Grazing Incidence Infrared Reflectivity of $La_{1.85}Sr_{0.15}CuO_4$ and NbN

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Infrared reflectivity measurements, using *p*-polarized light at a grazing angle of incidence, show an increased sensitivity to the optical conductivity of highly reflecting superconducting materials. We demonstrate that when this measurement technique is applied to the conventional *s*-wave superconductor NbN, the results are in perfect agreement with BCS theory. For the in-plane response of a $La_{1.85}Sr_{0.15}CuO_4$ single crystal, in the superconducting state, we find a reduction of the optical conductivity in the frequency range below 20 meV. The observed frequency dependence excludes an isotropic *s*-wave gap, but agrees well with model calculations assuming a *d*-wave order parameter.

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The symmetry and magnitude of the superconducting order parameter belong to the key elements of theoretical models of the superconducting state of the high T_c cuprates. The issue of the order parameter symmetry is intimately related to the question as to whether superconductivity is caused by local exchange correlations, antiferromagnetic spin fluctuatons, interlayer pairing, or electron-phonon interactions [1]. Much of the data which have been interpreted as evidence for *d*-wave pairing, using a wide variety of experimental techniques, were obtained on the double-layer compounds $Bi_2Sr_2Ca_1Cu_2O_8$ and $YBa_2Cu_3O_7$ [2]. However, for compounds with two or more CuO layers per unit cell the presence of several coupled charge reservoirs complicates the picture, and increases the number of possible interpretations of the experimental results [3], as was recently discussed [4] for, e.g., the experimentally observed sign reversals of the order parameter in $YBa_2Cu_3O_7$. On the other hand, the single-layer cuprate superconductors, such as $La_{1-x}Sr_xCuO_4$, have only a single band of electrons per unit cell, which in principle facilitates the interpretation of experimental data.

The experimental results on $La_{1-x}Sr_xCuO_4$ using Raman spectroscopy [5], specific heat measurements [6], and inelastic neutron scattering [7] indicate a strong anisotropy of the order parameter, possibly due to *d*-wave pairing. In this Letter we discuss a set of infrared experiments on $La_{1.85}Sr_{0.15}CuO_4$. The classical technique of infrared spectroscopy offers the advantage of sensitivity to the bulk of the material, high energy resolution, and the fact that the optical conductivity determined by this method can be interpreted in a theoretically well-defined way as the current-current correlation function.

Although mm-wave studies of the low-frequency penetration depth have been successfully used to probe, via the temperature dependence, the possible existence of nodes in the order parameter of $YBa_2Cu_3O_7$, a direct spectroscopic determination of the order parameter with infrared and mm-wave techniques has been limited so far by several experimental factors: (1) The low-frequency limiting behavior of the reflectivity of a (nonsuperconducting) metal is given by the Hagen-Rubens expression $R = 1 - 0.366\ (\nu\rho_{\mathrm{dc}})^{1/2}$ with ν in units of cm^{-1}, ρ in units of Ω cm, the reflectivity of a good conductor is high. For the high T_c cuprates $\rho \approx 100\ \mu\Omega$ cm, so that for frequencies of the order of $3.5k_BT_c$, and $T_c = 30$ K, $R = 0.97$. As a result, the changes in reflectivity upon entering the superconducting state are difficult to detect, especially because the changes take place gradually [8]. (2) The range of order-parameter-induced changes in conductivity coincides with the frequency range of optical phonons. The electronic conductivity in the *c* direction is very small in these materials, and therefore changes are masked by the rather strong contributions due to optical phonons [9,10].

In this paper we describe and demonstrate that the situation with respect to problem (1) can be improved by using polarized light incident at a grazing angle. For *p*-polarized light the reflectivity is given by the expression

$$R_p(\theta,\omega) = \left| \frac{\epsilon\cos\theta - \sqrt{\epsilon - \sin^2\theta}}{\epsilon\cos\theta + \sqrt{\epsilon - \sin^2\theta}} \right|^2 . \qquad (1)$$

For a metal in the limit where $\omega\tau \ll 1$, the absorptivity $A_p = 1 - R_p = 4/\cos\theta\sqrt{\omega/4\pi\sigma}$ is enhanced by a factor $1/\cos\theta$, up to an angle $\theta_c = \arccos\sqrt{\omega/4\pi\sigma}$ where it reaches a maximum. On the other hand, in the superconducting state the dielectric properties at low frequencies are dominated by the real part of the dielectric function, $\mathrm{Re}\ (\epsilon) = -c^2[\omega\lambda(T)]^{-2}$, where $\lambda(T)$ is the penetration depth. The absorbtivity $A_p = 4/\cos\theta c^{-3}\omega^2\lambda(T)^3 4\pi\sigma$

vanishes as $\sigma \to 0$ below the gap. Therefore, by measuring the reflectivity at a grazing angle of incidence with *p*-polarized light, we enhance our sensitivity to changes in σ with roughly a factor of $1/\cos\theta$. In the present study we have chosen an angle $\theta = 80° \pm 3°$, resulting in an enhancement factor of approximately 6. For the samples studied in this paper the superconductivity-induced changes in reflectivity are of the order of 1% at normal incidence. This is at the border of what can be measured experimentally (with a typical accuracy of about 0.5%). At $\theta = 80°$ the level of superconducting-induced changes is raised to a comfortable 10%. The grazing incidence method is different from, and complementary to, improvements in counting statistics, e.g., by using larger samples, brighter sources, etc.

$La_{1.85}Sr_{0.15}CuO_4$ single crystals with a T_c of 32 K were grown by the traveling solvent floating zone method, and cut along the *a*-*c* plane. The dimensions of the clean and polished crystal surface were approximately 7 mm along the *a* axis and 4 mm along the *c* axis. The samples were mounted such that the plane of scattering coincides with the CuO planes. The samples were mounted in a conventional flow cryostat using the two opposite windows for scattering in a cone of $80° \pm 3°$ relative to the surface normal. A wire grid polarizer was used to select the proper polarization. Special care was taken to prevent stray light from reaching the detectors. Although all the measurements reported here were taken with *p*-polarized light, by rotating the wire-grid polarizer by 90° we were able to direct $\vec{E} \parallel \vec{c}$ and detect the appearance of the *c*-axis plasmon as T drops below T_c [10]. This was used both as an *in situ* check for correct crystal orientation and as an "internal" indicator of the sample temperature. NbN films of 400 and 55 nm thickness were prepared on substrates of MgO by dc reactive magnetron sputtering, in a gas composition of 3.0% CH_4/30.0% N_2/Ar, at a temperature of approximately 840° C to produce high quality epitaxial growth [11]. The carbon addition improves film quality which was checked by x-ray diffraction and high resolution electron microscopy. The films had a superconducting transition temperature of 16.5 K, and a resistivity ratio (300 K/16.5 K) close to unity.

Reflectivities at 80° angle of incidence were measured at temperatures between 4 and 60 K. With a gold reference mirror we checked that the effects of thermal expansion of the cryostat on our results are very small within this range of temperatures. Initially, the normal incidence absolute reflectivity at 40 K was measured with high precision (inset of Fig. 1, upper panel), we then calculated the dielectric function using the Kramers-Kronig transformation, and from this, the reference reflectivity curve at 40 K and 80° angle of incidence. Absolute reflectivities at all temperatures were obtained by multiplying the reflectivity ratios to this reference curve, and by correcting for thermal expansion effects of the cryostat as detected with a gold reference mirror in a separate session. Although under conditions of *s* polarization the *c*-axis plasmon shows up very prominently below T_c, with $\vec{E}$ polarized parallel to the planes we observed no distinct gap feature in the case of $La_{1.85}Sr_{0.15}CuO_4$. Because the observed thermally induced changes are quite subtle, we reproduced the measurements several times on two different crystals.

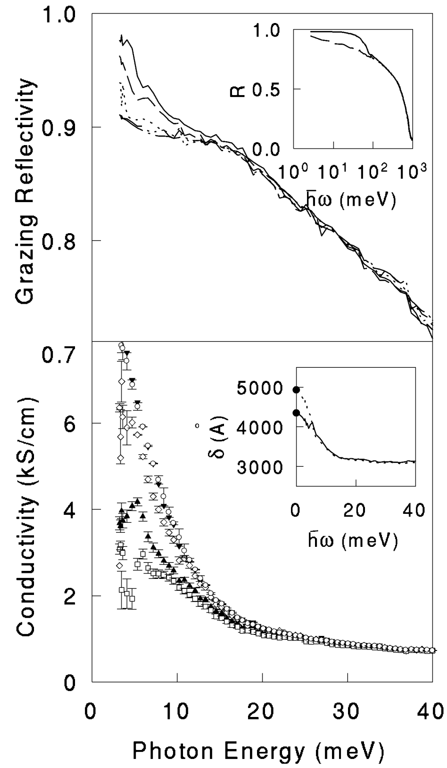

FIG. 1. Upper panel: Reflectivity of $La_{1.85}Sr_{0.15}CuO_4$ at 80° angle of incidence at 4 K (solid), 20 K (dashed), 27 K (dotted), 40 K (dash-double-dotted), and 50 K (chained). Inset: Reflectivity at normal angle of incidence for 40 K (solid) and 300 K (dashed). Lower panel: Optical conductivity at 50 K (inverted closed triangles), 40 K (circles), 27 K (lozenges), 20 K (closed triangles), and 4 K (squares) obtained from the reflectivities using Kramers-Kronig relations. Inset: Skin depth for 4 K (solid) and 20 K (dashed). The solid dots are the penetration depth obtained from the *f*-sum rule.

The absolute reflectivities are displayed in the upper panel of Fig. 1 for temperatures between 4 and 50 K. In the inset we show the reflectivity taken at normal incidence. Below 3 meV the extrapolation was based upon a two-fluid model as described in [12]. A Kramers-Kronig transformation gives the pseudodielectric function at 80°, and from this the dielectric function and the optical conductivity which is displayed in the lower panel of Fig. 1. In order to check the internal consistency of the analysis, as well as agreement with published values of the penetration depth, we calculated $\lambda(\omega)$ by two different methods. The skin depth, defined as $\delta = c/(\omega \operatorname{Im} \sqrt{\epsilon})$, must be taken in the limit $\omega \to 0$ to obtain the superconducting penetration depth (inset of

Fig. 1, lower panel). Alternatively, if the temperature dependence results from a transfer of spectral weight to the condensate peak at $\omega = 0$, the penetration depth follows from the Glover-Tinkham-Ferell sum rule formula $c^2\lambda(\omega)^{-2} = 8\int_{0^+}^{\infty}[\sigma_n(\omega') - \sigma_s(\omega')]d\omega'$. In our analysis these two values coincide with an accuracy better than 1%. We therefore conclude that the "missing" area in the conductivity is indeed transferred to the condensate peak, and is therefore inherently linked to the formation of the superconducting state. The values of $\lambda = 4300 \pm 30$ and 4900 ± 30 Å at 4 and 20 K, respectively, are in good agreement with measurements at 10 GHz [13].

It has been suggested [14] that the low-frequency electrodynamics can be understood as a sum of a temperature independent midinfrared (MIR) band and a Drude contribution which narrows upon lowering the temperature. This empirical decomposition of the data has been used to describe normal incidence reflectance and conductivity spectra for frequencies typically above 12 meV. For our sample the MIR band can be parametrized with the function $\sigma_M \,\mathrm{Re}\,\omega/(\omega + i[\omega_M^2 - \omega^2]\tau)$, where $\sigma_M = 800$ S/cm, $\hbar\omega_M \approx 0.16$ eV, and $\hbar\tau^{-1} = 0.66$ eV. Clearly for $\hbar\omega < 40$ meV the conductivity is dominated by the free carrier contribution. The suppression of conductivity below 18 meV is markedly different from a narrowing (or depletion) of the Drude peak on a constant MIR background. On the other hand, there is also no gap in the observed frequency range. If $La_{1.85}Sr_{0.15}CuO_4$ would be an isotropic s-wave superconductor, then BCS theory predicts that the gap should be at approximately 10 meV. As there is no spurious background in the present spectra, it is clear from these data that such a BCS gap is absent.

To verify that our experimental method will indeed show the presence of a gap if there is one, we show in Fig. 2 the conductivity obtained with the same grazing incidence technique on a thick (400 nm) film of NbN. NbN thin films deposited on MgO are suitable for IR transmission spectroscopy; our measurements show that this material behaves like a classical BCS superconductor, as can be seen from the quality of the fits in Fig. 2 (lower panel). With $T_c = 16.5$ K the gap is at approximately 6 meV [$2\Delta/k_BT_c \simeq 4$, which is now quite close to the lower limit of our window of observation (of 3 meV)]. In terms of "cleanliness" in the normal state, this material has an even higher reflectivity than high T_c superconductors as the dc conductivity is about 14 000 S/cm. In this case, however, the changes in the measured reflectivity at grazing incidence are quite large, and a clear gap opens up in the conductivity. As can be seen from the solid curves the agreement with simulations [15] assuming an isotropic s-wave gap of $2\Delta = 4k_BT_c$ for NbN [16] with intermediate scattering rate ($\hbar/\tau = 14$ meV) is excellent.

In Fig. 3 we display our experimental data at 4 and 40 K together with model calculations for $La_{1.85}Sr_{0.15}CuO_4$, based on BCS s-wave theory with finite scattering ($2\Delta = 3.5k_BT_c$) [15] and a weak coupling calculation with finite scattering rate assuming d-wave pairing [17]. As parameters we took $\hbar/\tau = 6$ meV, and $\omega_p = 0.73$ eV. By fixing T_c at 32 K we also fixed the value of the gap. For the case of d-wave pairing, T_c is quite strongly suppressed due to the presence of scattering [18]. In our calculations we had to take $T_{c0} = 64$ K, which is then reduced to 32 K due to our assumed scattering rate of 6 meV. There is an intrinsic ambiguity in the choice of the latter: Although the scattering rate needed to fit the data for $T < 50$ K and $\omega > 6$ meV is temperature independent, the linear temperature dependence of the decay rate still exists at lower (notably, dc) frequencies. Hence the physical origin of the scattering rate seems not to be solely due to impurity scattering. The present weak-coupling calculations do not faithfully represent this aspect of the problem, but have the advantage of using only a limited number of adjustable parameters. As T_c, $1/\tau$, and ω_p are fixed by experimental constraints, the only free parameter left is the scattering cross section $\sigma_{\rm sc} = \sin^2\eta$, where η is the phase shift. The comparison with experimental data in Fig. 3 strongly

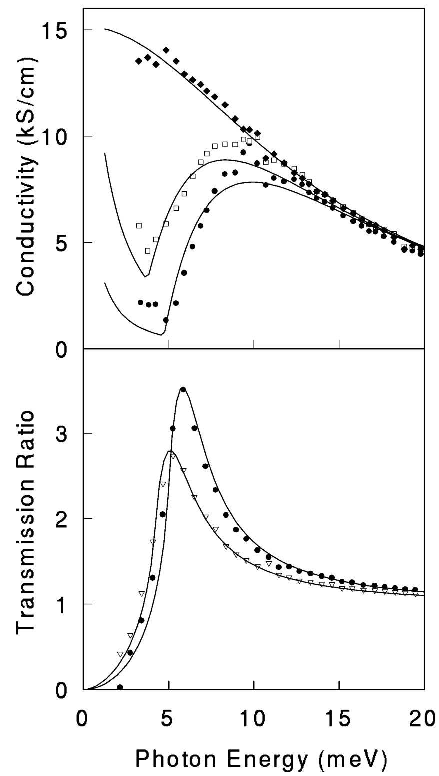

FIG. 2. Upper panel: Optical conductivity of NbN calculated from 80° angle of incidence reflection spectra for 9 K (closed circles), 13 K (open squares), and 18 K (closed diamonds). Solid curves: Theoretical calculations assuming isotropic s-wave pairing. Lower panel: Measured transmittivity ratios of a 55 nm thick NbN film on MgO [closed circles, $T(9\text{ K})/T(18\text{ K})$; open symbols, $T(13\text{ K})/T(18\text{ K})$]. The solid curves are calculated using the same parameters as for the conductivity of the top panel.

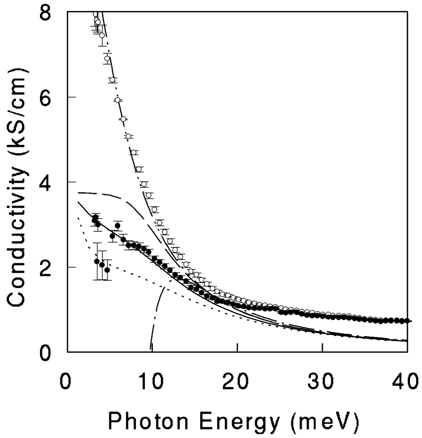

FIG. 3. Comparison of the experimental optical conductivity at 4 K (solid circles) and 40 K (open circles) to model calculations for the optical conductivity of $La_{1.85}Sr_{0.15}CuO_4$ assuming an intermediate impurity scattering rate at $T = 40$ K K (dash-double-dotted). The other curves are calculated for 4 K assuming isotropic *s*-wave pairing (chained), *d*-wave pairing with $\sigma = 0.1$ (dotted), *d*-wave with $\sigma = 0.4$ (solid), and *d*-wave with $\sigma = 0.8$ (dashed).

favors *d*-wave symmetry with $\sigma_{sc} = 0.4$, so that $\eta \approx 0.2\pi$. The analysis of microwave surface impedance measurements of $YBa_2Cu_3O_y$ between 4 and 40 GHz indicates that for these materials the elastic scattering is very small and close to the unitarity limit $(0.98 < \eta < 1)$ [19,20]. The temperature dependence of the *ab*-plane penetration depth of $La_{2-x}Sr_xCuO$ measured at 10 GHz drops slightly below the BCS prediction for *s*-wave pairing [13]. These data do not exclude the possibility of *d*-wave pairing in the presence of impurity scattering, in which case $\Delta\lambda \propto T^2$ [21]. Although an isotropic *s*-wave gap is clearly ruled out by our analysis, we cannot rule out the possibility of a strongly anisotropic gap, or an incoherent mixture of *s*- and *d*-wave symmetry $(s + d)$. In such cases a lower bound exists on the distribution of gap values along the Fermi surface. In the optical spectra a full gap opens only below the lower bound of this distribution. From our data we conclude that such a lower bound, if it exists, must be located below 3 meV $(1.3k_BT_c)$.

Using grazing incidence reflectivity, we determined the optical conductivity of $La_{1.85}Sr_{0.15}CuO_4$ and NbN below and near the superconducting phase transition down to a photon energy of 3 meV. In the case of NbN a clear BCS gap was observed. For $La_{1.85}Sr_{0.15}CuO_4$ good agreement was obtained with model calculations assuming *d*-wave pairing and scattering closer to the Born limit.

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