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Inelastic electron scattering in the high-T_c compound $YBa_2Cu_3O_{7-x}$

C. Tarrio and S. E. Schnatterly
Jesse Beams Laboratory of Physics, University of Virginia, Charlottesville, Virginia 22901
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We have carried out inelastic electron scattering transmission measurements on the high-T_c compound $YBa_2Cu_3O_{7-x}$ in the energy range 1–100 eV. We have directly observed the free-electron plasma peak at 1.1 eV in addition to the bound electron plasmon at 25.5 eV. The interband threshold is at 2.1 eV, above which the material behaves as a typical oxide insulator.

Since the discovery of superconductivity in the 30–90 K range,[1,2] intensified experimental and theoretical effort has ensued to determine various properties of the superconducting copper oxides. Much of this work has focused on the electronic and phonon properties. Photoemission experiments have determined binding energies of occupied electronic levels with good agreement among the different measurements.[3-6] Inverse photoemission[4,7] has been used to probe unfilled levels. Reflection electron energy loss[8] has been used to study transitions between these levels, while reflectivity measurements[9-11] have been used to determine the optical constants from the far infrared to near ultraviolet. Both reflectivity and transmittance have been measured on a series of oriented thin films.[12] We present inelastic electron scattering (IES) transmission measurements from 1 to 100 eV. By means of Kramers-Kronig (KK) analysis, we obtain dielectric and optical constants over the entire range. Our results extend the energies over which the optical constants are known. We also help to relate the photoemission and inverse photoemission to each other while providing the strengths of the transitions found in the reflection energy-loss measurements.

Samples of $YBa_2Cu_3O_{7-x}$ were obtained from Argonne National Laboratory. The critical temperatures of the samples studied were all in the 90 K range. Samples produced at the University of Virginia showed no consistent measurable differences in their spectra.

Normally, IES transmission measurements are performed with films of thickness 10–100 nm. However, because free-standing films are not yet available, we have used powdered samples for these experiments. 200 mesh electron-microscope grids were coated with sodium silicate solution of which the excess was removed by spinning. The bulk material was then powdered and brushed onto the grids. The powder was exposed to air for less than 30 min before going into the vacuum. Since IES measurements detect only electrons which have lost the energy being measured, the experiments are not in principle affected by the fact that only a very small fraction of the electrons pass through the samples. We have obtained good comparisons with published results using this method for a number of test materials. Sodium silicate spectra were also measured to determine if some of our signal was due to the substrate. Any spectra showing evidence of the strong 33-eV Na exciton were rejected.

Measurements were made on the IES accelerator at the University of Virginia, which has been described in Ref. 13. The primary-beam energy was 280 keV with a resolution of 0.2 eV. Spectra were taken at 0.15 Å^{-1} transverse-momentum transfer with a resolution of 0.04 Å^{-1} to avoid surface and Cherenkov radiation losses.

The IES cross section is proportional to

$$\frac{d^2\sigma}{d\omega\, d\Omega} \propto \frac{1}{q_\parallel^2+q_\perp^2}\,\mathrm{Im}\left(-\frac{1}{\epsilon(q,\omega)}\right),$$

where $q_\parallel$ and $q_\perp$ are the longitudinal- (energy-dependent) and transverse-momentum transfers, and ϵ is the complex dielectric function. The spectra are corrected for the $1/q^2$ dependence and multiple scattering following algorithms of Fields.[14] The final scale of the spectrum is determined by satisfying $\mathrm{Re}[-1/\epsilon(\omega=0)]=0$ and the oscillator strength sum rule. The KK analysis enables us to determine the real and imaginary dielectric functions and the optical constants.

Figure 1 shows the loss function of $YBa_2Cu_3O_{7-x}$ from 0 to 90 eV. Reference 9 presents a loss function from 0 to

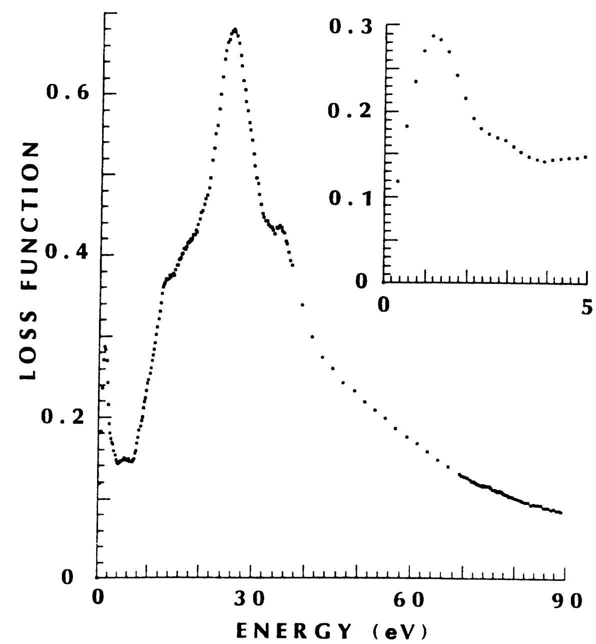

FIG. 1. Loss function of $YBa_2Cu_3O_{7-x}$ from 0 to 90 eV. Inset: same loss function from 0 to 5 eV.

5 eV obtained from a KK analysis of optical reflectivity data. The shapes agree well, with a major peak at 1.1 eV and a smaller feature at 3.0 eV. However, our values of the loss function are a factor of 1.5–3 higher in this energy range. Our 3-eV feature is also broader, but this feature can be affected by variations in stoichiometry which do not affect the superconducting properties.[15] Kamaras *et al.* report a similar feature at 2.5 eV rather than 3 eV.[10] From our data alone, we cannot determine the origin of the 1.1-eV peak. Below about 1 eV, the zero-energy-loss beam begins to dominate over the spectrum, so we must extrapolate to zero energy assuming a shape of the spectrum. We have carried out the extrapolation so as to approximate our loss function in the region near the peak. The data in the 0.8–2.2 eV range can be described by a modified Drude shape with a plasma frequency of 2.75 eV, corresponding to a free-electron density of 5.4×10^{21} cm^{-3} assuming an effective mass of unity, a half-width of 2.85 eV, and a background dielectric constant of 2.5. The plasma frequency is within the range of reported values of 2.6 eV in Refs. 9 and 12, and 3.0 eV in Ref. 11. These differences may be due to variations in the oxygen content. A slight change in the oxygen content has been shown to move the Fermi energy,[16,17] and thus will change the number of free carriers. This will affect the free-carrier plasma frequency, as well as the value of the loss function in the low-energy region. In the course of our KK analysis, we have also extrapolated to zero energy assuming a small band gap (e.g., 0.2 eV), and this leads to the 1.1 eV peak behaving as an exciton, showing a strong peak in ϵ_2 at 0.7 eV. However, this leaves the sample with no free carriers, which we know not to be the case.

Excitations observed near 0.4 eV in granular samples[9,10] but not in oriented film samples[12,15] could be due to the free carriers. In granular samples, one expects excitations related to grain size and surface effects at and below the plasma energy.[18,19] In the case of $YBa_2Cu_3O_{7-x}$ samples, the plasmon peak energy of 1.1 eV corresponds to a photon wavelength of about 1 μm, which is roughly the diameter of a grain.[20] Therefore, grain-size effects cannot be described by existing theories appropriate to either the long- or short-wavelength limit, and we cannot predict the position of any features associated with these effects.[18,19]

Figure 2 shows the interband contribution to the loss function, with the Drude contribution as estimated above, subtracted. The interband threshold is at 2.1 eV, in agreement with optical transmission measurements.[12] The band-structure calculation of Massida, Yu, Freeman, and Koelling[16] indicates that the first possible transition from the Fermi level into the conduction band is at 2.6 eV, while Mattheiss and Hamann[17] find this to be 3.4 eV. However, transitions from lower-lying valence bands to just above E_F may be possible.

ϵ_1 and ϵ_2 are shown in Fig. 3. Above the excitations at 1.1 and 3 eV, there is a weak transition at 5 eV, and both ϵ_2 and $\mathrm{Im}(-1/\epsilon)$ show a sharp increase at 6.6 eV. This is consistent with photoemission and inverse photoemission experiments: the highest-lying level observed in photoemission is at -2.3 eV (Ref. 3) to -2.5 eV (Ref. 6),

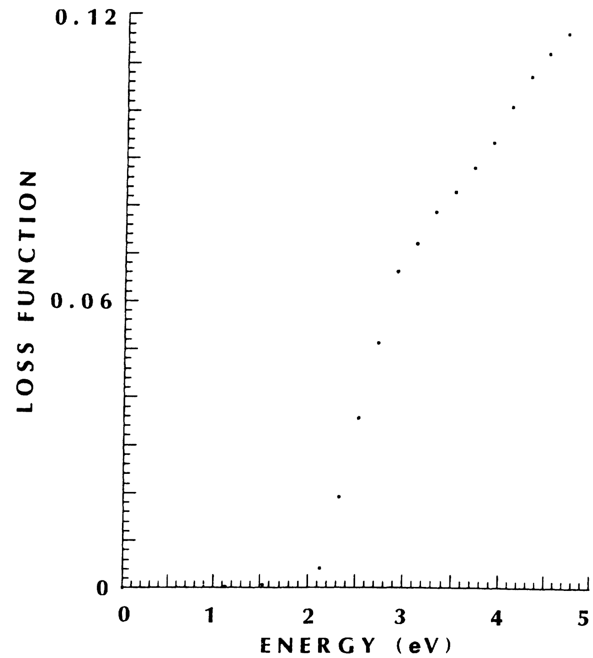

FIG. 2. Bound-electron contribution to the loss function of Fig. 1. The Drude free-electron contribution has been subtracted.

while inverse photoemission indicates a small density of states near the Fermi level which begins to increase sharply at 3.7 eV.[7] Our ϵ_2 spectrum shows a broad peak from 9–12 eV, which corresponds to the levels found at 8.7 and 11.8 eV by reflection energy-loss spectroscopy.[8] We also see the O 2*s* level at 22 eV, in agreement with Ref. 8, however, our bound-energy plasma frequency of 25.5 eV, and Y 4*p* level at 34 eV, are at somewhat higher energies

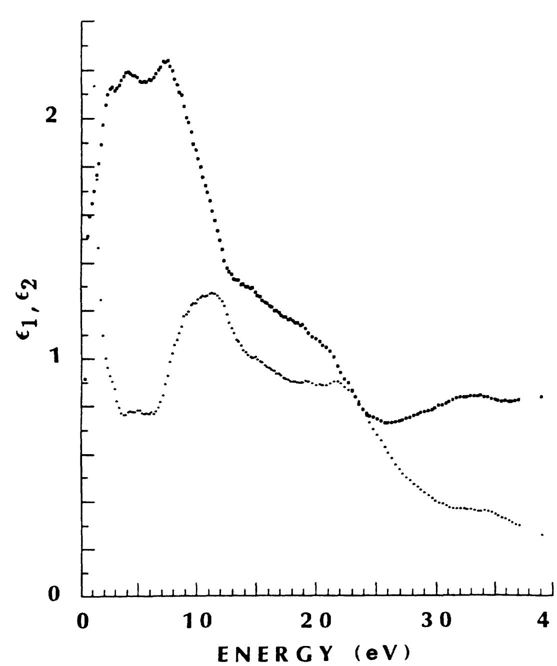

FIG. 3. ϵ_1 (squares) and ϵ_2 (triangles) calculated from the loss function of Fig. 1.

than in that measurement. The values of ϵ_1 and ϵ_2 at 25.5 eV are both close to 0.6, leading to the wide plasma peak which is typical of insulators. This is due to the proximity of core levels, most notably the O 2s electrons. The values of ϵ_1 and ϵ_2 are quite similar to those of other oxides we have measured in which the plasmon is very close in energy to the O 2s electrons (e.g., SiO_2, SiO).

From the ϵ_2 spectrum and calculated densities of states,[16,17] we can obtain information about the relative strengths of the interband versus intraband matrix elements. The material's behavior is between that of a good simple metal and a strong d-electron metal. The ratio of the matrix elements well into the interband region to those of intraband transitions is roughly a factor of 3 higher than the corresponding ratio in sodium, while it is about $\frac{1}{3}$ of the ratio in silver.

In the conductivity (Fig. 4), one can better distinguish the higher-energy excitations. Both the Y 4s, 43 eV, and the Cu 3p, 74 eV, thresholds are weak, with the oscillator strength spread out over a wide energy range. This is consistent with our measurements on related compounds such as YF_3, CuCl, and CuBr.

The oscillator strength sum rule is obtained from

$$N_{\text{eff}}(\omega) = \frac{2}{\pi\omega_p^2}\int_0^{\omega} \omega'\epsilon_2(\omega')d\omega' .$$

The oscillator strength derived from ϵ_2 is shown in Fig. 5. About 0.4 electrons per molecular unit contribute to the sum rule below the interband threshold. This corresponds to an electron density of 2.3×10^{21} cm^{-3}, which is about $\frac{1}{2}$ of the total free-electron density obtained from the Drude fit to the 1.1-eV peak. The number of electrons is not sensitive to the precise form of the extrapolation to zero energy. The number of electrons at 2 eV as obtained from the sum rule is expected to be somewhat lower than the total number of electrons participating in the plasma oscillation. The large difference in this case arises from the broadness of the plasmon. This leads to a very long high-energy tail, which is weighted by the energy in the sum-rule integral, and much of the strength of the plasmon will lie above the interband threshold. To evaluate the sum rule in the limit of infinite energy, a $1/E^3$ function was grafted onto the data both at 70 eV, below the Cu 3p threshold, and at 92 eV, between the Cu 3p and Ba 4d levels. Extrapolating above 70 eV yields a total of 110 electrons contributing per unit cell, while extrapolating above 92 eV yields 128 electrons. There are 106 electrons per unit cell with binding energy less than the Cu electrons, and 124 including the Cu 3p levels. One expects the measured oscillator strength to be slightly higher than the actual number of electrons. This is due to the negative oscillator strength for transitions into lower-energy levels, which are forbidden by the Pauli exclusion principle.[21] This effect causes higher-lying levels to carry more strength, while more tightly bound levels carry less. For example, in aluminum 3.1 rather than 3.0 electrons contribute below the 2p electrons, a 3% increase. In the present case, we have a 4% increase in the strength below the Cu 3p threshold, but we do obtain the expected 18 electrons in the Cu 3p shell.

We have reported the first direct measurement of the free-electron plasmon in $YBa_2Cu_3O_{7-x}$. The plasmon is heavily damped, with a full width at half maximum of almost the plasmon energy. We have determined the interband threshold to be 2.1 eV. A Drude fit of the conduction plasmon gives a free-electron density of 5.4×10^{21} cm^{-3}, similar to a very heavily doped semiconductor. Above the threshold, the material behaves as an insulator with a sharp increase in the strength of transitions at 6.6

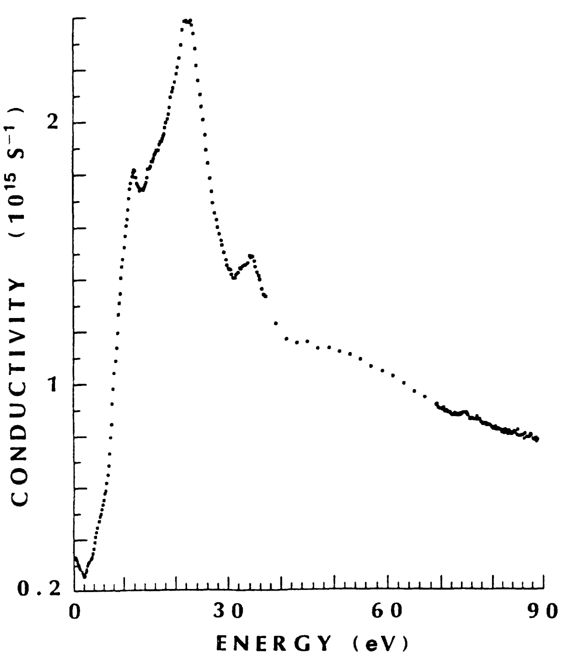

FIG. 4. Conductivity calculated from ϵ_2 of Fig. 3.

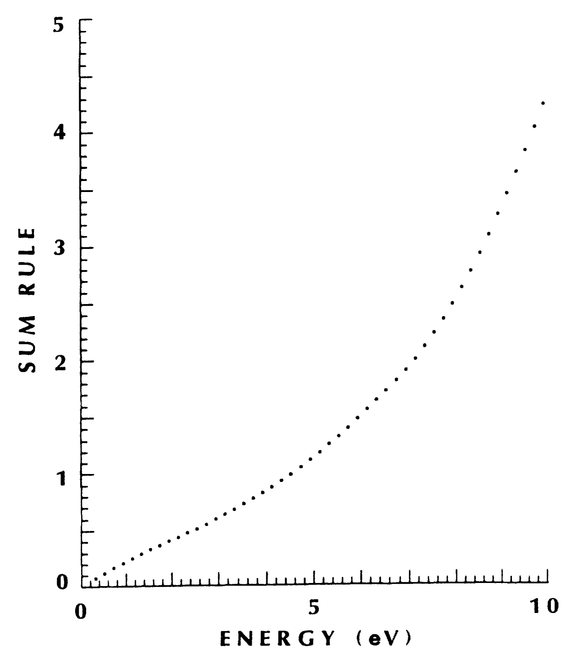

FIG. 5. Oscillator strength sum rule calculated from ϵ_2 of Fig. 3.

eV, and a heavily damped valence plasmon at 25.5 eV with no zero crossing of ϵ_1.

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