge-transfer reaction $3d^9 \rightarrow 3d^{10}\underline{L}$ (\underline{L} is a hole on a hybridized Cu $3d$ -O $2p$ ligand) rather than from the Mott gap $2d^9 \rightarrow d^8 + d^{10}$. Hybertsen, Schlüter, and Christensen¹ (HSC) point out that the Coulomb repulsion between a ligand hole and a hole on a neighbor Cu ion (d^9) can give rise to two charge-transfer bands: one corresponding to delocalized ligand holes which have only Cu d^9 ion neighbors and the second an excitonic charge transfer in which the ligand hole is localized in the neighborhood of the $3d^{10}$ ion. They estimate that the energy difference between the localized and delocalized charge-transfer reactions is ~ 1.2 eV in La_2CuO_4 . In this paper we measure the optical properties of $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (2:2:0:1) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2:2:1:2) by transmission electron-energy-loss spectroscopy (EELS) and observe two excitations centered at ~ 2.7 and 3.6 eV in the Cu-O₂ layers of both materials which may be the excitonic and band charge-transfer reactions predicted by HSC. If correct, then the parameters $\epsilon = \epsilon_p - \epsilon_d$ and U_{pd} of the three-band Hubbard model are $\epsilon = 1.8$ eV and $U_{pd} = 0.9$ eV (ϵ is the energy difference between the O $2p$ and Cu $3d$ levels and U_{pd} is the Coulomb repulsion between neighbor holes occupying these two levels).

We are able to determine whether an optical transition is associated with Cu-O₂ or Bi-O sheets by comparing the oscillator strengths of the excitations in the two materials. In addition to the free-carrier optical response at zero en-

ergy, we find that the next two excitations centered at ~ 2.7 and 3.6 eV are associated with the Cu-O₂ sheets. The next excitation at ~ 4.6 eV occurs in the Bi-O sheets. There is general agreement that the broad optical band centered at 2.7 eV is associated with excitations in the Cu-O₂ sheets,²⁻⁵ but identification of the 3.6 -eV excitation with transitions in the Cu-O₂ sheets is controversial. In particular, Kelly *et al.*² assigned the 3.6 - and 4.6 -eV excitations to the Bi-O planes on the basis of their dependence on chemical substitutions. Garriga *et al.*⁵ suggested these two excitations might be transitions to an atomiclike Bi $6p$ spin-orbit doublet. But Humlíček *et al.*⁴ found that the polarization dependence of the 3.6 -eV excitation was not consistent with this hypothesis. We will consider some of these papers in more detail after presenting and discussing our data.

The $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ crystal was prepared by melting the constituents (nominal proportion of Bi:Sr:Cu equaled 2:2:1) in an alumina crucible in air at 900°C . The temperature was turned down at a rate of $0.6^\circ\text{C}/\text{min}$ to 830°C . Then the furnace was turned off to cool to room temperature. An x-ray analysis of the bulk material indicated that it was single phase. The material was not superconducting above 1.9 K. Thin films of the material were prepared by a modification of the method of Ref. 6. The $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ sample was prepared from Bi_2O_3 , SrCO_3 , CaO , and CuO in the molar proportion 2:2:1:2 using the flux method reported by Schneemeyer *et al.*⁷ Details regarding the preparation of this sample are given in Ref. 8. The electron-energy-loss measurements were taken with a transmission electron-energy-loss spectrometer (nonimaging) similar to the instrument described by Gibbons, Ritsko, and Schnatterly.⁹ The incident-beam ener-

gy is 80 keV and the energy resolution is 0.17 eV [full width at half maximum (FWHM)]. The momentum resolution is 0.04 \AA^{-1} (FWHM). The momentum transfer for measurements reported in this paper was 0.1 \AA^{-1} and was nearly perpendicular to the c axis of the sample. Thus, the component of the dielectric tensor derived from these measurements is in the a - b plane of the crystal.

The EELS spectra, after correcting for multiple scattering, is proportional to the loss function, $\text{Im}(-1/\epsilon)$. The thickness of the sample is unknown, so we determine the proportionality constant from the Kramers-Kronig condition

$$\text{Re}(1 - 1/\epsilon_0) = \frac{2}{\pi} \int_0^\infty \text{Im}(-1/\epsilon) \frac{dE'}{E'}, \quad (1)$$

where $\text{Re}(1 - 1/\epsilon_0) = 1$ for a conductor. The 2:2:1:2 sample is unambiguously a conductor, but the conductivity of our 2:2:0:1 sample is not known. We did measure the infrared reflectivity of the 2:2:0:1 sample and found that it had a Drude-like reflectivity edge at 0.6 eV which implies that the carrier density is $n = 4 \times 10^{21} \text{ cm}^{-3}$ assuming $\epsilon_\infty = 5.0$ and $m^*/m = 2.0$. Thus, if the sample is a semiconductor, the gap is very small and, therefore, $\text{Re}(1 - 1/\epsilon_0)$ differs from 1 by less than a few percent. Setting $\text{Re}(1 - 1/\epsilon_0) = 1$, the proportionality constant between the data and $\text{Im}(-1/\epsilon)$ can be determined. The real and imaginary parts of the dielectric function, $\epsilon = \epsilon_1 + i\epsilon_2$, are obtained from the loss function by a Kramers-Kronig analysis. Then, from the optical sum rule, one obtains the mass-weighted differential-oscillator strength (MDOS) at an energy E (atomic units, $Ry = 27.2 \text{ eV}$)

$$\frac{m}{m^*} \frac{dN}{dE} = \frac{1}{2\pi^2} V E \epsilon_2, \quad (2)$$

where V is the volume of a cell containing one formula unit of the compound and dN/dE is the differential number of charges in that volume with transition energies between E and $E + dE$. If the same transition occurs in 2:2:1:2 and 2:2:0:1 at energy E with the same width Γ then the ratio of the respective mass-weighted effective charge,

$$\left. \frac{m}{m^*} N_{\text{eff}} \sim \Gamma \frac{m}{m^*} \frac{dN}{dE} \right|_E,$$

will be 2/1 for excitations well localized in the Cu-O₂ layers and 1/1 for excitations localized in the Bi-O planes. The ratio should be close to integers 1 or 2 for core-level transitions, but may be significantly different from an integer if the excitation is delocalized over several planes or if the oscillator strength depends on the oxygen doping. The effective number of free carriers, for example, varies continuously with doping.

The MDOS for 2:2:0:1 and 2:2:1:2 from 0 to 40 eV are shown in Fig. 1. The important features to note in this figure are the transitions from the Bi 5*d* spin-orbit doublet in the energy region 25–30 eV. The differential oscillator strengths for these excitations ride on a continuum of transitions represented by the dashed line in the figure. With respect to this background, the differential oscillator strengths for these transitions are equal (within 10%) in

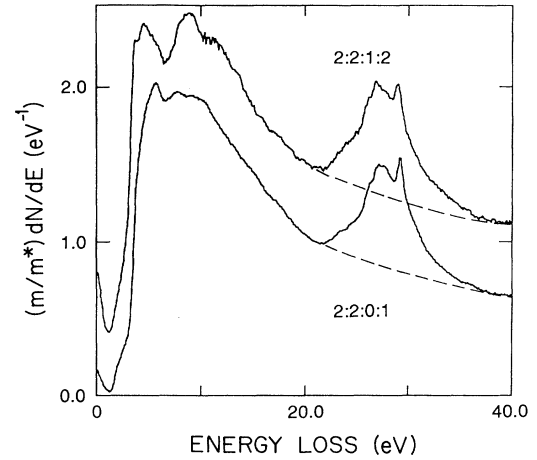


FIG. 1. The mass-weighted differential-oscillator strength from 0–40 eV for $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (2:2:0:1) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2:2:1:2).

2:2:0:1 and 2:2:1:2 as they should be for localized core-level transitions within the Bi-O layer. This agreement with theory for known transitions confirms that the data has been scaled properly.

The MDOS for 2:2:0:1 (solid line) and 2:2:1:2 (dashed line) in the region 0–6.0 eV are shown in Fig. 2(a). We observe the following transitions: (1) the free-carrier transition at zero energy loss, (2) a broad excitation centered at 2.7 eV, (3) a strong, relatively narrow transition at 3.6 eV, and (4) a less well-defined excitation at 4.6 eV. The excitations at 3.6 and 4.6 eV can be seen more clearly in our normal-incidence reflectivity measurements shown in Fig. 3. We fit the reflectivity data with three Lorentz

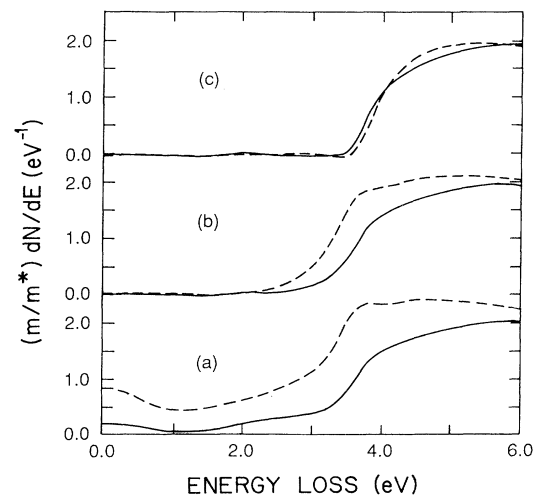


FIG. 2. The mass-weighted differential-oscillator strength from 0–6.0 eV for $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (solid line) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (dashed line), (a) the full data, (b) the data with Drude term and Lorentz oscillator (center frequency = 2.7 eV) subtracted, and (c) the data with Drude term and two Lorentz oscillators (center frequencies = 2.7 and 3.6 eV) subtracted.

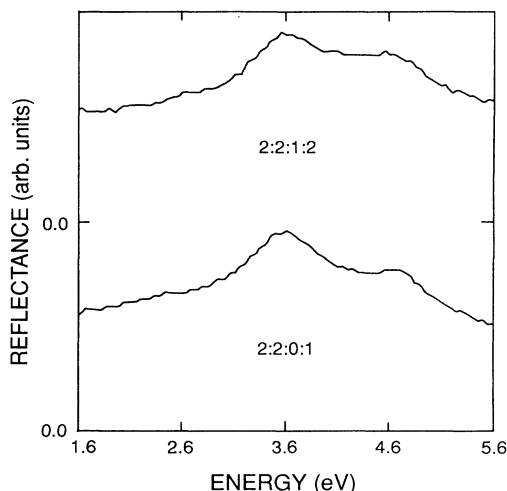


FIG. 3. Normal-incidence reflectivity from 1.6–5.6 eV for $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (2:2:0:1) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2:2:1:2).

oscillators; a very broad oscillator for the background and two oscillators centered at 3.6 eV (width = 0.8 eV) and 4.6 eV (width = 1.0 eV). The oscillator strengths in the two materials depend sensitively on the background which is uncertain, but the center frequencies and transition widths are relatively insensitive to the background and are the same in both materials.

The low-energy ($E < 3$ eV) electron-energy-loss data for 2:2:1:2 has been analyzed in detail.⁸ A plasmonlike excitation is observed at ~ 1.0 eV in the EELS spectra. A similar feature is observed in 2:2:0:1 at ~ 0.6 eV. The EELS spectra is uncertain for $E \leq 0.5$ eV because of the overlapping quasielastic peak. If we assume the plasmonlike excitations in these two materials are due to free carriers, then the MDOS for 2:2:0:1 and 2:2:1:2 extrapolates, respectively, to 0.16/eV and 0.80/eV at zero energy giving an effective-charge ratio $N_{\text{eff}, 2:2:1:2}/N_{\text{eff}, 2:2:0:1} = 5.0$ for the free carriers. Maeda *et al.*¹⁰ find the ratio of the carrier densities in the two materials is close to 1 from their measurement of the Hall coefficient. This disagreement may be due to differences in the stoichiometries of our sample and theirs or may reflect a fundamental difference between the carrier density derived at zero frequency (dc Hall effect) versus the density derived at optical frequencies. Considering now the excitation at 2.7 eV, the MDOS for 2:2:0:1 and 2:2:1:2 at that energy are 0.31/eV and 0.9/eV, respectively. There is a contribution to the MDOS at 2.7 eV from the tail of the 3.6-eV oscillator which we estimate by the following procedure. The free carrier and 2.7-eV excitations in 2:2:0:1 and 2:2:1:2 are modeled by a Drude term and a Lorentz oscillator. The MDOS is calculated from the models and subtracted from the data. The parameters of the models are adjusted until the absolute value of the difference between data and model MDOS is minimized in the energy range 0–2.7 eV. The results are shown in Fig. 2(b). The tail of the 3.6-eV excitation at 2.7 eV is 0.055/eV in 2:2:0:1 and 0.23/eV in 2:2:1:2. Thus, correcting the value of MDOS at 2.7 eV for contributions from the 3.6-eV transition, we obtain a

ratio of the effective charge $N_{\text{eff}, 2:2:1:2}/N_{\text{eff}, 2:2:0:1} = 2.6$. Though deviating significantly from an integer, this ratio certainly is closer to 2/1 than 1/1 verifying, as other investigators have concluded, that the 2.7-eV excitation is located in the Cu-O₂ planes rather than in the Bi-O layers. Next, we consider the 3.6 and 4.6-eV excitations, again separating the overlapping tail of the 4.6-eV transition from the peak at 3.6 eV by the same procedure. The MDOS for Lorentz oscillators with center frequencies equal to 3.6 eV and widths equal to 0.8 eV (determined from fitting the reflectivity spectra) are subtracted from the 2:2:0:1 and 2:2:1:2 spectra shown in Fig. 2(b). The oscillator strengths for the two models are adjusted to minimize the difference spectra below 3.6 eV. The results are shown in Fig. 2(c). The MDOS for the 3.6-eV excitations in 2:2:0:1 and 2:2:1:2, corrected for the overlap with the 4.6-eV transitions, are 0.63/eV and 1.62/eV, respectively, giving a charge ratio $N_{\text{eff}, 2:2:1:2}/N_{\text{eff}, 2:2:0:1} = 2.6$. The exact agreement with the ratio at 2.7 eV is probably coincidental, but the result is strongly suggestive that both excitations have a common origin in the Cu-O₂ planes. Finally, the MDOS for the 4.6-eV excitations, corrected for the tails from the 3.6-eV transitions, are 1.8 and 1.6 for 2:2:0:1 and 2:2:1:2, respectively, giving a charge ratio $N_{\text{eff}, 2:2:1:2}/N_{\text{eff}, 2:2:0:1} = 0.9$. Clearly, the transition is associated with the Bi-O layers in agreement with the conclusions of other investigators. We note that the charge ratios could have been determined from the oscillator strengths derived by fitting the data with Lorentz oscillators, but these parameters were not tightly constrained by the fitting procedure. The MDOS ratio, in contrast, is relatively insensitive to the oscillator parameters and is, therefore, a less model-dependent result.

Our final assignments for the four transitions are: (1) $E = 0$, where we cannot distinguish whether carriers are in the Cu-O₂ or Bi-O planes, (2) $E = 2.7$ eV, Cu-O₂ layers, (3) $E = 3.6$ eV, Cu-O₂ layers, and (4) $E = 4.6$ eV, Bi-O layers. The only controversial assignment is the 3.6-eV excitation. Some investigators⁵ have speculated that the 3.6- and 4.6-eV transitions are associated with an unoccupied Bi 6*p* spin-orbit doublet since the atomic Bi 6*p* spin-orbit splitting, $\Delta E = 1.7$ eV, is comparable to the energy difference between these two transitions. But these investigators point out that the strong polarization dependence of the 3.6-eV excitation does not seem consistent with a rotationally invariant final state. The strongest argument for assigning the 3.6-eV transition to the Bi-O layers was made by Kelly *et al.*² They made a detailed optical study of several perovskite superconductors and attempted to identify the source of various excitations by analyzing the influence of chemical substitutions on the optical spectra. They observe relatively sharp features in 2:2:0:1 and 2:2:1:2 at 3.8 and 4.8 eV (corresponding, presumably, to our structure at 3.6 and 4.6 eV) which are not seen at those energies in La_2CuO_4 or in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. These two excitations are associated with the Bi-O planes because substitution of Co or Fe for Cu has minimal effect on the spectra, while replacing Bi, Sr by Tl, Ba changes the spectra significantly. We have no explanation for the weak dependence of the spectra on transition-metal cation, but do interpret differently the changes in spectra

from the Bi,Sr to the Tl,Ba compounds. A strong feature does exist in the Tl,Ba compound at ~ 3.5 eV while the 4.8-eV excitation in this material is much weaker than in the Bi,Sr compound. Thus, the spectral change resulting from the substitution of Tl,Ba for Bi,Sr can be interpreted as redshifting the Cu-O₂-based feature at 3.8 eV down to 3.5 eV and removing the Bi-O-based feature at 4.8 eV.

The excitations at 2.7 and 3.6 eV in the Cu-O₂ sheets can be interpreted in several ways. A strong feature in the neighborhood of 4 eV is observed in several Cu-O₂ based perovskite structures and has been associated with the charge-transfer reaction $3d^9 \rightarrow 3d^{10}\underline{L}$ [or $3d^{10} \rightarrow 3d^{10}s\underline{L}$ in the Cu-O chains of YBa₂Cu₃O₆ (Ref. 2)]. It also may be an intra-atomic $d-d^*$ excitation of Cu, but Humlicek *et al.* and Kelley *et al.* have argued against this assignment based on the association of this excitation with oxygen bonding and on the temperature dependence of the spectra. If the transition at 3.6 eV is the charge-transfer gap shifted down from 4 eV, then this leaves in question the identity of the broad 2.7-eV excitation. Kelly *et al.* suggested that this broad feature is an interband transition which is found at ~ 2 eV in the optical spectra calculated from band structure.¹¹ HSC, on the other hand, conjectured that a similar feature seen at the same energy in La₂CuO₄ may be an excitonic charge transfer transition. The width of the transition may be due to hybridization and/or large fluctuations in the local electric field due to the random doping of oxygen. In their model, HSC distinguish between two final states of the charge-transfer reaction $d^9 \rightarrow d^{10}\underline{L}$: one a localized ligand hole in the neighborhood of the d^{10} copper ion (an exciton) and the other a delocalized band where the ligand hole has two d^9 copper-ion neighbors. In the first case, the excitation energy (assuming the hopping matrix element is zero) is

$\varepsilon + U_{pd}$ and in the second case it is $\varepsilon + 2U_{pd}$. If the 2.7- and 3.6-eV excitations are described correctly by this model, then $\varepsilon = 1.8$ eV and $U_{pd} = 0.9$ eV for both 2:2:0:1 and 2:2:1:2. Large uncertainty (approximately ± 0.5 eV) exists in these numbers because of the width of the 2.7-eV excitation, but they are in good agreement with the estimates ($\varepsilon = 2-4$ eV and $U_{pd} = 1.2 \pm 0.5$ eV) calculated by HSC for La₂CuO₄.

In conclusion, we have compared the mass-weighted differential-oscillator strengths of Bi₂Sr₂CuO₆ and Bi₂Sr₂CaCu₂O₈ in order to distinguish between optical excitations in the Cu-O₂ planes and excitations localized in the Bi-O layers. The free carriers undoubtedly exist in the Cu-O₂ sheets, but we are unable to rule out the possibility that pockets of electrons in the Bi-O sheets also may be contributing free carriers. The effective charge ratios at 2.7 and 3.6 eV imply that these excitations are both in the Cu-O₂ planes while the ratio at 4.6 eV indicates that this transition is localized in the Bi-O layers. We suggest, based on the calculations of Hybertsen *et al.*, that the excitation at 2.7 eV is a localized (excitonic) charge-transfer reaction while the transition at 3.6 eV is a charge-transfer reaction into a delocalized final state. It follows from this hypothesis that the two parameters, $\varepsilon = \varepsilon_p - \varepsilon_d$ and U_{pd} , of the three-band Mott-Hubbard model (neglecting the hopping matrix element) are 1.8 and 0.9 eV, respectively, for these two materials with an experimental uncertainty of approximately ± 0.5 eV.

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