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Optical reflectivity spectra of single-crystal $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ ($n=1$ and 2)

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The optical reflectivity spectra of the single-crystal Bi-based cuprates, $Bi_2Sr_2CaCu_2O_{8+x}$ and $Bi_2Sr_2CuO_{6+x}$, were measured in a wide energy range from 0.05 to 40 eV, and analyzed through the Kramers-Kronig relation. The obtained spectra are different from other superconducting cuprates, such as $(La,Sr)_2CuO_4$ and $YBa_2Cu_3O_x$, which might be ascribed to the existence of the characteristic Bi_2O_2 layer. The optical excitations within Bi_2O_2 layer start from 2 eV or higher energy, so it is unlikely that the electrons in the Bi_2O_2 layer contribute to low-energy excitation or dc conduction in this family of high-T_c superconductors.

The Bi-based cuprates, $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ ($n=1$, 2, and 3) form a class of high-temperature superconducting oxides which have no rare-earth atoms in compositions.[1,2] They have a two-dimensional square lattice of Cu atoms interconnected by O atoms as in the case of $(La,Sr)_2CuO_4$ (La-Sr-Cu-O) and $YBa_2Cu_3O_x$ (Y-Ba-Cu-O), but also possess a characteristic structure made from Bi and O, a so-called "Bi_2O_2 layer." Therefore, much interest has been focused on how the presence of the Bi_2O_2 layer affects the physical properties of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ system as compared with previously known La-Sr-Cu-O and Y-Ba-Cu-O. The results of the band calculations have shown that the Bi_2O_2 layer supplies holes to the conducting CuO_2 layer, i.e., self-doping.[3-6] The transport measurement of single-crystal $Bi_2Sr_2CaCu_2O_{8+x}$ has revealed enormous anisotropy of the resistivity between the directions parallel and perpendicular to the c axis ($\rho_\parallel/\rho_\perp \sim 10^5$),[7] which suggests that the conducting CuO_2 layers are well isolated along the c axis by the Bi_2O_2 layer. Since the Bi-based cuprates can be easily cleaved and the clean surface of the sample can be obtained, many experiments on photoemission spectroscopy have been reported.[8-10]

The optical reflectivity measurement is a powerful probe for the study of the electronic structure of solids. It can provide much information on the conduction bands as well as the valence bands of the crystal through interband transitions. It is an interesting problem for Bi-based cuprates how the excitations within the Bi_2O_2 layer affect those within the CuO_2 layer and how the optical transitions differ from those of Y-Ba-Cu-O and La-Sr-Cu-O. In this paper, we report the results of the optical reflectivity measurement of single-crystal $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-Sr-Ca-Cu-O) and $Bi_2Sr_2CuO_{6+x}$ (Bi-Sr-Cu-O) over a wide energy range from 0.05 to 40 eV.

Single crystals of Bi-Sr-Ca-Cu-O and Bi-Sr-Cu-O were prepared by a usual CuO flux method. Typical dimension of the sample is about $2\times1\times0.1$ mm^3. The sample of Bi-Sr-Ca-Cu-O becomes superconducting at 80 K. The sample of Bi-Sr-Cu-O is metallic but does not show superconductivity above 4.2 K. More detailed fabrication technique and the characterization of the sample were reported in Ref. 11. The reflectivity was measured only with the electric field E of incident light perpendicular to the c axis ($E \perp c$), because the sample was too thin to be measured in the configuration $E \parallel c$. The reflectivity above 2 eV was measured by using the synchrotron radiation as a light source and a 1-m Seya-Namioka monochromator with a typical resolution of 2 Å. Photomultipliers were used as a detector and the absolute value of reflectivity was determined by signal-voltage characteristics of the photomultipliers.

The reflectivity spectra of Bi-Sr-Ca-Cu-O and Bi-Sr-Cu-O are shown in Fig. 1(a). The gross features of the spectra of Bi-Sr-Ca-Cu-O and Bi-Sr-Cu-O are almost the same except for one difference. It is the lowest edge near 1 eV, marked with a filled triangle in Fig. 1(a), which

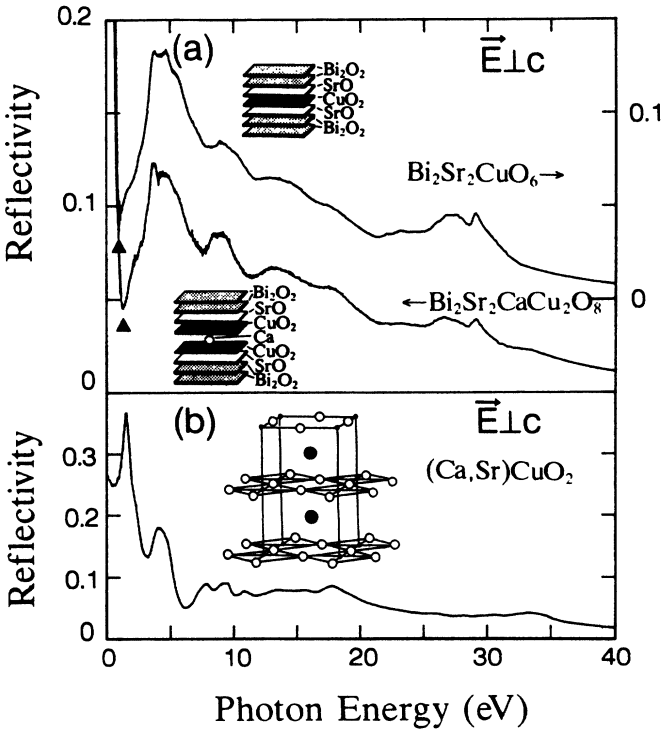

FIG. 1. The optical reflectivity of single-crystal cuprates. The electronic field E of incident light is perpendicular to the c axis of the crystals: (a) $Bi_2Sr_2CuO_{6+x}$ and $Bi_2Sr_2CaCu_2O_{8+x}$; (b) $(Ca,Sr)CuO_2$.

presumably corresponds to the plasma excitation of the free carriers. The position of the edge of Bi-Sr-Ca-Cu-O is about 1 eV, and slightly higher than that of Bi-Sr-Cu-O (~0.9 eV).

One would notice that the spectra of the Bi-based cuprates are different from those of La-Sr-Cu-O and Y-Ba-Cu-O which share common features.[12] The reflectivity spectrum of Bi-Sr-Cu-O is compared with that of La-Sr-Cu-O (from Ref. 12) as shown in Fig. 2. The most distinct feature of the spectra of the Bi-based cuprates is the presence of the peak around 4–5 eV. The definite assignment of this peak is difficult because of the complexity of the crystal structure of the Bi-based cuprates. There are two possible candidates for the origin of the peak at the moment. One is the optical transition within the Bi_2O_2 and/or SrO layers, e.g., between Bi $6p$ and O $2p$, and the other in the CuO_2 layer, e.g., between Cu $3d$ and O $2p$. Of course, it is possible that both excitations overlap with each other.

Fujimori *et al.* have observed the excitations below 6 eV for single-crystal Bi-Sr-Ca-Cu-O by using electron-energy-loss spectroscopy (EELS), and assigned them to the excitations associated with Bi and O.[8] Kelly *et al.* have reported the existence of similar features at 4–5 eV for polycrystalline $Bi_2Sr_2CoO_6$ and $Bi_2Sr_3Fe_2O_9$ as well as those of Bi-Sr-Cu-O and Bi-Sr-Ca-Cu-O through ellipsometry, and speculated that the transition around 4 eV is assigned to the excitation in the Bi_2O_2 layer.[13]

Other cuprates without the Bi_2O_2 layer sometimes show a weak feature near 4 eV in the reflectivity spectrum. An example is the spectrum of single-crystal $(Ca,Sr)CuO_2$, which is regarded as the parent material of the Bi- and Tl-based cuprates, as shown in Fig. 1(b). The oxide $(Ca,Sr)CuO_2$ is an insulating cuprate, and has the layered structure in the sense that CuO_2 and Ca/Sr layers are alternately stacked along the c axis. The transitions associated with Ca and Sr may have little effect on the reflectivity spectrum below ~10 eV for $E \perp c$, because the oxygens around Ca and Sr are completely vacant. So the peak near 4 eV in $(Ca,Sr)CuO_2$ should be assigned to some excitation in the CuO_2 layer.

In the lower-energy region, the spectrum of $(Ca,Sr)CuO_2$ exhibits a pronounced peak at 1.5 eV. The corresponding peak is observable at nearly the same energy for every insulating cuprate including the parent compounds of high-T_c superconductors, such as La_2CuO_4, Nd_2CuO_4, and $YBa_2Cu_3O_6$.[12,13] This peak is observed only when the electric field of light is parallel to the CuO_2 layer,[12,14] so it is reasonably assigned to the charge-transfer excitation from O $2p$ to Cu $3d$ states. The insulating $Bi_2Sr_2YCu_2O_8$ also shows a similar peak at 1.7 eV.[13] The 4-eV peak in $(Ca,Sr)CuO_2$ would thus be the second lowest excitations in the CuO_2 layer (a possible candidate is the transition between Cu $3d_{z^2}$ and $3d_{x^2-y^2}$). The 1.7-eV peak of $Bi_2Sr_2YCu_2O_8$ rapidly loses its intensity when doped with carriers[15] as was also shown in the reflectivity of $(La,Sr)_2CuO_4$ and $(Nd,Ce)_2CuO_4$.[14]

From the fact that the 4-eV feature in Bi-Sr-Ca-Cu-O and Bi-Sr-Cu-O consists of a few peaks and forms relatively stronger and broader absorption band than that in $(Ca,Sr)CuO_2$, excitations in the CuO_2 layer as well as the Bi_2O_2/SrO layers likely contribute to this broad absorption peak. Then it follows that the optical transition around 4 eV is the lowest-energy excitation in the Bi_2O_2/SrO layers and thus the spectrum in the lower-energy region ($\hbar\omega < 2$ eV) is determined only by the excitations in the CuO_2 layer. Actually there are no clear absorptions below 2 eV for Bi-based cuprates except for the plasma excitation of carriers in the CuO_2 layer, as shown in Fig. 3(b). In this regard, the Bi_2O_2/SrO layers might be insulating and have no direct relevance to superconductivity in this system.

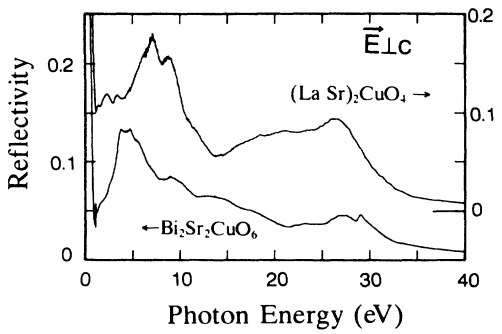

FIG. 2. The optical reflectivity of single-crystal $Bi_2Sr_2CuO_{6+x}$ and $(La,Sr)_2CuO_4$.

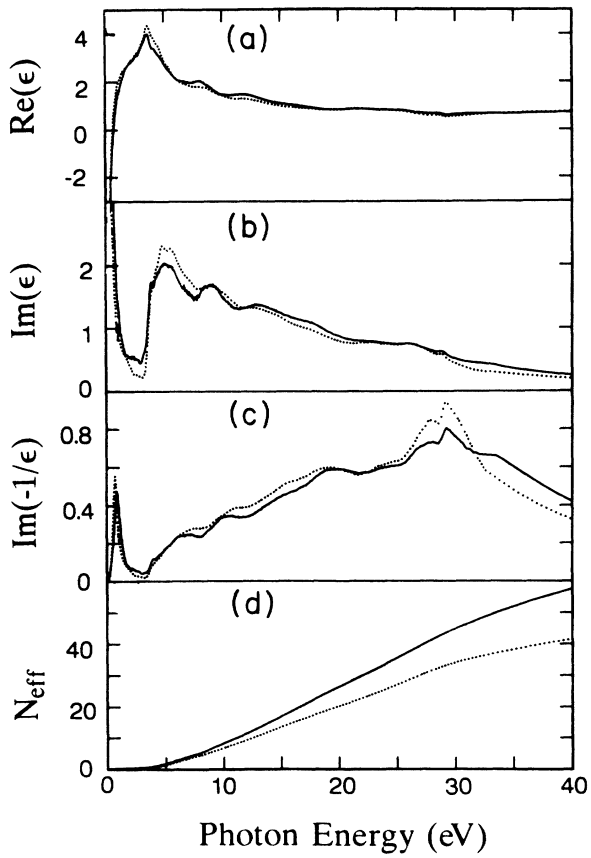

FIG. 3. Results of Kramers-Kronig analysis for $Bi_2Sr_2CaCu_2O_{8+x}$ (solid line) and $Bi_2Sr_2CuO_{6+x}$ (dotted line): (a) real part of $\varepsilon(\omega)$, (b) imaginary part of $\varepsilon(\omega)$, (c) the loss function, and (d) the effective electron number (see text).

Another notable feature is that the spectra in the higher-energy region are different from that of La-Sr-Cu-O or Y-Ba-Cu-O where two distinct reflectivity edges are observed [one is 12–13 eV, and the other is 25–30 eV (Ref. 12)]. The previous paper has revealed that the spectra of La-Sr-Cu-O and Y-Ba-Cu-O in the high-energy region ($\hbar\omega > 4$ eV) are in excellent agreement with the band calculations and are predominantly due to the transitions to the conduction bands composed of La $5d/4f$ in La-Sr-Cu-O and Ba $5d$ in Y-Ba-Cu-O.[12] Both La and Ba atoms are located in the planes including apical sites of oxygen octahedra or pyramids surrounding Cu atoms. Corresponding conduction bands should be derived from Sr $4d$ for the Bi-based cuprates. The circumstances are, however, a little different in Bi-Sr-Ca-Cu-O and Bi-Sr-Cu-O because the O $2p$ orbitals in the SrO layer are strongly hybridized with Bi $6p$ in the Bi_2O_2 layer. As a consequence the strength of the optical transition between O $2p$ and Sr $4d$ becomes weak. This is also the case with $(Ca,Sr)CuO_2$ where the oxygen sites in the Ca/Sr layer are vacant, so that the spectral feature associated with the transitions to the Ca $3d$/Sr $4d$ conduction bands is very weak.

The conduction bands of Bi-based cuprates are more complicated than those of La-Sr-Cu-O and Y-Ba-Cu-O because of the presence of the Bi_2O_2 layer. While the lowest conduction bands of La-Sr-Cu-O and Y-Ba-Cu-O mainly consist of La $5d/4f$ and Ba $5d$, respectively, those of Bi-based cuprates are predominantly composed of Bi $6p$ and O $2p$, according to the band calculations. (O $2p$ is mainly made of O $2p_{x,y}$ in the Bi_2O_2 layer and partially O $2p_z$ in the SrO layer.) Since Bi $6p$ and O $2p$ are strongly hybridized with each other, the lowest conduction bands for Bi-Sr-Cu-O and Bi-Sr-Ca-Cu-O are broader than those for La-Sr-Cu-O and Y-Ba-Cu-O. Although the spectral weight associated with the transitions to these conduction bands seems concentrated in the energy region around 4–5 eV, the interband transitions within the Bi_2O_2 and SrO layers should extend to higher energies and overlap other excitations in the CuO_2 layer.

The Kramers-Kronig (KK) analysis was performed with the measured spectra, and the calculated dielectric functions are shown in Figs. 3(a)–3(d). Since the KK analysis requires the spectra for the entire energy region, the low-energy spectra ($\hbar\omega < 0.05$ eV) were extrapolated by using the Hagen-Rubens fit and the high-energy spectra ($\hbar\omega > 40$ eV) were extrapolated by using the relation $R(\omega) \propto \omega^{-4}$. In Fig. 3(a), the plasma excitations of free carriers are clearly shown at $\mathrm{Re}[\varepsilon(\omega)] = 0$. The plasma frequency for Bi-Sr-Ca-Cu-O is larger than that for Bi-Sr-Cu-O, as was already described. In Fig. 3(b), no clear absorption is seen below 3 eV except for that centered at $\hbar\omega \sim 0$ eV. So it can safely be said that the low-energy excitation is dominated by the carriers in the conducting CuO_2 layer. In $\mathrm{Im}[-1/\varepsilon(\omega)]$ spectrum [Fig. 3(c)], a peak is observed near 20 eV, which can be assigned to the end of the excitations involving all the valence electrons in the CuO_2 layer. Since the excitations in the Bi_2O_2 and SrO layers are present and extending to higher-energy region, the peak near 20 eV is not isolated. Above 20 eV, the transitions from the core levels of Bi as well as the valence bands dominate in the spectra. Sharp structures near 26–27 and 29 eV are clearly seen both in Bi-Sr-Ca-Cu-O and Bi-Sr-Cu-O, which are assigned to the transitions from spin-orbit split Bi $5d$ to Bi $6p$ and/or O $2p$. The energy difference of the peaks coincides with the spin-orbit splitting of Bi $5d$.[16]

The obtained spectrum of $\mathrm{Im}[-1/\varepsilon(\omega)]$ for Bi-Sr-Ca-Cu-O is in agreement with the results measured by Nucker *et al.* with EELS.[9] The peaks in $\mathrm{Im}[-1/\varepsilon(\omega)]$ obtained from EELS seem to be more emphasized than those from the optical measurement. The effective electron number $N_{\mathrm{eff}}(\omega)$ is calculated through the relation as

$$N_{\mathrm{eff}}(\omega) = \frac{m}{2\pi^2 e^2} \int_0^{\omega} \omega' \mathrm{Im}[\varepsilon(\omega')] d\omega' .$$

As is shown in Fig. 3(d), N_{eff}'s at 40 eV are about 41 and 57 for Bi-Sr-Cu-O and Bi-Sr-Ca-Cu-O, respectively. The formal numbers of the valence electrons per unit cell for Bi-Sr-Cu-O and Bi-Sr-Ca-Cu-O (N_{total}) are 45 and 66, respectively. (We assume that the valence bands consist only of Cu $3d$ and O $2p$, and valence electrons are composed of nine $3d$ electrons per Cu and six $2p$ electrons per O. For example, N_{total} of $Bi_2Sr_2CuO_6$ is $1\times9+6\times6 = 45$.) It has already been found out that N_{eff} at 40 eV roughly represents the number of the valence electrons in the case of La-Sr-Cu-O and Y-Ba-Cu-O,[12] but the electronic states of the Bi-based cuprates are more complicated because the contributions of the excitations from the Bi_2O_2 layer overlap. As a matter of fact, the transitions from Bi $5d$ are clearly seen above 20 eV. $N_{\mathrm{eff}}(\omega)$'s of Bi-Sr-Ca-Cu-O and Bi-Sr-Cu-O are not well saturated, which means that the excitations of valence electrons extend above 40 eV. Therefore, it is difficult to compare $N_{\mathrm{eff}}(\omega)$ at 40 eV with N_{total} for Bi-based cuprates. Nonetheless, we emphasize that $N_{\mathrm{eff}}(\omega)$ at 40 eV correlates well with N_{total}. Table I lists the calculated $N_{\mathrm{eff}}(\omega)$ at 40 eV and N_{total} for La-Sr-Cu-O, Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, and Bi-Sr-Cu-O. The material which has larger N_{total} shows larger $N_{\mathrm{eff}}(\omega)$, therefore the correlation between $N_{\mathrm{eff}}(\omega)$ and N_{total} is also valid for the Bi-based cuprates.

In summary, we have measured and analyzed the optical reflectivity spectra of single-crystal Bi-based cuprates, $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ ($n = 1$ and 2). The obtained spectra are apparently different from $(La,Sr)_2CuO_4$ and $YBa_2Cu_3O_x$, and the reason may be as follows: The lowest conduction band consists of Bi $6p$ and O $2p$ in

TABLE I. The calculated effective electron number $N_{\mathrm{eff}}(\omega)$ at 40 eV and the formal valence electron number N_{total} in Cu $3d$ and O $2p$ states for various superconducting cuprates (see text).

Material	$N_{\mathrm{eff}}(\omega)$ at 40 eV	N_{total}
$(La,Sr)_2CuO_4$ [a]	27	33
$YBa_2Cu_3O_7$ [a]	58	69
$Bi_2Sr_2CaCu_2O_8$	57	66
$Bi_2Sr_2CuO_6$	41	45

[a]Reference 12.

Bi_2O_2/SrO layers and the position is lower in energy as compared with the La $5d/4f$ or Ba $5d$ conduction bands in $(La,Sr)_2CuO_4$ or $YBa_2Cu_3O_x$ (but perhaps does not cross the Fermi level). Since the CuO_2 layer is well separated in space from the Bi_2O_2 layer, the excitations within Bi_2O_2 and SrO layers are rather independent of those in CuO_2 layer, and form characteristic and complicated reflectivity spectra. The Kramers-Kronig analysis has been performed, and the obtained dielectric function is in agreement with the results of the electron-energy-loss spectroscopy measurement.

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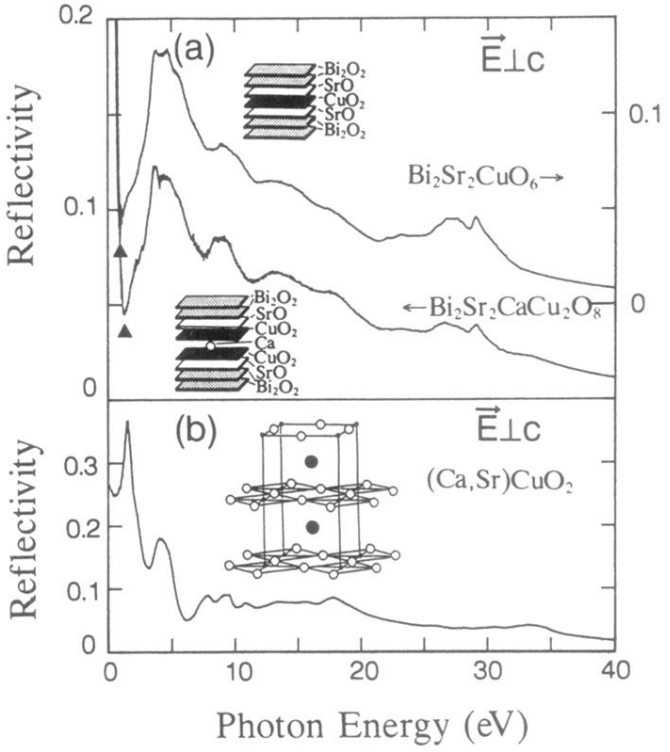

FIG. 1. The optical reflectivity of single-crystal cuprates. The electronic field E of incident light is perpendicular to the c axis of the crystals: (a) $Bi_2Sr_2CuO_{6+x}$ and $Bi_2Sr_2CaCu_2O_{8+x}$; (b) $(Ca,Sr)CuO_2$.