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Theoretical calculation of optical properties of Y-Ba-Cu-O superconductors

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The optical properties of orthorhombic $YBa_2Cu_3O_7$ crystal are studied by a first-principles method. The interband optical conductivity shows strong directional anisotropy in the 0–3.0 eV range. A plasmon energy of 2.8 eV is predicted. Analysis of the static dielectric constant in the case of a semiconductorlike band structure supports the excitonic-enhanced superconducting mechanism in the Y-Ba-Cu-O system.

The discovery of the superconducting La-*M*-Cu-O and Y-Ba-Cu-O systems with superconducting transition temperatures T_c above 35 and 90 K, respectively, has spurred great deal of experimental and theoretical investigations on these materials.[1-5] The nature of electron states in these materials plays a key role in understanding the properties and the possible superconducting mechanism in these complex ceramic oxides. The electronic structure of $YBa_2Cu_3O_7$ has been studied by the linearized augmented plane wave method[6-8] and the linear combination of atomic orbitals (LCAO) method.[9] In this paper, we report the first calculation on the optical properties of $YBa_2Cu_3O_7$ crystal in order to gain a deeper understanding of the unusual electronic structure of this material and to provide further evidence of the possible superconducting mechanism in $YBa_2Cu_3O_{7-\delta}$. Because of the difficulty in obtaining sufficiently large single-phase crystals and of performing the proper surface treatment, no experimentally measured optical data on $YBa_2Cu_3O_{7-\delta}$ in the ultraviolet or visible frequency range exists in the literature. Optical measurements in the far-infrared region[10] and Raman spectra[11] on $YBa_2Cu_3O_{7-\delta}$ have been reported. Only very recently, additional results on optical measurements on the Y-Ba-Cu-O system in a more extended spurred frequency range have appeared.[12-15]

Our theoretical calculation of optical properties is done for $YBa_2Cu_3O_7$ in the orthorhombic phase using the crystal-structure data of Beno *et al.*[16] The band structure of this crystal has been calculated using the first-principles self-consistent orthogonalized LCAO method and detailed results will be reported elsewhere in a longer paper.[17] The band structure along the symmetry lines Γ-*X*-*S*-*Y*-Γ of the lower plane of the Brillouin zone (BZ) is shown in Fig. 1. The band structure in the upper plane (*Z*-*U*-*R*-*T*-*Z*) is almost identical and there is very little band dispersion along the vertical k_z direction. Using the wave functions obtained at 147 **k** points in $\frac{1}{8}$ of the BZ, the momentum matrix elements $\langle\psi_n(k)|\mathbf{P}|\psi_l(\mathbf{k})\rangle$ between the occupied state $\psi_n(\mathbf{k})$ and the unoccupied state $\psi_l(\mathbf{k})$ for $|E_n(\mathbf{k})-E_l(\mathbf{k})|<10.0$ eV were evaluated. The interband optical conductivity was then calculated in the dipole approximation according to the Kubo-Greenword formalism:[18]

$$\sigma_I(\omega)=\frac{2\pi e^2\hbar}{3m^2\omega\Omega}\sum_{n,l}\int d\mathbf{k}\,|\langle\psi_n(\mathbf{k})|\mathbf{P}|\psi_l(\mathbf{k})\rangle|^2 f_l(\mathbf{k})[1-f_n(\mathbf{k})]\delta(E_n(\mathbf{k})-E_l(\mathbf{k})-\hbar\omega). \quad (1)$$

The linear analytic tetrahedron method was used for the BZ integration in (1) based on 432 tetrahedrons generated by the 147 **k** points in the irreducible portion of the BZ. No attempt was made to include the effect of finite-lifetime broadening. Because the crystal is highly anisotropic, it is necessary to present the σ_{xx}, σ_{yy}, σ_{zz} components of σ_I, which are shown in Fig. 2. It is evident that σ_{zz} is very much different from σ_{xx} and σ_{yy} in the region of 0–3 eV which is related to the quasi-two-dimensional characteristic of the electronic structure of $YBa_2Cu_3O_7$. The absorption in the *z* direction is much larger than in either the *x* or *y* direction in this region. A crossover occurs at about 5.2 eV, above which the absorption in the *z* direction becomes smaller than in the perpendicular directions. There are some subtle differences between σ_{xx} and σ_{yy}, as well as in this energy range, reflecting the presence of the

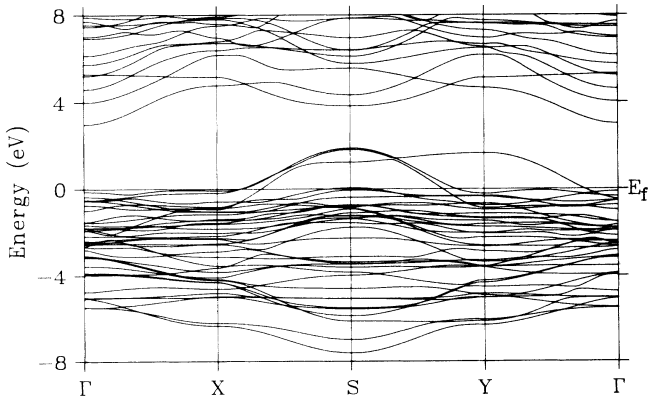

Fig. 1. Energy bands of $YBa_2Cu_3O_7$.

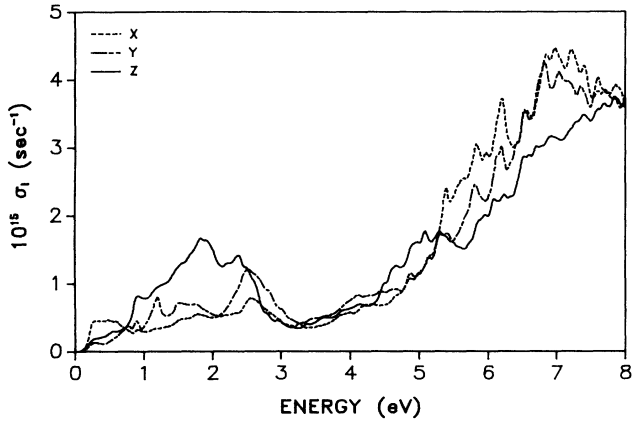

FIG. 2. x,y,z components of interband optical conductivity in $YBa_2Cu_3O_7$.

one-dimensional O_1-Cu_1 chain along the **b** axis and the absence of O atoms along the **a** axis in the $z=0$ plane. It is difficult to associate the structures in the optical conductivity curve with transitions involving specific pairs of bands because of the multiplicity in the manifold band structures. In order to investigate further the nature of optical anisotropy in $YBa_2Cu_3O_7$, we plot in Fig. 3 the energy dependence of the square of the components of the optical matrix elements in the same energy range. Below 5 eV, the variation of the squares of the components is much smaller than the variation in the optical-absorption spectra of Fig. 2. Thus, the anisotropy in the optical-absorption is not entirely due to the symmetry of the wave functions of the states involved in the optical transitions, as reflected by the selection rules, but is mostly due to the distribution of the states of different symmetries near the Fermi level and in the vicinity of the semiconductorlike gap. The peak at 2 eV in Fig. 2 is a direct reflection of the transitions from the high-density-of-states (DOS) region between 0 to -2.0 eV to the relatively flat, low-density hole region from 0–1.9 eV.

From the interband optical conductivity, the real and imaginary part of the dielectric function, ϵ_1 and ϵ_2 were evaluated through the Kramers-Kronig relation. From ϵ_1 and ϵ_2, the energy-loss function (ELF) $F(\omega)$ defined as

$$F(\omega) = -\mathrm{Im}\left[\frac{1}{\epsilon}\right] = \frac{\epsilon_2(\omega)}{\epsilon_1^2(\omega)+\epsilon_2^2(\omega)}, \tag{2}$$

was extracted (see Fig. 4). $F(\omega)$ has a well-defined peak at $\omega_p = 2.8$ eV which is the plasmon frequency for $YBa_2Cu_3O_7$. This plasma frequency is much smaller than those of a typical semiconductor such as Si ($\omega_p \approx 17$ eV). This plasmon peak has a full width at half maximum of 0.9 eV and there is another smaller peak at 2.0 eV. From Fig. 3, it is clear that this value of the plasmon frequency is due to the fact that ϵ_1 and ϵ_2 have minima at roughly 2.7 and 3.3 eV, respectively. The reason for the minimum in ϵ_2 can be traced to the semiconductorlike band structure of $YBa_2Cu_3O_7$ shown in Fig. 1. Although the Fermi surface is located about 1.9 eV below the top of the valence band at S, there exists a well-defined gap above S. The bottom of the conduction band is at Γ with an indirect band gap of 1.06 eV and a direct band gap of 1.54 eV at S. The unoccupied region below the top of the valence band (VB) accommodates exactly four holes, and transition of occupied electrons to this hole region accounts for most of the low-energy optical absorption below 3 eV. The presence of the gap between 1.9–3.0 eV above E_f results in a minimum in the optical absorption near 3 eV and ultimately gives rise to a plasmon peak at 2.8 eV. The existence of another plasmon peak at higher energy, where ϵ_1 cuts through zero, should not be ruled out. A recent muon-spin-relaxation measurement[19] indicates that ω_p in $YBa_2Cu_3O_{7-\delta}$ is probably in the range of 1.2–1.6 eV. In analyzing the optical transition data in the high-frequency range, Sulewski *et al.*[14] found they have to use the plasmon frequency value of 2.6 eV to obtain a good fit. Similarly, Orenstein *et al.*[12] used $\omega_p = 3.0$ eV and obtained an excellent fit to their reflectivity spectrum up to 3 eV. These ω_p values are fully consistent with our calculated value of 2.8 eV.

The intraband optical transition is more difficult to treat. Far-infrared optical data from different work-

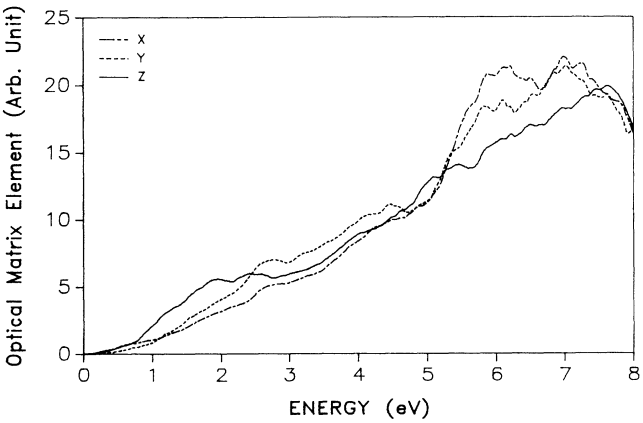

FIG. 3. x,y,z components of the square of the interband optical matrix elements in $YBa_2Cu_3O_7$.

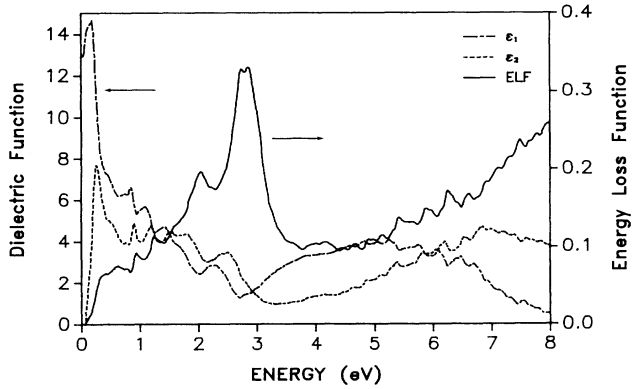

FIG. 4. The real and imaginary parts of the dielectric constants ϵ_1 and ϵ_2 and the electron energy-loss function in $YBa_2Cu_3O_7$.

ers[12-15] are not all consistent and have led to different interpretations. A lot of these inconsistencies have to do with different sample conditions and different ways to correct them. Kamaras *et al.*[15] concluded that the frequency-dependent conductivity is decidedly non-Drude in form while the reflectivity spectrum of Wrobel *et al.*[13] shows a smooth, Drude-like decrease over the frequency range up to 700 cm^{-1}. But Orenstein *et al.*[12] are of the opinion that optical transitions in both $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ cannot be described by the nearly free-electron model. Sulewski *et al.*[14] argued that free carriers are present and conductivity can be analyzed in terms of the Drude model with a frequency-dependent scattering rate. All these indicate that electron states of the carriers near the Fermi energy in $YBa_2Cu_3O_{7-\delta}$ are very different from those of a conventional free-electronlike metal such as copper. Obviously, more theoretical work is needed to address the intraband optical process in this class of materials where the carriers may be both electrons and holes with large effective masses. Nevertheless, even though the intraband transitions from both electron-electron and hole-hole contribution may be present, it is probably limited to a very low-energy range (<0.1 eV). The interband transitions should dominate the whole frequency range above the far-infrared region.

The static dielectric function ϵ_0 of $YBa_2Cu_3O_7$ can be obtained from the sum rule

$$\epsilon_0=\epsilon_1(0)=1+\frac{2}{\pi}\int_0^\infty \frac{\epsilon_2(\omega')}{\omega'}d\omega'. \tag{3}$$

For pure interband transition averaged over the three directions, a value of 12.9 for ϵ_0 is obtained. This value is lower than most of the semimetals. If a finite value of intraband contribution at $\omega=0$ is to be included, the value of ϵ_0 will be increased. In evaluating Eq. (3), the upper integral limit is set at 15 eV, however, because of the ω^{-1} dependence of the integrand and the fact that the oscillator strength starts to drop for energy higher than 8 eV, it is estimated that the higher-frequency contribution of the integral in Eq. (3) is generally less than 1.5%.

In a recent Letter,[9] we presented an argument for an excitonic-enhanced high-T_c superconducting mechanism in $YBa_2Cu_3O_{7-\delta}$. The original model was suggested more than two decades ago by Jerome, Rice, and Kohn[20] and was subsequently studied in considerable detail by Wong and co-workers.[21,22] The idea is based on the formation of excitons between electrons in the conduction-band (CB) minimum and holes at the maximum of the unfilled VB such that the binding energy $|E_B|$ is slightly larger than E_g, the "band gap" in the semiconductorlike band structure. The excitation gap Δ_{ex}, due to the formation of exciton, enhances the BCS gap Δ_{BCS} to obtain the total excitation gap according to $\Delta_T^2=\Delta_{BCS}^2+\Delta_{ex}^2$, thus providing a possible mechanism for high T_c. Since $|E_B|$ is approximately given by[23]

$$|E_B|\approx hc(\mu^*/m)\left[\frac{1}{\epsilon_0^2}\right]\mathcal{R}\ , \tag{4}$$

where $\mathcal{R}$ is the Rydberg constant, and μ^* is the effective mass of the exciton, μ^* can be accurately estimated from the calculated band structure and E_B must be very close to E_g, so it was concluded that ϵ_0 for $YBa_2Cu_3O_{7-\delta}$ should be in the range of 3–7 in order for the excitonic-enhancement mechanism to be operational. It should be pointed out that ϵ_0 in (4) is the pure interband part associated with a semiconductorlike band structure with a well-defined "gap." The presence of O defect in $YBa_2Cu_3O_{7-\delta}$, or the replacement of O by F,[24] makes the materials superconducting with high T_c. In the absence of detailed electronic structure and optical calculation for $YBa_2Cu_3O_{7-\delta}$ or Y-Ba-Cu-F-O system, it is fair to conclude that the effect of these on the band structure of $YBa_2Cu_3O_7$ is to raise the Fermi level, thereby reducing the hole region near the top of the unfilled VB and making the band structure more semiconductorlike. In order to estimate the possible value of ϵ_0 for such systems, we have repeated our calculation of $\epsilon_2(\omega)$ (and hence ϵ_0) by shifting E_F to be at the top of VB at S, while keeping all the states unchanged. We have obtained a value of 3.21 for ϵ_0. Thus, it appears that the interband part of the static dielectric function for the high-T_c oxide systems falls into the range required for the excitonic-enhanced superconducting mechanism to be operational.

In conclusion, we have calculated the interband optical properties of $YBa_2Cu_3O_7$ from first principles. The results show a strong anisotropic effect due to the two-dimensional characteristic of the band structure. From the computed electron-energy-loss spectra, a plasmon frequency of 2.8 eV is predicted. Analysis of the interband part of the static dielectric function for a semiconductorlike band structure supports the excitonic-enhanced superconducting mechanism for $YBa_2Cu_3O_{7-\delta}$.

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