Superconductivity-Induced Transfer of In-Plane Spectral Weight in $Bi_2Sr_2CaCu_2O_{8+\delta}$

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Optical data are reported on a spectral weight transfer over a broad frequency range of $Bi_2Sr_2CaCu_2O_{8+\delta}$, when this material became superconducting. Using spectroscopic ellipsometry, we observed the removal of a small amount of spectral weight in a broad frequency band from 10^4 cm^{-1} to at least 2×10^4 cm^{-1}, due to the onset of superconductivity. We observed a blue shift of the *ab*-plane plasma frequency when the material became superconducting, indicating that the spectral weight was transferred to the infrared range. Our observations are in agreement with models in which superconductivity is accompanied by an increased charge carrier spectral weight. The measured spectral weight transfer is large enough to account for the condensation energy in these compounds.

A universal property of the superconducting state is the condensation of pairs of electrons into a single macroscopic quantum state. Superconductivity in conventional models was described by Bardeen, Cooper, and Schrieffer (BCS theory) and has been understood to result from an effective attractive interaction between electrons (*1*). When the material becomes superconducting, this causes a reduction of the potential energy and a slight increase of the kinetic energy. The net amount of energy released is defined as the condensation energy. In many materials, the pairs have a fully symmetric, or *s*-wave, internal symmetry, which is a natural consequence of phonon-mediated pairing. In the cuprate high transition temperature (high T_c) superconductors, the condensed pairs have a *d*-wave symmetry, which is an indication of an unconventional mechanism. Therefore, new models have been proposed in which the "glue" that binds the carriers consists of something different from phonons (*2–10*). The model by Hirsch predicts a reduction of kinetic energy when two holes are nearby (*4*, *5*) and provides quantitative predictions for superconductivity-induced spectral weight transfer, in agreement with the experimental data we present here. Various other models predict that in the cuprates, the normal state is not a Fermi liquid and that superconductivity is driven by recovering frustrated kinetic energy of single charge carriers when pairs are formed (*7*, *8*), by lowering the *ab*-plane zero-point kinetic energy (*9*), or by Bose-Einstein condensing pairs already present in the normal state (*10*).

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Experimental study of the optical conductivity may help to identify different contributions to the condensation energy. It has previously been shown (*11–15*) that the superconductivity-induced change of kinetic energy perpendicular to the planes, as revealed by the *c*-axis plasma resonance and penetration depth, is two orders of magnitude too small to account for the condensation energy in $Tl_2Ba_2CuO_6$. This was used to rule out interlayer tunneling (*2*, *3*) as a generic mechanism of superconductivity in the cuprates, although it is still true that the *c*-axis kinetic energy is lowered (*16*). Recent observations that the intensity of the single-particle excitation spectra of $Bi_2Sr_2CaCu_2O_{8+\delta}$ scales like the superfluid density (*17*, *18*) cannot be reconciled by conventional pairing models.

Based on general principles, the spectral weight contained in the optical conductivity, $\sigma(\omega)$, satisfies the frequency-sum, or f-sum, rule

$$\int_0^\infty \sigma(\omega)d\omega = \pi ne^2/(2m) = A, \text{ where } n, e,$$

and m are the electron density, charge, and mass, respectively, and ω is the photon angular frequency. For all temperatures, the total spectral weight A is constant, which depends only on the density of electrons in the system. In a superconductor, the presence of a condensate causes a δ function at zero frequency in the conductivity. The spectral weight of this δ function, D, is revealed at finite frequencies as a contribution to the dielectric function of the form $\varepsilon_L(\omega) = -8D/\omega^2$. Thus, the optical conductivity of a superconductor has both a regular ($\omega > 0$) part and a singular part, $D\delta(\omega)$. The spectral weight of the regular part consists of the contributions from free carrier ("Drude") intraband transitions (A_l) and from interband transitions (A_h). Here we use

$$A_l = \int_{0+}^{\Omega} \sigma(\omega)d\omega \text{ with } \Omega/(2\pi c) = 10{,}000$$

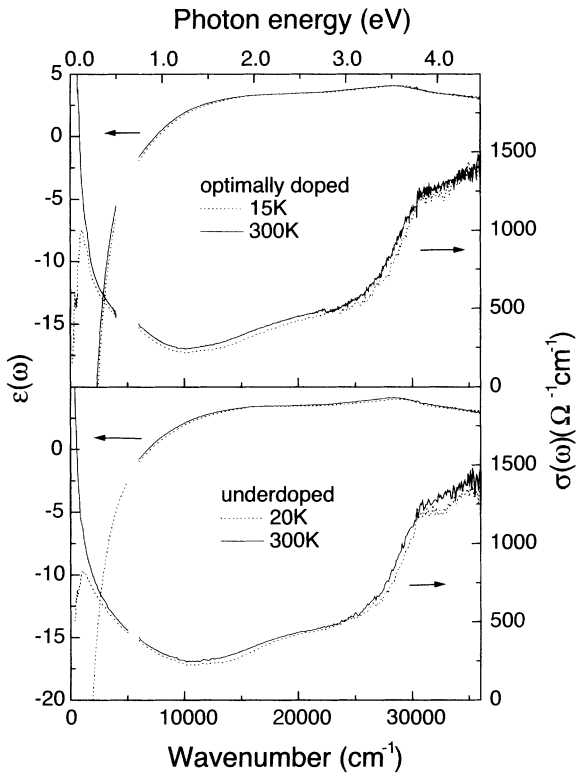
cm^{-1} which corresponds to the minimum of $\sigma(\omega)$ between the intraband and the interband transitions, and $A_h = \int_{\Omega}^{\infty} \sigma(\omega)d\omega$. In experimental practice, the upper limit of the latter integral has to be finite. Here we will integrate up to 20,000 cm^{-1}, which corresponds to the range where the noise of our spectrometer is still sufficiently low. In the superconducting state, an energy gap opens up in the optical conductivity, observable as a suppression of $\sigma(\omega)$ for frequencies in the gap region. The corresponding spectral weight removed from A appears as the δ function at zero frequency. The conservation of spectral weight can be expressed as the Ferrell-Glover-Tinkham (FGT) sum rule (*1*, *19*)

$$D = A_l^n - A_l^s + A_h^n - A_h^s \quad (1)$$

Here the superscript s refers to the superconducting state, and the superscript n refers to the normal state. In the conventional approach according to BCS theory, the value of the interband spectral weight A_h is not affected by the superconducting phase transition; that is, $A_h^s = A_h^n$. Quijada *et al.* (*20*, *21*) have verified Eq. 1 for the *ab*-plane optical conductivity of $Bi_2Sr_2CaCu_2O_{8+\delta}$ and other high-T_c cuprates, with an experimental accuracy of ~0.04 eV^2. Optical thin film absorption (*22*, *23*), thermal difference reflectance (*24*), femtosecond spectroscopy (*25*, *26*), and ellipsometry (*27*) have indicated that, for light polarized along the *ab* plane, an influence of superconductivity on the optical constants exists at frequencies exceeding 10^4 cm^{-1}.

If the spectral weight is transferred from A_h to $D + A_l$, this should show up for frequencies intermediate between the intraband region and the interband region as a contribution to $\varepsilon(\omega)$ proportional to $-\omega^{-2}$. The plasma frequency ω_p, the frequency where ε crosses zero, would therefore be blue-shifted, reflecting an increase of $D + A_l$. Our data are consistent with this effect for the *ab*-plane optical conductivity of $Bi_2Sr_2CaCu_2O_{8+\delta}$.

We investigated optimally doped (T_c = 88 K) and underdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ (T_c = 66 K) single crystals. The crystals have a small *a-b* anisotropy, and changes with temperature are independent of the crystallographic direction (*28*). The dielectric function was measured with spectroscopic ellipsometry between 6000 and 36,000 cm^{-1}, with detailed temperature dependence up to 20,000 cm^{-1}. In the infrared frequency range between 200 and 6000 cm^{-1}, we measured the reflectivity at normal incidence, using in situ gold evaporation as a reference. The complex dielectric function was



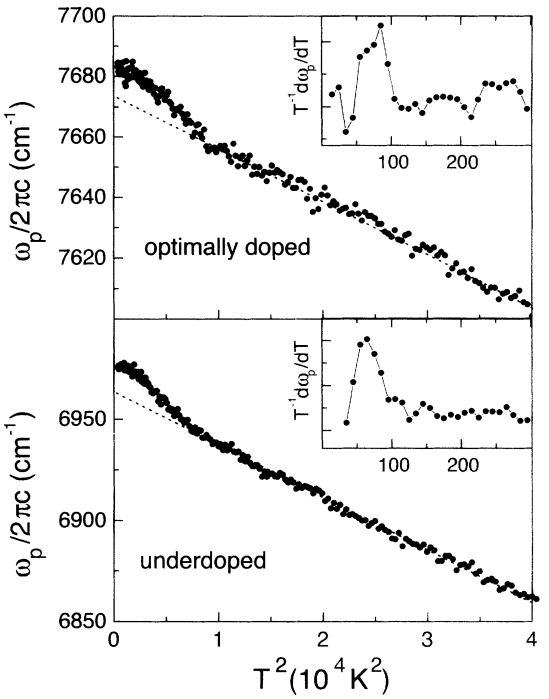


Fig. 1 (left). Dielectric function $\varepsilon(\omega)$ and optical conductivity $\sigma(\omega)$ of optimally doped (top) and underdoped (bottom) $Bi_2Sr_2CaCu_2O_{8-\delta}$ versus photon energy in the superconducting state and at 300 K. **Fig. 2 (right).** Temperature dependence of the screened plasma frequency ω_p for optimally doped (top) and underdoped (bottom) $Bi_2Sr_2CaCu_2O_{8-\delta}$. **(Insets)** Derivatives $T^{-1}d\omega_p/dT$.

then calculated from the reflectivity spectrum by means of Kramers-Kronig analysis, in which the experimental dielectric function between 6000 and 36,000 cm^{-1} was used to anchor the phase spectrum according to the procedure in (*29*). For both crystals, all spectra were recorded in 2 K intervals between 10 and 300 K, thus providing, for 150 different temperatures, the real $[\varepsilon'(\omega)]$ and imaginary $[\varepsilon''(\omega) = 4\pi\sigma(\omega)/\omega]$ part of the *ab*-plane dielectric function covering the range from 200 to 20,000 cm^{-1}.

The dielectric function and the optical conductivity are displayed as a function of photon energy for 15 and 300 K (Fig. 1), where it is seen that the plasma resonance frequency ω_p exhibits a blue shift when the temperature decreases. In Fig. 2 we present the temperature dependence of ω_p for the two samples. In the insets, the temperature derivatives are displayed, showing a maximum at the phase transition. At T_c, the temperature dependence of $\partial\omega_p/\partial T$ exhibits nonmonotonic behavior: We observe that $\omega_p(T)$ breaks away from the (approximately T^2) temperature dependence of the normal state when superconducting correlations begin to develop.

To illustrate the suppression of spectral weight in the visible range, we display in Fig. 3 the measured spectral weight integrated from

$$10{,}000 \text{ to } 20{,}000 \text{ cm}^{-1},\ A_h = \int_{10{,}000}^{20{,}000} d\omega\sigma(\omega)$$

as a function of temperature, showing a progressive reduction of spectral weight as the temperature is lowered and an acceleration of the spectral weight removal as the material enters the superconducting state. The insets show the derivative with a peak at the phase transition.

What could be the reason for this temperature dependence? The most obvious candidate would be an overall increase of low-frequency spectral weight in the superconducting state. To explore this possibility, we calculate $A_{1+D} = A_1 + D$ for each temperature in two different ways: (i) We fit a set of Drude-Lorentz oscillators simultaneously to $\varepsilon'(\omega,T)$ and $\varepsilon''(\omega,T)$ in the frequency range from 6000 to 20,000 cm^{-1} and to the infrared reflectivity $R(\omega,T)$ in the range from 200 to 6000 cm^{-1}. Direct integration of the Drude-Lorentz oscillators (including the condensate δ peak) provides $A_{1+D}(T)$. (ii) Using Kramers-Kronig analysis of the infrared reflection spectra and the spectra in the visible range, we obtain the real and imaginary parts of $\varepsilon(\omega)$ with high accuracy, from which the low-frequency spectral weight $A_{1+D}(T)$ is obtained directly. The results are displayed in Figs. 3 and 4. Both the absolute value of A_{1+D} and the kink at T_c are the same for methods (i) and (ii) (*30*). We see that in both samples, $A_h(T)$ and $A_{1+D}(T)$ have opposite temperature dependencies. In the normal state and in the superconducting state, the spectral weight removed from $A_h(T)$ upon reducing temperature is recovered in $A_{1+D}(T)$. As temperature is reduced, $A_{1+D}(T)$ increases about 6% between 300 and 4 K. In addition, there is a slight extra increase of $A_{1+D}(T)$ below the superconducting phase transition, whereas $A_h(T)$ slightly decreases, indicating that spectral weight is transferred from the 10,000 to 20,000 cm^{-1} frequency range to low frequencies when the material becomes superconducting.

In two dimensions, the relation between the intraband optical spectral weight and the kinetic properties of the charge carriers is formalized by (*31*)

$$\frac{2\hbar^2 V_{Cu}}{\pi e^2} A_{1+D} = \sum_k \frac{2\hbar^2 n_k}{m_{xx}(k)a^2} = -K \quad (2)$$

where a is the lattice parameter, V_{Cu} is the cell volume per Cu atom, and n_k and $1/m_{xx}(k) = \partial^2\varepsilon/\partial k_x^2$ are the momentum occupation number and the reciprocal mass of the conduction electrons. In the case of nearest-neighbor hopping,

$K = \sum_k n_k\varepsilon_k$ corresponds to the kinetic energy

(*5*, *32*). A nonzero value of the quantity $A_{1+D}^S - A_1^n$ means that the GFT sum rule is not satisfied within the intraband region. The spectral weight transferred from A_h to A_{1+D} is then proportional to the change in kinetic energy. We estimate that for optimally doped $Bi_2Sr_2CaCu_2O_{8-\delta}$, $K^s - K^n$ is about -1 meV per copper atom (*33*). For the underdoped sample, the order of magnitude appears to be the same, although the rounded behavior near T_c makes an estimate of $K^s - K^n$ more ambiguous. A value of -1 meV is certainly large enough to account for the condensation energy: Estimates of the condensation energy of $Bi_2Sr_2CaCu_2O_{8-\delta}$ vary from 0.06 to 0.25 meV per copper atom,

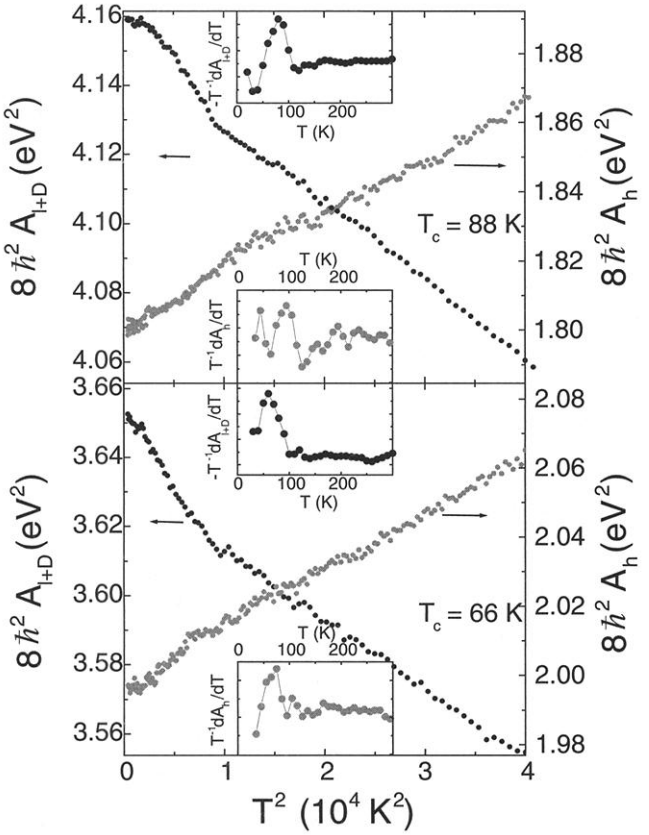


Fig. 3 (left). Temperature dependence of the low-frequency spectral weight $A_{1+D}(T)$ and the high-frequency spectral weight $A_h(T)$, for optimally doped (top) and underdoped (bottom) $Bi_2Sr_2CaCu_2O_{8-\delta}$. **(Insets)** Derivatives $-T^{-1}dA_{1+D}/dT$ and $T^{-1}dA_h/dT$.

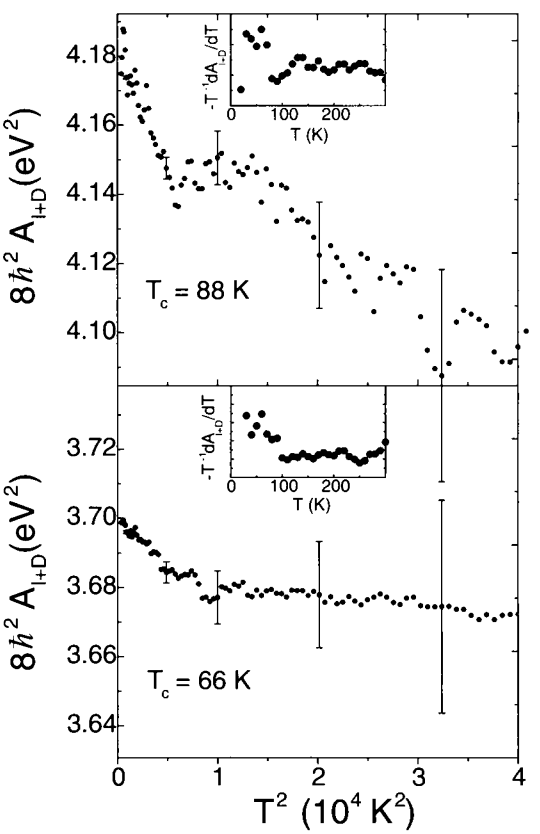


Fig. 4 (right). Temperature dependence of the low-frequency spectral weight $A_{1+D}(T)$ for optimally doped (top) and underdoped (bottom) $Bi_2Sr_2CaCu_2O_{8-\delta}$. The infrared optical conductivity was obtained by a Kramers-Kronig transformation of the reflection data. **(Insets)** Derivatives $-T^{-1}dA_{1+D}/dT$.

depending on the doping (*34*). The question of whether the observed spectral weight transfer is a generic property of the cuprates or a specific property of $Bi_2Sr_2CaCu_2O_{8-\delta}$ needs to be addressed by further experiments.

We see that in underdoped and optimally doped $Bi_2Sr_2CaCu_2O_{8-\delta}$ the onset of superconductivity is accompanied by a transfer of spectral weight from the spectral region above 10,000 cm^{-1} to the intraband optical spectrum. This behavior contradicts that expected from traditional models of superconductivity and is a strong indication that superconductivity in the cuprates is unconventional.

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28. The crystals were 1 by 3 mm in size and 0.1 mm in thickness, with mirror-like *ab* planes, and were grown by the traveling solvent floating zone method in an argon/oxygen mixture. Underdoped crystals were obtained by annealing in flowing nitrogen at 700°C and optimally doped crystals were obtained by annealing in flowing air at 750°C for several days. Between 6000 and 36,000 cm^{-1}, the *ab*-plane pseudodielectric function was measured with spectroscopic ellipsometry, at an angle of incidence of 80° and a pressure below 2×10^{-9} mbar. The pseudodielectric functions were then corrected for the admixture of *c*-axis polarization by means of *c*-axis optical constants [see also S. Tajima, D. G. Gu, S. Miyamoto, A. Odagawa, N. Koshizuka, *Phys. Rev. B.* **48**, 16164 (1993)].
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30. The overall temperature dependence appears to be somewhat different for the two methods. Ellipsometry measures relative amplitudes for different polarizer settings and is therefore self-aligned. Reflectometry is more strongly affected by instrumental drift. The error bars in Fig. 4 indicate the range within which the traces as a function of temperature of method (ii) can vary due to a gradual drift of the detected signal.
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33. By extrapolating the normal state $A_1^n(T)$ to 4 K, the difference spectral weight, $\Delta A_1 = A_{1+D}^s(4\text{ K}) - A_1^n(4\text{ K})$, can be calculated. To make the conversion from the units of eV^2 used in Fig. 3 to units of meV per Cu atom, we have to multiply $8\hbar^2 A$ with a factor $-10^3 V_u / (4\pi e^2 a^2) = -83$ (meV/eV^2).
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