Microscopic Studies of the Optical Spectra of $YBa_2Cu_3O_7$

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Microscopic studies of the optical spectra of $YBa_2Cu_3O_7$ have been done using the linear-muffin-tin-orbital (LMTO) method for solving the band-structure problem. Special attention has been paid to the midinfrared and visible spectral range where a number of peculiarities including the large anisotropy of the optical reflectance was observed. It is shown that the overall features of the observed optical spectra can be well explained in the framework of the usual band-structure approach. Moreover, the anisotropy of the reflectance in the *a-b* planes and the positions of the main interband transitions are also in good agreement with available experimental data.

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One of the most important problems arising in studies of the high-T_c superconductors is the electronic structure of these compounds. It has been the subject of intense study using a number of different methods. Various forms of both high-energy and low-energy spectroscopies have been applied. The investigation of optical spectra has an advantage due to the long penetration depth of the light. The early investigations of ceramics were not so representative due to the very anisotropic character of these compounds. Recently a number of investigations of oriented films and twinned crystals has been published.[1-5] But only a few publications exist on single-domain reflectance from crystals. $EuBa_2Cu_3O_7$ [6,7] and $YBa_2Cu_3O_7$ [8,9] both show a rather large anisotropy in the reflectance for *a*-axis and *b*-axis polarizations.

The experimental data concerning oriented films and twinned crystals and their interpretations are rather contradictory. The main disagreement concerns the infrared spectral range and, in particular, the frequency and temperature dependence of the conductivity. But a central question regarding the normal-state infrared properties is whether the conductivity is most appropriately described in terms of a frequency-independent scattering rate and carrier mass, or as a superposition of a free-carrier band with a frequency-dependent scattering rate and some type of midinfrared interband transitions. In the energy region above 5 eV, there is sufficiently good agreement between all the investigations. For this energy region, as it was shown for La compounds,[3] there is also excellent agreement between the experimental data and theoretical calculations[10] based on the linear-muffin-tin-orbital (LMTO) method.

In this work, we have calculated the optical spectra of $YBa_2Cu_3O_7$ over a wide spectral range (up to 40 eV). In the energy region above 5 eV, we also find good agreement with both the optical reflectivity spectra and the electron-energy-loss spectra obtained experimentally. The details of our work will be published elsewhere, but we would like to concentrate here on the infrared and visible range of the optical spectra. To obtain the optical spectra we have calculated first the electronic structure of $YBa_2Cu_3O_7$ using the self-consistent LMTO method[11] with the local-density approximation for the exchange and correlation potential. Our result for the band structure agrees well with the calculations made by others.[12,13] The calculation of the imaginary part of the dielectric function (DF) $\epsilon_2(\omega)$ was performed by the method described previously.[14,15] We used 242 points in $\frac{1}{8}$ of the Brillouin zone. The LMTO basis set was chosen as *s*, *p*, *d*, and *f* orbitals for YBa and Cu and *s*, *p*, and *d* orbitals for O. The integration over the Brillouin zone was made using 600 tetrahedrons. The real part of the DF $\epsilon_1(\omega)$ was obtained by the Kramers-Kronig relation. It allows us to obtain the conductivity $\sigma(\omega)$, and the reflectivity $R(\omega)$. We have used the Drude model for the description of the intraband contribution to DF

$$\epsilon(\omega)=1-\frac{\omega_p^2}{\omega(\omega+i\gamma)},$$

where ω_p and γ are the plasma frequency and the scattering rate of the Drude carriers. The plasma energy was calculated in terms of the mean-square value of the electron velocity at the Fermi surface, while the scattering rate was fitted to the resistivity at $T=300$ K. Because of the orthorhombic structure of $YBa_2Cu_3O_7$ the DF becomes a tensor quantity with three nonequal components $\epsilon_{xx}(\omega)\neq\epsilon_{yy}(\omega)\neq\epsilon_{zz}(\omega)$. We calculated all three of these components.

Figure 1 shows the interband conductivity for the three axes in the energy interval $0\leq\hbar\omega\leq 6$ eV. Comparing the conductivity for the different polarizations, we note first the large anisotropy of these quantities. The conductivity for the *a* axis shows the pronounced peak at 0.2 eV and following background up to 4 eV. These transitions arise from the excitations of electrons in the Cu(2)-O(2) planes. The same maximum in $\sigma(\omega)$ exists also for the *b* axis. However, there are two additional peaks for the *b*-axis polarization at energies 0.45 and 0.75 eV. These transitions have a very large oscillator strength with corresponding effective electron number

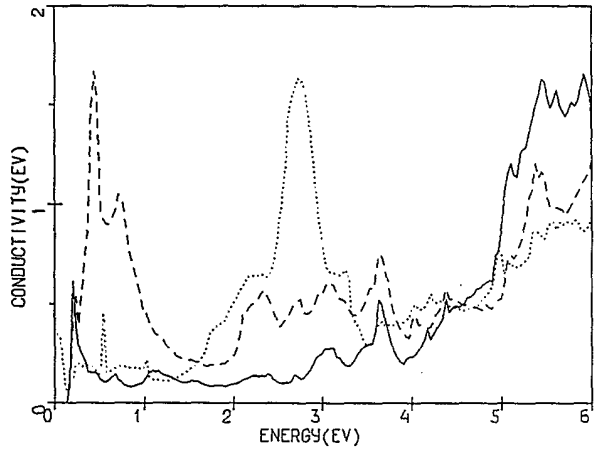

FIG. 1. The conductivity for the a axis (solid curve), b axis (dashed curve), and c axis (dotted curve).

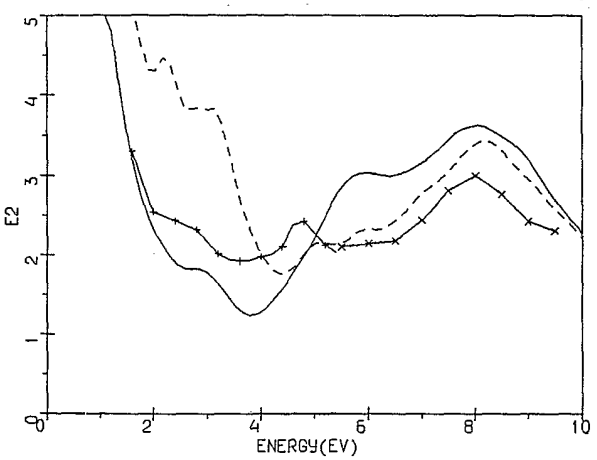

FIG. 2. The imaginary part of the dielectric function $\epsilon_2(\omega)$ for the polarization along the a axis (solid curve), b axis (dashed curve), and the experimental results obtained by Garriga *et al.* (Ref. 16) (crosses).

N^{eff} equal to 0.4 and 0.25 per cell, respectively. The value N^{eff} is determined as

$$N^{\text{eff}} = \frac{m}{2\pi^2 e^2}\int_{\omega_1}^{\omega_2} \omega\epsilon_2(\omega)d\omega,$$

where ω_1 and ω_2 represent the beginning and the end of a transition. The oscillator strength for the transition in the a-axis spectrum at 0.2 eV is 1 order of magnitude smaller. Both these transitions (0.45 and 0.75 eV) involve electrons in the Cu(1)-O(1) chains. The difference in the oscillator strength between the transitions along the a and b axes is caused by the states in the region near the Fermi energy. As can be seen easily from the work Krakauer, Pickett, and Cohen[13] the state density in the interval 1 eV below the Fermi energy belongs mainly to the chain states.

For the polarization $\mathbf{E}\parallel\mathbf{c}$, the interband transitions start from very low energies ≈ 0.03 eV. These transitions exist in the energy interval $0.03 \leq \hbar\omega \leq 0.1$ eV and have $N_{\text{eff}} = 0.02$. The origin of these transitions is the existence of two nearly degenerate quasi-two-dimensional bands related to the existence of two Cu(2)-O(2) planes per unit cell. As a result of the weak interaction between these planes, the bands are split by a small value which determines the characteristic energies of these transitions. We also note the existence of the narrow peak at 0.55 eV caused by the excitation of electrons in the bridge Cu(1)-O(4)-Cu(2) linking chains and planes. Finally we should point out the very intense peak at the energy $=2.8$ eV with $N_{\text{eff}} = 1.3$. This peak is also caused by electron excitations in the bridge Cu(1)-O(4)-Cu(2) first of all due to the polarization of the oxygen O(4). In conclusion, we should mention that the intraband transitions are also very anisotropic. The intraband plasma energies are $\hbar\omega_p^a = 3.51$ eV, $\hbar\omega_p^b = 4.2$ eV, and $\hbar\omega_p^c = 1.05$ eV for a, b, and c axes, respectively.

Because of the large anisotropy it is very hard to give a direct interpretation of the data obtained on twinned films and crystals even for light polarization parallel to the a-b plane. These data are some unknown average along the a and b axes. Figures 2 and 3 show the calculated values $\epsilon_2(\omega)$ and $\epsilon_1(\omega)$ for the polarizations $\mathbf{E}\parallel\mathbf{a}$ and $\mathbf{E}\parallel\mathbf{b}$. Also shown on the same figures are the results of the ellipsometric measurements made by Garriga *et al.*[16] on twinned crystals for $\mathbf{E}\perp\mathbf{c}$ in the energy interval $1.7 \leq \hbar\omega \leq 5.5$ eV and on ceramic samples in the energy interval $5.5 \leq \hbar\omega \leq 9.5$ eV. It can be seen that there is good agreement between the calculated values and the experimental ones. It is interesting to note that the experimental curve is closer to the theoretical one obtained for a-axis polarization. We speculate that the chains in the samples used by Garriga *et al.* were damaged moderately by the oxygen deficiency.

Figure 4 shows the calculated curves for the reflectivity $R(\omega)$ for the polarizations $\mathbf{E}\parallel\mathbf{b}$ and $\mathbf{E}\parallel\mathbf{a}$. We

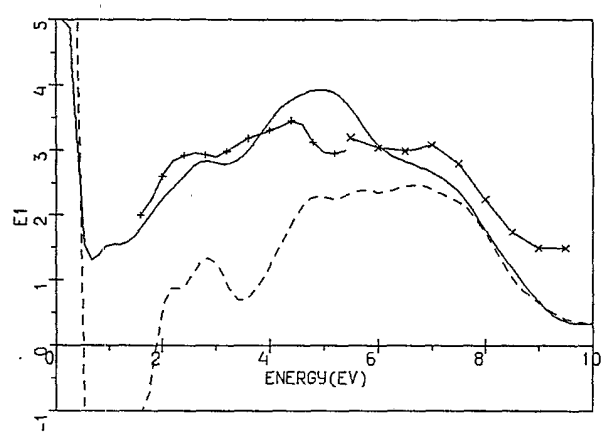

FIG. 3. The real part of dielectric function $\epsilon_1(\omega)$. The symbols are the same as in Fig. 2.

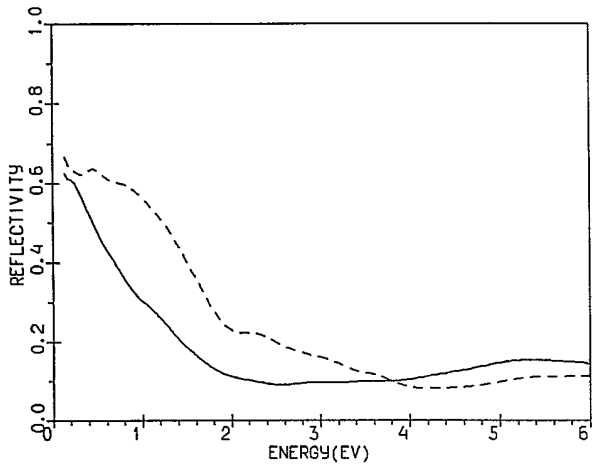

FIG. 4. The reflectivity along the a axis (solid curve) and b axis (dashed curve).

would like to emphasize two main peculiarities of these curves. First, the reflectivity $R^b(\omega)$ in the b direction exceeds appreciably the value $R^a(\omega)$ in the energy interval $0.1 \leq \hbar\omega \leq 3$ eV. The same behavior of $R^b(\omega)$ and $R^a(\omega)$ was observed experimentally in Refs. 6–9. However, the curves $R^b(\omega)$ and $R^a(\omega)$ were observed to cross in these papers at some low energy $\simeq$1.5–2.8 eV. Second, there is a pronounced peculiarity on the curve $R^b(\omega)$ in the energy region $\simeq$0.4 eV connected with the strong interband transition. The very similar behavior of $R^b(\omega)$ was also observed previously.[6–9] The position of this anomaly does not coincide with the calculated one. But the experimental evidence of this anomaly is also contradictory. There is some evidence[5,17] about the existence of this anomaly, namely, at 0.4 eV.

The experimental data have also confirmed the calculated difference of the oscillator strength for the interband transitions in the a and b axes.

We would emphasize that the energy and the oscillator strength of the midinfrared transitions in the a-b planes depend crucially on the oxygen content in $YBa_2Cu_3O_{7-x}$. An oxygen removal from the chains can lead to the shift of the Fermi level and a destruction of electronic states near the Fermi level. As a result the midinfrared transitions can change radically or disappear altogether.

In conclusion, we have calculated the optical properties of $YBa_2Cu_3O_7$ and obtained good agreement with the overall features of the observed spectra at least for the energies above 0.2 eV. Returning to the previously mentioned discussion about the normal-state infrared properties, we would like to note that the existence of the midinfrared transitions in the a-b planes above 0.1 eV cannot be questioned. But the interband transitions give both the rather narrow peaks in the conductivity $\sigma(\omega)$ and the pronounced background, as can be seen from Fig. 1. We should emphasize again that the very existence of the peaks and the values of their width depend crucially on the quality of crystals and on the oxygen content. The destroyed peaks together with the background can be easily interpreted as the broad interband transitions with the width $\simeq$1 eV.[5] The interband transitions for the $\mathbf{E} \| \mathbf{c}$ exist even at lower energies and they can also give the contribution in the reflectivity for the polydomain crystals even though the main part of the reflectivity connects with the a-b plane. Additional measurements of the single-domain reflectance are very important for understanding the electron structure of the new superconductors. But, on the other hand, it is clear that the optical spectra at energies lower than 0.1 eV cannot be described in terms of free-carrier band. The processes of the dynamic interaction at energies comparable with the characteristic phonon and spin-wave frequencies are very important but they go beyond the possibilities of first-principle calculations.

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