Optical properties of metal oxides of the La_2CuO_4 type

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The electronic structure and optical spectra of the compound La_2CuO_4 in the tetragonal phase are calculated "from first principles." The results show that all the basic features of the observed reflection spectrum can be explained by the conventional band approach.

Measurements of the frequency dependence of the optical reflection coefficient $R(\omega)$ of the surface of polycrystalline $La_{2-x}Sr_xCuO_4$ have yielded several unexpected results[1–4] (Fig. 1).

In the first place, two sharp dips ("plasma edges") in $R(\omega)$ are found, at $\hbar\omega \approx 0.08$ eV and $\hbar\omega \approx 0.8$ eV. Second, slight oscillations due to optical phonons are observed in $R(\omega)$. Furthermore, there is an anomalously large structural feature of the phonon type at $\hbar\omega \approx 0.07$ eV (ordinarily, even in very poor metals, the phonon contribution is difficult to discern against the background of the large intraband dielectric constant). The dielectric constant reconstructed with the help of the Kramers-Kronig relations, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, exhibits a strong absorption with an energy $\hbar\omega \approx 0.5$ eV, contradicting the band structure calculated for La_2CuO_4 "from first principles."[5–7] In this connection, it has been concluded in several papers that the ordinary band picture does not apply to this compound and that it contains some special multielectron low-energy excitations. We should state at the outset that the highly anisotropic compound La_2CuO_4 cannot be described by a single dielectric constant $\epsilon(\omega)$, and it becomes necessary to deal with a dielectric-constant matrix $\epsilon_{\alpha\beta}(\omega)$. We know that in the case of tetragonal crystals, two of the diagonal elements of this matrix are the same, and they differ from the third: $\epsilon_{xx} = \epsilon_{yy} \neq \epsilon_{zz}$. Since the relationship between $R(\omega)$ and $\epsilon(\omega)$ is strongly nonlinear ($R = |(\sqrt{\epsilon} - 1)/(\sqrt{\epsilon} + 1)|^2$), the application of the isotropic Kramers-Kronig procedure to $R(\omega)$ found from polycrystalline samples, with a pronounced local anisotropy, is incorrect. The dielectric constant $\epsilon(\omega)$ found by such a procedure is not a dielectric constant averaged over polarizations; it is in fact totally devoid of physical meaning.

In order to analyze this situation, we carried out some calculations on the optical spectra of La_2CuO_4 single crystals in the tetragonal phase. We calculated the diagonal elements of the tensor $\epsilon_{\alpha\beta}(\omega)$ ($\epsilon^{\parallel}$ and $\epsilon^{\perp}$), which describe the response to an electromagnetic field with polarizations $\mathbf{E}\|\mathbf{c}$ and $\mathbf{E}\perp\mathbf{c}$, respectively ($c$ is the optic axis). These calculations were carried out on the basis of the band structure found by the conventional method.[7] The procedure is described in Ref. 8. As we will see below, the results of these calculations give an essentially comprehensive description of the features in

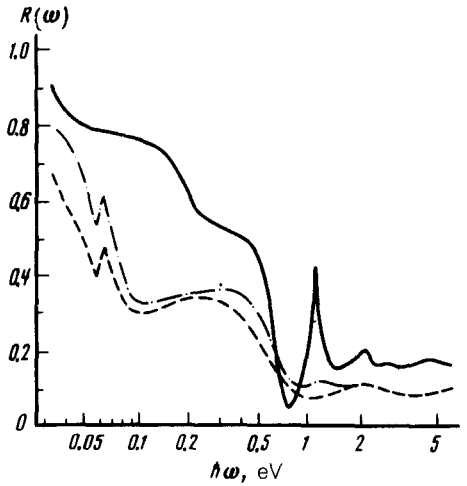

FIG. 1. Experimental and theoretical curves of the reflection coefficient of a polycrystalline sample. Solid line—Theoretical; dashed line—experimental[1]; dot-dashed line—experimental.[4]

the observed $R(\omega)$ spectra which we have mentioned, without the need to appeal to the specific multielectron effects.

In analyzing our results, we note a difference in the positions of thc plasma edges: In the case $\mathbf{E}\|\mathbf{c}$ the energy of this edge is 0.2 eV, while in the case $\mathbf{E}\perp\mathbf{c}$ it is 0.6 eV (Figs. 2 and 3). This difference is due primarily to the different velocities of the electrons along and across the layers. According to the Drude formula,

$$\epsilon(\omega) = \epsilon_{inter}(\omega) - \tilde{\omega}_p^2/[\omega(\omega + i\gamma)], \tag{1}$$

where ϵ_{inter} is the interband-transition component of ϵ, and

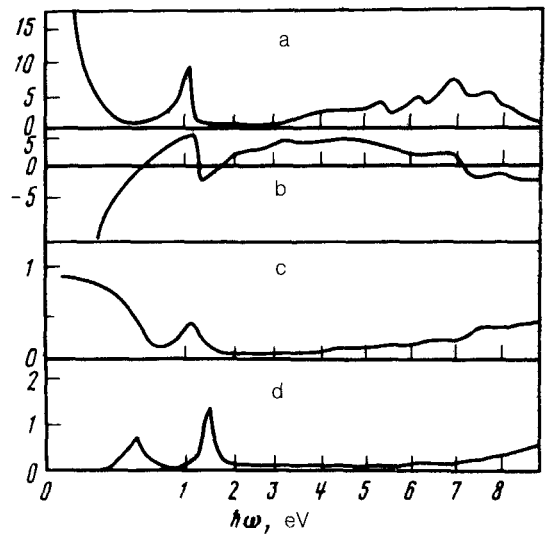

FIG. 2. Optical characteristics for the polarization $\mathbf{E}\perp\mathbf{c}$. a—$\epsilon_2(\omega)$; b—$\epsilon_1(\omega)$; c—$R(\omega)$; d—$\mathrm{Im}[-1/\epsilon(\omega)]$.

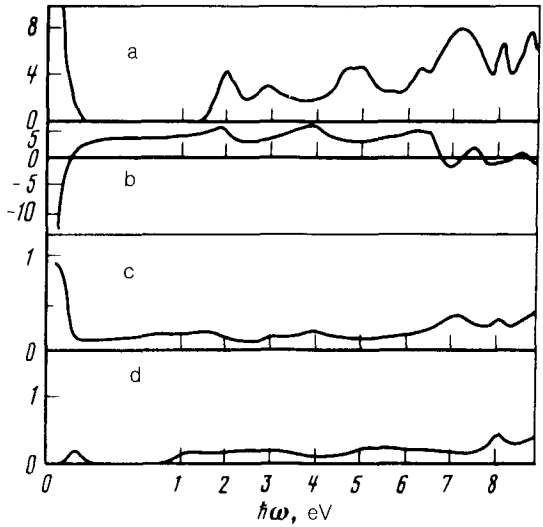

FIG. 3. The same as in Fig. 2, but for the polarization $\mathbf{E}\|\mathbf{c}$.

$\hbar\tilde{\omega}_p = [4\pi e^2 N(E_F)\langle v_\alpha^2\rangle/\Omega m]^{1/2}$, where $v_\alpha = v_\parallel, v_\perp$ are the projections of the Fermi velocity, m is the mass of the electron, Ω is the volume of the unit cell, and $N(E_F)$ is the state density at the Fermi level. For La_2CuO_4 we have $\hbar\tilde{\omega}_p^\perp = 1.86$ eV, $\hbar\tilde{\omega}_p^\parallel = 0.44$ eV, $\hbar\gamma^\perp \approx \hbar\gamma^\parallel = 0.064$ eV (these figures correspond to resistivities $\rho_\perp \approx 1.5\times 10^2$ and $\rho_\parallel \approx 2.4\times 10^3\ \mu\Omega\cdot$cm), $\epsilon_{\text{inter}}^\parallel(\omega=0) = 3.9$ and $\epsilon_{\text{inter}}^\perp(\omega=0) = 6.5$. In both directions ($\perp\mathbf{c}$ and $\|\mathbf{c}$), the decrease in $R(\omega)$ coincides with $\epsilon_1(\omega)\approx 0$ and with a maximum of $\text{Im}\{-1/\epsilon(\omega)\}$. In other words, it is indeed a plasma edge. Because of the additional polarization caused by interband transitions, we have $\epsilon_{\text{inter}}(\omega=0)\neq 1$, and the energy of the plasma edge is significantly lower than $\hbar\tilde{\omega}_p$. We might also note that the quasi-two-dimensional nature of the crystal makes the energy $\hbar\omega_p^\parallel$ extremely small in magnitude and very sensitive to the calculation details. For this reason, we can claim no more than the correct order of magnitude for the frequency of the plasma edge in the direction $\|\mathbf{c}$, while the errors in the determinations of the positions of the other structural features do not exceed 10%, according to our estimates. Another consequence of the quasi-two-dimensional nature of the crystal is that the frequency of the plasma edge in the direction $\|\mathbf{c}$, which corresponds to a zero of $\epsilon_i^\parallel(\omega)$, is anomalously low and falls in the region of phonon frequencies. The contribution of an ordinary phonon with a frequency close to the frequency of the plasma edge can thus be seen particularly clearly against the background of $\epsilon_1(\omega)\approx 0$. We can thus conclude that the extremely strong phonon structural feature observed at $\hbar\omega\approx 0.07$ eV (≈ 550 cm^{-1}) in the polycrystalline samples corresponds to an optically active phonon with a polarization $\mathbf{e}\|\mathbf{c}$.

The primary causes of the structural features in $R(\omega)$ at higher frequencies are interband transitions. The large maximum in $\epsilon_2^\perp(\omega)$ at $\hbar\omega = 1.2$ eV is caused by a polarization of Cu and O_{ab} atoms (i.e., O atoms lying in conducting layers). In k space, these transitions are localized near the Fermi surface. Below and above this maximum, $\epsilon_1^\perp(\omega)$ crosses zero, and $\text{Im}\{-1/\epsilon(\omega)\}$ has peaks. Correspondingly,

$R_\perp(\omega)$ increases sharply at $1.0 \lesssim \hbar\omega \lesssim 1.7$ eV, as if it were being squeezed between two plasma edges. Interestingly, in the case $\mathbf{E}\|\mathbf{c}$, this group of electronic transitions is essentially absent. On the other hand, there is a maximum in $\epsilon_2^{\|}(\omega)$ at $\hbar\omega \sim 2$–3 eV, associated with the excitation of La atoms and (to a lesser extent) Cu atoms. This maximum is in turn missing from $\epsilon_2^{\perp}(\omega)$. At higher energies, the electronic transitions for both $\mathbf{E}\perp\mathbf{c}$ and $\mathbf{E}\|\mathbf{c}$ are caused by an excitation of La atoms. The O_c atoms play a very minor role throughout this spectral region and can be ignored in a first approximation.

The literature so far reveals no reports of measurements of the optical spectra of $La_{2-x}Sr_xCuO_4$ single crystals. The incorrect interpretation of the polycrystalline measurements has given life to several hypotheses which link the superconductivity in this system to an electronic excitation which allegedly exists at $\hbar\omega \sim 0.5$ eV. We accordingly compared the curves which we calculated with the experimental data from polycrystalline samples. We make the natural assumption that the individual crystallites are oriented in an absolutely random way and that we have $R(\omega) \approx 2/3R^{\perp}(\omega) + 1/3R^{\|}(\omega)$ in the polycrystalline sample.

The $R(\omega)$ curve calculated by this method is shown in Fig. 1. The primary conclusion which can be drawn from the comparison of theory and experiment is that all the characteristic structural features on the experimental curve can be completely explained in terms of the ordinary band picture. There are some quantitative differences between the theoretical and experimental curves. The lower plasma edge in the calculated results lies 0.12 eV higher than the experimental edge, apparently because of the inaccuracy of the calculation of $\tilde{\omega}_p^{\|}$, which we have already mentioned. The calculations ignored interband relaxation, which accounts for the conversion of the peak in $R(\omega)$ at $\hbar\omega \sim 1.2$ eV into an experimental step with a small bump. Finally, the difficulties in preparing a mirror-finish surface on ceramic samples reduced the absolute value of $R(\omega)$. Reducing $\tilde{\omega}_p^{\|}$ by 0.1–0.15 eV and introducing an interband relaxation with a frequency $\hbar\gamma_{\text{inter}} \sim 0.25$ eV bring the theoretical results into essentially complete agreement with the experimental results (phonons have of course been ignored).

It can thus be seen that the erroneous conclusion that there is a peak in $\epsilon_2(\omega)$ at $\hbar\omega \sim 0.5$ eV is a consequence of an incorrect analysis of the average $R(\omega)$ curve. The sole nonphonon excitation in $La_{2-x}Sr_xCuO_4$ at low energies is a classical plasmon along the direction of the c axis. It is highly unlikely that this plasmon would play a special role in the mechanism for the superconductivity in this system.

Note added. After this paper had been submitted for publication, we learned of a preprint of a study by a Japanese group led by J. Tanaka. They reported measurements of the reflection coefficient of $La_{2-x}Sr_xCuO_4$ single crystals and reached the conclusion that there is no peak in $\epsilon_2(\omega)$ at $\hbar\omega \sim 0.5$ eV.

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