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Plasmons and interband transitions in $Bi_2Sr_2CaCu_2O_8$

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Electron energy-loss spectroscopy has been used to investigate the electronic structure of single-crystalline $Bi_2Sr_2CaCu_2O_8$. The dielectric function was derived in the energy range of 0.2–48 eV. Information on interband transitions and low-lying core levels is obtained. The charge-carrier plasmon shows a quadratic dispersion in momentum transfer. From the dispersion constant the Fermi velocity of the charge carriers could be derived.

The class of high-T_c superconductors first discovered by Bednorz and Müller[1] has recently been extended[2] by the Bi-Sr-Ca-Cu-O system having T_c's up to 105 K. Information on the electronic structure of $Bi_2Sr_2CaCu_2O_8$ has been obtained by photoelectron spectroscopy,[3–5] inverse photoemission,[6,7] x-ray-absorption spectroscopy (XAS),[8,9] core-level electron energy-loss spectroscopy (EELS),[10] and by optical spectroscopy.[11,12] In this Rapid Communication we report on EELS studies of valence-band and low-lying core-level excitations. The dielectric function has been obtained for momentum transfer parallel to the CuO_2 planes. We present for the first time information on the momentum-transfer dependence of the charge-carrier plasmon of a high-T_c superconductor. Part of the results have been published previously.[13]

EELS spectra were taken in transmission with a high-resolution 170-keV spectrometer described elsewhere.[14] The full width at half maximum energy and momentum resolution was chosen to be 0.15 eV and 0.04 $Å^{-1}$, respectively. Measurements were performed at room temperature and at 30 K. The preparation of single crystals of $Bi_2Sr_2CaCu_2O_8$ was described elsewhere.[15] From x-ray diffraction and from the T_c value (83 K) derived from ac susceptibility measurements, it was concluded that the crystal was predominantly in the $n=2$ phase.[16] Thin films with a thickness of about 1000 Å were obtained by peeling them from single crystals with a tape and mounting them on standard electron-microscope grids. The crystal structure of the films was controlled by electron diffraction. We emphasize that EELS in transmission is not a surface-sensitive method as, e.g., photoelectron spectroscopy or XAS in the partial yield mode. Therefore, problems of preparing surfaces representing bulk properties are avoided.

In Fig. 1(a) we present a typical loss function $\mathrm{Im}[-1/\epsilon(\mathbf{q},\omega)]$ for a single crystal of $Bi_2Sr_2CaCu_2O_8$ in the energy range 0–48 eV. The momentum transfer $\mathbf{q}$ was chosen to be 0.1 $Å^{-1}$ to suppress contributions from surface losses. This value is small in comparison with the extension of the Brillouin zone, and therefore the data derived from the loss function can be compared directly with optical spectra. The direction of the momentum transfer $\mathbf{q}$ was in the **a**,**b** plane (CuO_2 plane). Thus, an element of the dielectric tensor, namely $\epsilon_{xx}=\epsilon_{yy}=\epsilon$, can be determined from the present EELS measurements while this is, in principle, not possible for polycrystalline[17,18] and twinned single-crystalline[13] $YBa_2Cu_3O_7$. The loss function was derived from an EELS spectrum by subtracting contributions from the quasielastic peak and double scattering. The absolute value of the loss function was obtained by satisfying $\mathrm{Re}[-1/\epsilon(0,0)]=0$. By a Kramers-Kronig analysis the real and imaginary parts of the dielectric function (ϵ_1 and ϵ_2) were calculated. In Fig. 1(a) we show ϵ_1 and the optical conductivity σ which is proportional to $\omega\epsilon_2$. In Fig. 1(b) we show the low-energy part ($E<6$ eV) of the loss function ϵ_1 and σ (dashed line). The solid line corresponds to data where the Drude part, which is due to the charge carriers, was subtracted. In Fig. 2 we show the momentum dependence of the charge-carrier plasmon. There is more background at higher momentum transfer due to the quasielastic line, which obscures the spectra below ~ 1 eV. Therefore, the extrapolation to zero energy is shown by a dashed line. In the inset we show the charge-carrier plasmon dispersion, i.e., the momentum dependence of the maximum of the loss function.

Discussing the experimental results, we begin with the loss function of $Bi_2Sr_2CaCu_2O_8$ which is dominated by a broad peak with a maximum near 19.5 eV. It can be assigned to a collective excitation of all valence electrons. A calculation of the energy of this highly damped valence-band plasmon in a free-electron model yields about 25 eV. The shift to lower energy is caused by strong excitations of Bi 5*d* electrons in the energy range 26–29 eV, which will be discussed later. The plasmon at 1 eV [see Fig. 1(b)] has already been detected by optical-reflectivity measurements.[11] It is well described by a Drude plasmon having a width of 0.7 eV. The background dielectric function ϵ_∞ in the plasmon energy range is about 4.5 as shown in the ϵ_1 curve where the Drude part is subtracted. By using the charge-carrier density $n=3\times10^{21}$ cm^{-3} (0.7*e* per formula unit) derived from Hall-effect measurements[19] (the simple relation $R_H=1/ne$ was applied) the effective mass m^* is calculated from $E_p=\hbar(ne^2/\epsilon_\infty m^*)^{1/2}$ to be close to

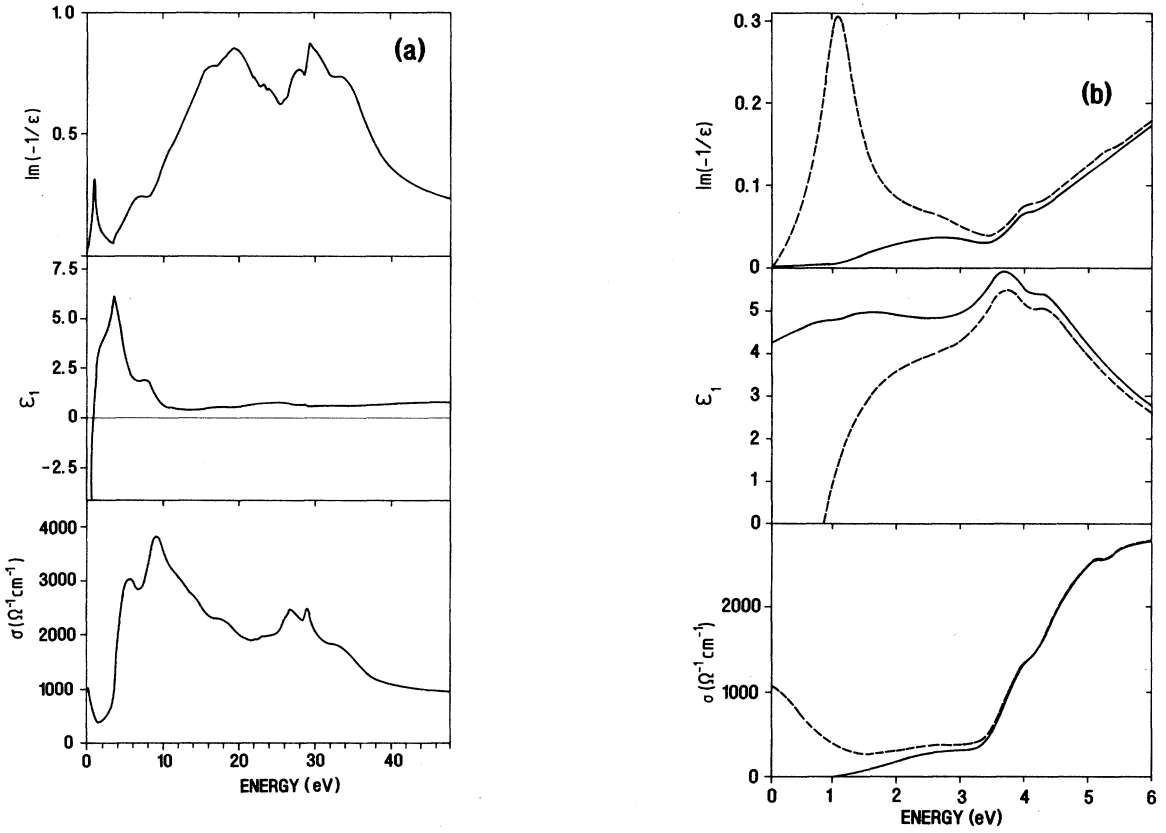

FIG. 1. Loss function $\mathrm{Im}[-1/\epsilon(\mathbf{q}\omega)]$, real part of the dielectric function $[\epsilon_1(\mathbf{q},\omega)]$, and optical conductivity $\sigma(\mathbf{q},\omega)$ of a single crystal of $Bi_2Sr_2CaCu_2O_8$ for $\mathbf{q} \| \mathbf{a},\mathbf{b}$. The value of $q = 0.1$ Å^{-1} is small in comparison to the Brillouin zone. (a) Energy range 0–48 eV, (b) low-energy part: including the Drude part (dashed line), without the Drude part (solid line).

the free-electron mass m. We are aware that at much lower energy, considerably higher effective masses may be obtained as, e.g., from optical data[20] on $YBa_2Cu_3O_7$. Next we discuss the dispersion of the plasmon. As shown in Fig. 2, the plasmon is strongly damped at higher momentum transfer q. The width increases with the third power of q. This damping is probably due to a decay into interband transitions. As in the present measurements, the momentum transfer q_z perpendicular to the CuO_2 layers was rather small ($q_z < 0.01$ Å^{-1} given by the misorientation of the sample), the electrons move in phase on different planes, and therefore the measured plasmon dispersion can be evaluated as in a usual three-dimensional sample. The plasmon dispersion as a function of momentum transfer q is then given in a first approximation by $E_p(q) = E_p(0) + (\hbar^2/m)\alpha q^2$ where the dispersion coefficient α is $\frac{3}{10}[mv_F^2/E_p(0)]$ with v_F being the Fermi velocity. From the experiment (see Fig. 2) $E_p(0) = 1.0$ eV and $\alpha = 0.6$ is derived. Then the Fermi velocity is calculated to be $v_F = 0.6 \times 10^8$ cm/sec which is slightly smaller than values for normal metals. With use of $m^* = m$, the Fermi energy $E_F = 1.0$ eV, which is half the value expected for the half-filled antibonding $Cu\,3d_{x^2-y^2}$–$O\,2p_{x,y}$ band derived from band-structure calculations,[21] thus further supporting the importance of correlation effects. In this case the Cu $3d$ band is split into a lower (occupied) and an upper (unoccupied) Hubbard band. An O $2p$ band (occupied) remains between the two Hubbard bands.[22,23] Upon self-doping by BiO planes, holes are formed in the O $2p$ band. In this picture the observed plasmon is caused by the charge carriers which are predominantly holes on O sites. According to the data derived above, these holes move almost as free particles. This is probably related to the fact that according to band-structure calculations, the O $2p$ states alone (without Cu $3d$ states) form a band of width of more than 2 eV in the CuO_2 planes.[21]

There are strong discussions on pairing mechanisms related to two-dimensional acoustic plasmons.[24] Therefore, it would be highly interesting to perform measurements as a function of the momentum transfer q_z perpendicular to the CuO_2 layers. This would yield information on the existence of acoustic plasmons, i.e., out-of-plane motion of charge carriers on adjacent planes. First measurements with nonzero q_z indicate that with increasing q_z the plasmon energy decreases as expected for two-dimensional plasmons. Further systematic studies of this problem are under way.

Besides the collective excitations of all valence electrons and the charge carriers, there are a series of interband transitions which can be discussed in the context of optical conductivity. Using an oscillator strength sum rule, one finds the Drude part to contain about $n_{\mathrm{eff}} = 0.8$ electrons

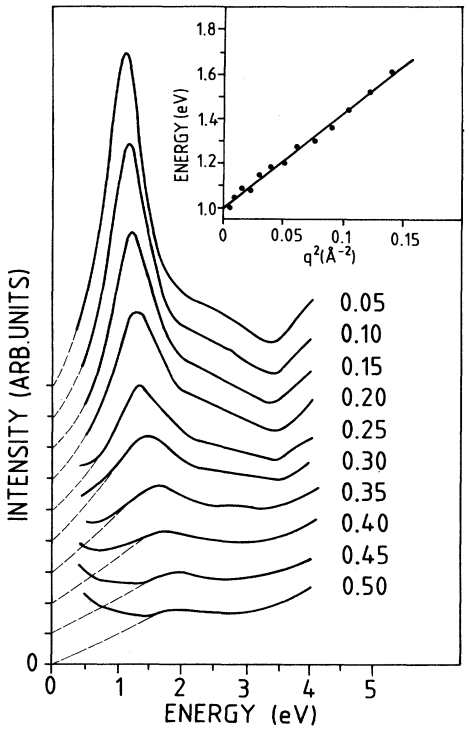

FIG. 2. Low-energy loss function as a function of momentum transfer $\mathbf{q} \| \mathbf{a},\mathbf{b}$ for $Bi_2Sr_2CaCu_2O_8$ showing the plasmon caused by the charge carriers (holes on O sites). The curves are labeled by the momentum transfer given in $Å^{-1}$. Inset: Dispersion of the charge-carrier plasmon as a function of the squared momentum transfer.

per formula unit (for $E < 2$ eV). Removing the Drude part, we realize that interband transitions start at 1.2 eV. There may be low-intensity transitions below 1.2 eV, e.g., *d-d* excitations which are not resolved in our spectra. As pointed out before, below 0.5 eV there are contributions from the quasielastic line, and therefore in this energy range the data are not very reliable. The broad onset of interband transitions may be explained in the electronic structure model given above by charge transfer transitions in the CuO_2 planes between the O $2p$ band and the upper Cu $3d$ Hubbard band. The number of electrons corresponding to these transitions in the energy range 2.0 to 3.5 eV is about 0.5 per formula unit. The steep rise in σ at 3.5 eV was also detected in ellipsometric measurements and was assigned to excitations in the BiO and SrO planes.[12] Strong maxima in the optical conductivity are observed at 6 and 9 eV. According to recent resonant inverse photoemission measurements,[6] the latter maximum can be ascribed to an excitation into empty Ca $3d$ states. At 7 eV, n_{eff} is about 7.5, and at 10 eV about 15. Low-lying core-level excitations are expected according to photoemission measurements[3] at 17.7 eV due to the Sr $4d$ level, at 18 eV due to the O $2s$ level, and at 23.4 eV due to the Ca $3p$ level, where peaks in the loss function can be seen. Further core-level excitations are expected in this energy range from the Bi $5d_{5/2}$ and $5d_{3/2}$ core levels separated by 3.1 eV due to spin-orbit splitting. From photoemission spectroscopy[5] the binding energies of the two levels have been determined to be 25.2 and 28.2 eV, respectively. In the atomic limit Bi $5d_{5/2}$-$6p_{1/2}$ transitions are not allowed, and Bi $5d_{3/2}$-$6p_{3/2}$ transitions are five times weaker than Bi $5d_{3/2}$-$6p_{1/2}$ transitions. Therefore, the lower part of the structures in the loss function should be related to Bi $5d_{5/2}$-$6p_{3/2}$ transitions. The upper part is predominantly caused by $5d_{3/2}$-$6p_{1/2}$ transitions. One may think that the steep rise in the loss function at 29.1 eV with a total width of only 0.3 eV is related to the Fermi edge of the Bi $6p$ electrons. However, according to band-structure calculations,[21] XAS studies,[8] EELS measurements,[10] and inverse photoelectron spectroscopy,[7] there should be a much higher second rise 2 eV above E_F due to flat antibonding Bi $6p$–O $2p$ bands of the BiO planes. As this second rise is not observed we ascribe the rise at 29.1 eV to transitions from the Bi $5d_{3/2}$ level into these flat BiO bands having $6p_{1/2}$ character. This assignment is supported by the fact that the binding energy of the Bi $5d_{3/2}$ level has been determined to be at lower energy. Furthermore, orientation-dependent measurements (not shown) indicate almost no anisotropy of the edge at 29.1 eV. Recent measurements by XAS (Ref. 8) and EELS (Ref. 10) of the O $1s$ edge, showing no anisotropy for the flat Bi $6p$–O $2p$ states, but strong anisotropy for the states near E_F, support the present assignment. The Fermi edge of the wide bands of the BiO planes may be somewhere at 26.8 eV and probably obscured by $5d_{5/2}$ transitions. The latter excitations, however, show no edge due to flat BiO bands. The reason for this may be that the bottom of these bands has predominantly Bi $6p_{1/2}$ character, and therefore the $5d_{5/2}$-$6p_{1/2}$ transitions are rather low in intensity and start at 26.0 eV or below. The maximum at 28 eV, which only appears for $\mathbf{q} \| \mathbf{a},\mathbf{b}$, can be assigned to $5d_{5/2}$-$6p_{3/2}$ transitions. At present it is not clear whether the small edge at 23.2 eV, which again appears only for $\mathbf{q} \| \mathbf{a},\mathbf{b}$, is caused by the $5d_{5/2}$-$6p_{1/2}$ transition to the Fermi edge of the wide BiO bands or by Ca $3d$ excitations. Further orientation-dependent measurements are necessary to obtain information from these edges on Bi states near E_F.

Finally, we would like to mention that we have performed similar measurements on excitations of valence and core electrons at 30 K which is well below the superconducting transitions temperature $T_c = 83$ K. Neither the loss function nor the plasmon dispersion show a significant difference between room temperature and 30 K. This indicates that changes of the electronic structure as a function of temperature are well below our energy resolution of 0.15 eV.

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