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Anisotropy of the dielectric function in $YBa_2Cu_3O_6$

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Experimental data for the anisotropy of the dielectric tensor $\epsilon=\epsilon_1+i\epsilon_2$ in $YBa_2Cu_3O_6$ are presented and interpreted. The spectra in the range between 1.7 and 5.2 eV were obtained by rotating-analyzer ellipsometry using a single crystal. It is found that the component of ϵ_2 in the *ab* plane ($\epsilon_2^{\parallel}$) displays a sharp peak at 4.1 eV, while the component along the *c* axis ($\epsilon_2^{\perp}$) has a less pronounced peak at 3.8 eV, a small peak at 4.2 eV, and a broad maximum near 5 eV. Similar structures were found in the interband spectra calculated using the local-density approximation. The 4-eV optical structure is caused by nearly parallel initial- and final-state bands whose wave functions are located, respectively in the O-Cu-O dumbbells and in the BaO-Cu-OBa triple layers. Intraionic $3d\rightarrow 4p$ transitions in dumbbell Cu contribute 90% of the optical matrix elements.

The removal of oxygen from $YBa_2Cu_3O_7$ causes not only a dramatic change in transport properties ($YBa_2Cu_3O_6$ is a semiconductor rather than a superconductor) but also in the optical properties.[1,2] In the superconductor the imaginary part of the dielectric function is relatively flat, with weak and broad structures at 2.8 and 4.7 eV. With decreasing oxygen content three features appear in the imaginary part of the dielectric function, namely a relatively sharp peak at 4.1 eV and two smaller peaks at 1.7 and 2.6 eV. The origin of these peaks, particularly the one at 4.1 eV, has been the object of some speculations.[1-5]

Experimental results obtained by analysis of the optical properties of compounds containing O-Cu-O dumbbells similar to those in $YBa_2Cu_3O_6$ indicate that the 4.1-eV peak may be associated with the existence of the O(IV)-Cu(I)-O(IV) complex.[2,3] In $YCuO_2$ for instance, a peak at 4.2 eV is observed. Reportedly, the peak also persists when the Ba is replaced by Sr in $YBa_2Cu_3O_6$,[3] supporting this interpretation. On the other hand, results for the polarization of the structure suggest that the origin of the peak is an O$\rightarrow$ Ba transition. Among these are electron-energy-loss-spectroscopy data[4] and reflectance data.[5] The hypothesis that the peak is caused by a O$\rightarrow$ Ba transition rather than the O-Cu-O gains support from the fact that ellipsometric measurements in ceramic $YBa_{2-x}Sr_xCu_3O_6$ ($x\approx 1$) (i.e., Ba partially replaced by Sr) yielded a peak weakened in intensity by about 50%,[6] which appears to be in contradiction with Ref. 3. This discrepancy has not yet been resolved. The experimental results leading to these assumptions, however, have been obtained by using sintered samples or thin films with the *c* axis perpendicular to the surface. The investigation of the anisotropy of the dielectric function in single crystals has been proposed as a means to obtain additional information on the origin of the peak.[1]

In this paper we report measurements of the dielectric-function anisotropy, as well as its interpretation based on a band-structure calculation. The samples were highly oriented multicrystal blocks prepared by the K_2CO_3 method.[7] They are obtained by heating a mixture of Y_2O_3, $BaCO_3$, K_2CO_3, and CuO in the molar ratio (0.5):(1.8-2.0):(0.1-0.5):(3.0) at 1270 K for 40 h in a recrystallized alumina crucible, followed by slow cooling. The lower part of the reacted charge is a porous mixture of polycrystalline $YBa_2Cu_3O_{7-\delta}$ contaminated with Al, K, "green phase," and other phases (like $BaCuO_2$ and CuO) while the upper portion contains many crystals grown adjacent to each other (with up to five neighboring crystals having the same orientation). Each of these crystals consists of layers ($d=20$–100 μm) of single crystals of $YBa_2Cu_3O_{7-\delta}$ with the *c* axes approximately aligned. Deviations from the average *c* direction were less than 5° [estimate by scanning electron microscopy (SEM) microstructure analysis] while the directions of the *a* and *b* axes were not determined exactly and might vary between different layers. SEM investigations on free-standing crystals, however, indicate that the *a* and *b* axes are also largely oriented. The superconducting transition temperature of this material (after oxygen annealing at 820 K for 48 h and subsequent cooling) was found to be 90 K with a transition width of 2 K (as obtained by resistivity measurements).

From the upper portion of the material so obtained, a sample large enough for various experiments was cut ($4\times4\times10$ mm^3). The sample consisted of two similarly oriented grains (as seen in a polarizing microscope) separated by a clearly visible grain boundary perpendicular to the *c* axis (as determined by x-ray investigations). We used the grain boundary to determine geometrically the exact orientation of the *c* axis that was found to be approximately parallel to one of the surfaces of the crystal with a tilt angle of 3–6°. This sample was then argon annealed at 1020 K for 48 h, polished, and checked to have an oxygen content of ≈ 6.0 ($\delta\approx 1.0$) by Raman spectroscopy.[8]

Using rotating-analyzer ellipsometry we obtained ϵ spectra for $\phi=n(\pi/2)$ ($n=0,1,2,3$) where ϕ is the angle between the *c* axis of the crystal and the plane of incidence. The spectra for $n=1$ and 3 are indistinguishable,

while there appeared some minor differences between the spectra for $n=0$ and 2. This effect can be explained by the fact that the c axis does not lie exactly in the reflecting surface. For simplification of the subsequent evaluation of the data, however, we assumed the c axis to lie in this surface. Spectra for $\phi=\pi/18$ were also obtained to probe the sensitivity of the experiment to small misorientations. No such sensitivity was observed. From the data for two high-symmetry orientations ($n=0,1$) the dielectric tensor components along the principal axes can be extracted numerically.[9,10] The component ϵ_2^a perpendicular to the c axis is shown as the dashed curve in Fig. 1, and the component ϵ_2^c along the c axis in Fig. 2. The dielectric function was used to calculate the reflectivity (see Fig. 3) which is in nice agreement with the spectra found elsewhere.[5]

In order to interpret the experimental spectra, we performed a standard, self-consistent band-structure calculation for $YBa_2Cu_3O_6$ using the spin-restricted local-density approximation[11] (LDA). The linear-muffin-tin-orbital method was used in the atomic-sphere approximation[12] with *spd* orbitals on the oxygens and *spdf* orbitals on all other atoms. We used the LDA energy eigenvalues and wave functions for the calculation of the interband contribution to the imaginary part of the components (ϵ_2^a and ϵ_2^c) of the dielectric tensor in the limit of vanishing lifetime broadening.[13,14] The Brillouin-zone (BZ) integrations were performed with the tetrahedron method using 147 points in the irreducible BZ. The solid curves in Figs. 1 and 2 give the calculated ϵ_2^a and ϵ_2^c spectra, which we now compare with their measured counterparts.

The dominant peak in the measured ϵ_2^a spectrum is reproduced by the calculation, although the position is shifted down by 0.5 eV from 4.1 to 3.6 eV. This shift towards lower energies of the calculated spectra is hardly surprising in view of the fact that the LDA bands have no gap. Excitonic interactions have, on the other hand, been neglected in the calculation as well, although the experimental data suggest them being of importance, at least for the 4.1-eV peak. The measured ϵ_2^c spectrum has a peak at 3.8 eV, plus a smaller one at 4.2 eV. About 0.5 eV further

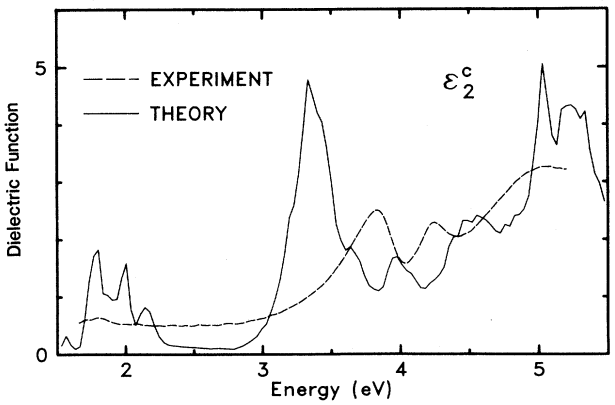

FIG. 2. Same as Fig. 1 with the exception of the polarization in the c direction.

down in energy the calculated ϵ_2^c spectrum also has two peaks, but the ratio of their amplitudes is much larger than that of the experimental peaks. At higher energies the experimental ϵ_2^c spectrum rises towards a broad maximum around 5 eV, whereas the ϵ_2^a spectrum is fairly flat. The calculation exhibits similar behavior. At low energies, the measured ϵ_2^a has maxima at 2.5 and 1.8 eV, whereas ϵ_2^c is featureless. In this low-energy region the LDA bands are highly inaccurate (gap problem).

We judge that, for energies between 3 and 5 eV, the agreement between the measured and the calculated spectra is sufficiently close, that the causes for the peaks in the former can be found by analysis of the latter.

The calculated 4-eV peaks are contributed by initial- and final-state bands which are nearly parallel near the boundary of the tetragonal BZ. In Fig. 4 we show the bands along the line from X (e.g., [100]) to M (e.g., [110]) in a 6-eV range around E_F, as well as the squares of the absolute values of the wave functions for the bands labeled 1, 2, and 4, midway between X and M. The peaks arise from the relatively flat bands labeled 1, 2, and 4, and from bands 3 and 5 near M. (The two unlabeled, dispersive bands extending from -5 to -2 eV are the bands from the two CuO_2 planes. These bands have saddle

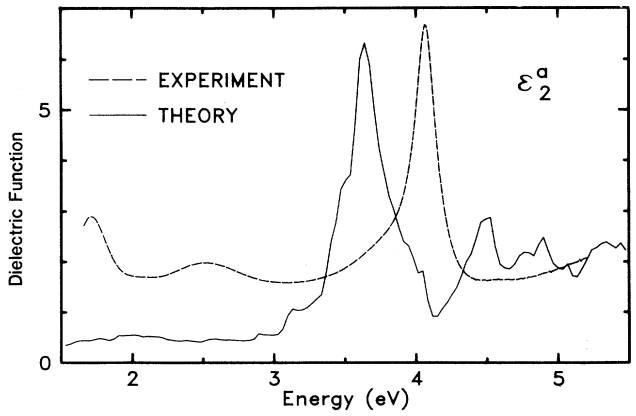

FIG. 1. Imaginary part of the dielectric function for $YBa_2Cu_3O_6$ with the polarization in the *ab* plane, as obtained by ellipsometry (dashed line) and by LDA band theory (solid line).

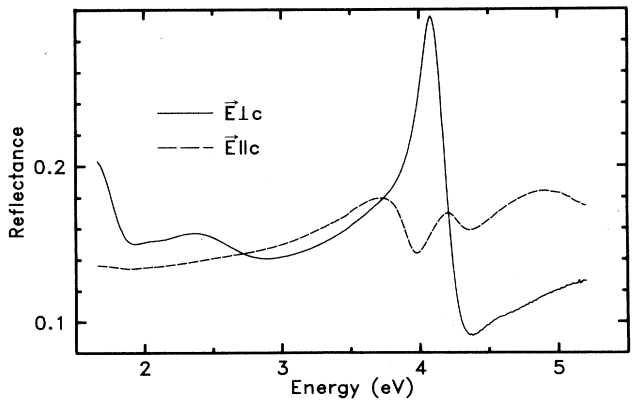

FIG. 3. Reflectance spectra of $YBa_2Cu_3O_6$ calculated from the experimentally obtained dielectric functions.

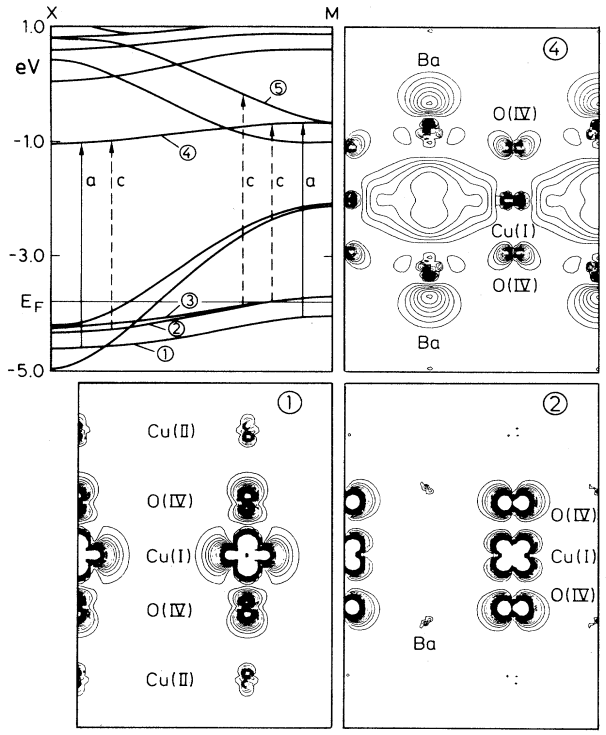

FIG. 4. Calculated LDA energy bands along the line from X (e.g., [100]) to M (e.g., [110]) in the tetragonal BZ. The transitions between the bands labeled 1–5 are responsible for the structures around 4 eV in the calculated ϵ_2^g and ϵ_2^c. The contour plots in the [1$\bar{1}$0] plane passing through Cu(II), O(IV), Cu(I), Ba, and Y give the square of the absolute value of the wave functions at the midpoint between X and M for bands 1, 2, and 4.

points at X and maxima at M. In the antiferromagnetic structure these bands will split, so that from X to M they are shifted upwards by 1–2 eV.) The initial states are confined to the O(IV)-Cu(I)-O(IV) dumbbell: Band 1 has antibonding $pd\sigma$ character (Cu $3d_{3z^2-1}$ O $2p_z$), and bands 2 and 3 have antibonding $pd\pi$ character (Cu $3d_{xz}$ O $2p_x$ and Cu $3d_{yz}$ O $2p_y$). The final states (bands 4 and 5) are mostly confined to the Ba-O(VI)-Cu(I)-O(VI)-Ba triple layers and consist of bonding linear combinations of Ba ($\approx 40\%$)$5d_{3z^2-1}$ orbitals (band 4 near X), $5d_{xz}$ and $4f$ orbitals (band 4 near M), or $5d_{yz}$ and $4f$ orbitals (band 5 near M), and Cu ($\approx 30\%$)$4p_x$ orbitals (band 4) or $4p_y$ orbitals (band 5 near M).

The dominant peak in the calculated ϵ_2^g is caused by transitions from band 1 to band 4, and we find that the dumbbell intraionic Cu $3d_{3z^2-1} \rightarrow$ Cu $4p_x$ transitions contribute to the optical matrix elements by an order of magnitude more than the Cu $3d_{3z^2-1} \rightarrow$ Ba transitions. The leading peak in ϵ_2^c is caused by transitions from band 2 to band 4, and the calculation thus explains the observed 0.3-eV distance between the positions of the ϵ_2^g peak and the leading ϵ_2^c peak by assigning them to the same final-state band (4) and to initial-state bands (1 and 2) which are displaced by 0.3 eV. The transitions responsible for the leading peak in ϵ_2^c are thus $\approx 90\%$ dumbbell intraionic Cu $3d_{xz} \rightarrow$ Cu $4p_x$ transitions and $\approx 10\%$ Cu $3d_{xz} \rightarrow$ Ba transitions. The structure calculated in ϵ_2^c on the high-energy side of the peak is due to Cu $3d_{yz} \rightarrow$ Cu $4p_y$ transitions from band 3 to band 5 near M. The origin of the broad peak in ϵ_2^c at 5 eV involves manifolds of initial-state bands which makes it difficult to associate it to specific interband transitions. A detailed discussion of its various components will be presented elsewhere.[15]

In conclusion, we have presented experimental as well as LDA band-theoretical results for the anisotropy of the dielectric function of $YBa_2Cu_3O_6$ which show reasonable agreement with the structure in the observed optical spectra between 3 and 5 eV. Moreover, we believe that we have been able to explain a major part of the remaining disagreement between theory and experiment. At low energies (1.5–3 eV) the well-known gap problem can be held responsible for the rather poor agreement. Since damping has not been included in the theoretical data, too-large values for the calculated absorption are unavoidable. The reason why, nevertheless, the 4-eV peak in ϵ_2^g is well reproduced, is probably that damping and electron-hole correlations (excitonic effects) tend to cancel for this specific feature. An assignment of the controversial peak at 4 eV has been attempted using the LDA band structure. We have found that it is related mainly to $3d^{10} \rightarrow 3d^9 4p$ transitions in the Cu ion of the O-Cu-O dumbbell and, to a minor extent, to dumbbell Cu $\rightarrow$ Ba charge-transfer transitions. Charge-transfer transitions in either the O-Cu-O dumbbell or in the Ba-O plane can be ruled out.

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