Far-infrared and submillimeter-wave conductivity in electron-doped cuprate \( \text{La}_{2-x}\text{Ce}_x\text{CuO}_4 \)

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We performed far-infrared and submillimeter-wave conductivity experiments in the electron-doped cuprate \( \text{La}_{2-x}\text{Ce}_x\text{CuO}_4 \) with \( x = 0.081 \) (underdoped regime, \( T_c = 25 \text{ K} \)). The onset of the absorption in the superconducting state is gradual in frequency and is inconsistent with the isotropic s-wave gap. Instead, a narrow quasiparticle peak is observed at zero frequency and a second peak at finite frequencies, clear fingerprints of the conductivity in a d-wave superconductor. A far-infrared conductivity peak can be attributed to \( 2\Delta_0 \), or to \( 2\Delta_0 + \Delta_{\text{spin}} \), where \( \Delta_{\text{spin}} \) is the resonance frequency of the spin-fluctuations. The infrared conductivity as well as the suppression of the quasiparticle scattering rate below \( T_c \) are qualitatively similar to the results in the hole-doped cuprates.

I. INTRODUCTION

The interest in the physical properties of electron-doped superconductors [1] has revived recently concerning the symmetry of the superconducting order parameter. Earlier results in these compounds on penetration depth [2], Raman [3] and tunneling spectroscopies [4] were explained in terms of conventional (s-wave) symmetry of the superconducting order parameter. However, later experiments, including half-flux effect [5], penetration-depth measurements [6], and photoemission [7] provided strong evidences for d-wave type symmetry. This contradiction can possibly be resolved on the basis of recent microwave experiments [8] and point-contact spectroscopy [9], which suggest changes of the gap symmetry as a function of doping.

Electron doping of the high-\( T_c \) cuprates can be achieved by substituting \( \text{Ce}^{4+} \) into \( \text{La}_2\text{CuO}_4 \) with \( \text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{and Eu} \) [10]. Among these family \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \) is the earliest known and best studied compound [11]. The highest transition temperatures for electron-doped cuprates (\( T_c = 30 \text{ K} \)) can be achieved in \( \text{La}_{2-x}\text{Ce}_x\text{CuO}_4 \) (LCCO) [10]. The temperature of the superconducting transition in LCCO is close to \( T_c = 39 \text{ K} \) in a recently-discovered superconductor \( \text{MgB}_2 \) [12], which is believed to be of BCS-type [13]. In order to obtain valuable information about the gap symmetry in LCCO, a direct comparison of the physical properties of these compounds can be carried out. Such analysis is provided by the low-frequency electrodynamics which directly visualizes many important features of superconductors as energy gap [13, 16] or quasiparticle scattering rate [17].

In this paper we present the far-infrared and submillimeter-wave conductivity of underdoped (\( x = 0.081, T_c = 25 \text{ K} \)) LCCO thin film. In order to obtain the complex conductivity above and below the superconducting gap energy, two different experimental methods have been applied using the same sample. For frequencies below 40 cm\(^{-1} \) the complex conductivity has been obtained by the submillimeter transmission spectroscopy. At higher frequencies the reflectance was measured using standard far-infrared techniques and the conductivity has been obtained via a Kramers-Kronig analysis of the spectra.

II. EXPERIMENTAL DETAILS

High quality \( \text{La}_{2-x}\text{Ce}_x\text{CuO}_4 \) film with \( x = 0.081 \pm 0.01 \) (underdoped regime), were deposited by molecular-beam epitaxy [14] on transparent (001) \( \text{SrLaAlO}_4 \) substrates \( 10 \times 10 \times 0.5 \text{ mm}^3 \) in size. The thickness of the present film was 140 nm and the film revealed a sharp transition into the superconducting state (\( \Delta T_c < 1 \text{ K} \)) at \( T_c = 25 \text{ K} \). Lower transition temperature compared to the optimal doping (\( x \approx 0.11, T_c = 30 \text{ K} \) [15]) confirms the underdoped character of the sample.

The transmission experiments for frequencies \( 5 \text{ cm}^{-1} < \nu < 40 \text{ cm}^{-1} \) were carried out in a Mach-Zehnder interferometer arrangement [15] which allows both, the measurements of the transmittance and the phase shift of a film on a substrate. The properties of the blank substrate were determined in a separate experiment. Utilizing the Fresnel optical formulas for the complex transmission coefficient of the substrate-film system, the absolute values of the complex conductivity \( \sigma^* = \sigma_1 + i\sigma_2 \) were determined directly from the measured spectra. In the frequency range \( 40 < \nu < 4000 \text{ cm}^{-1} \) reflectance measurements were performed using a Bruker IFS-113v Fourier-transform spectrometer. In addition, the reflectance for frequencies \( 5 < \nu < 40 \text{ cm}^{-1} \) was calculated from the complex conductivity data of the same samples, which was obtained by the submillimeter transmission. This substantially improves the quality of the subsequent Kramers-Kronig analysis of the reflectance and therefore the reliability of the data especially at low frequencies. A similar technique has been applied recently to the films of newly discovered \( \text{MgB}_2 \) [16, 20], leading to the observation of a superconducting absorption edge. Reference [18] gives
The reflectance of a thin metallic film on a dielectric substrate can be obtained from the Maxwell equations [21]:

\[
r = \frac{r_{0f} + r_{fs} \exp(4\pi i n_f d/\lambda)}{1 + r_{0f} r_{fs} \exp(4\pi i n_f d/\lambda)},
\]

with \( r_{0f} = (1-n_f)/(1+n_f) \) and \( r_{fs} = (n_f-n_s)/(n_f+n_s) \) being the Fresnel reflection coefficients at the air-film (\( r_{0f} \)) and film-substrate (\( r_{fs} \)) interface. Here \( n_f = (\sigma^*/\varepsilon_0 \omega^*)^{1/2} \) and \( n_s \) are the complex refractive indices of the film and substrate, respectively, \( \lambda \) is the radiation wavelength, \( d \) is the film thickness, \( \omega = 2\pi \nu \) is the angular frequency, \( \sigma^* = \sigma_1 + i\sigma_2 \) is the complex conductivity of the film, and \( \varepsilon_0 \) is the permittivity of free space. Eq. (1) is written neglecting the multiple reflections from the opposite sides of the substrate.

If the film thickness is smaller than the penetration depth \( (|n_f| d \ll \lambda) \) and if \( |n_f| \gg |n_s| \), Eq. (1) can be simplified to:

\[
r \approx \frac{1 - \sigma^* d Z_0 - n_s}{1 + \sigma^* d Z_0 + n_s},
\]

where \( Z_0 = \sqrt{\mu_0/\varepsilon_0} \approx 377 \Omega \) is the impedance of free space. Eq. (2) provides a good approximation of the reflectance at submillimeter frequencies. For higher frequencies Eq. (2) has to be used.

III. RESULTS AND DISCUSSION

The middle panel of Fig. 1 shows the far-infrared reflectance of the underdoped LCCO film at different temperatures. A common feature of all spectra is a sharp structure above 200 cm\(^{-1}\) which is due to the phonons of the substrate (upper panel). The influence of the substrate is reduced substantially by calculating the complex conductivity via Eq. (4) but cannot be fully removed. At low frequencies and in the normally-conducting state the reflectance is approximately frequency independent. This is in agreement with Eq. (4) for a metal at low frequencies with \( \sigma^* \approx \sigma_1 \). In the superconducting state, the low-frequency reflectance of the LCCO film becomes frequency dependent and follows approximately \( 1 - |r|^2 \propto \nu^2 \). This behavior follows directly from Eq. (4): in the superconducting state the complex conductivity can be approximated by \( \sigma^* \approx i\nu \sigma_2 \approx i/\nu \), which leads to \( 1 - |r|^2 \propto \nu^2 \). Comparing the reflectance of LCO in the superconducting state (Fig. 1) with the spectra of a s-wave superconductor with comparable transition temperature, e.g., with the reflectance spectra of MgB\(_2\) (lower panel) [14, 16], significant differences can be observed. In the spectra of MgB\(_2\) the s-wave symmetry of the superconducting order parameter leads to a sharp "knee" in the reflectance around \( h\nu \approx 2\Delta_0 \), which is in contrast to the spectra of LCCO where only a gradual decrease is observed. Thus, already the analysis of the reflectance spectra reveals a first indication of an unconventional gap-symmetry in LCCO.

Figure 2 shows the far-infrared conductivity of the underdoped LCCO film in the normally-conducting state. The results above 40 cm\(^{-1}\) were obtained applying the Kramers-Kronig analysis to the reflectance data and solving Eq. (4). Below 40 cm\(^{-1}\) the complex conductivity was calculated directly from the transmittance and phase shift. We recall that the resonance-like structures between 200 and 700 cm\(^{-1}\) are due to the residual influence of the substrate. In this frequency range only the overall frequency dependence of the conductivity is significant. The far-infrared conductivity in the normally-conducting state can well be described by the Drude model with a frequency-independent scattering rate \( 1/\tau \). At low frequencies, \( \sigma_1 \) is frequency-independent and \( \sigma_2 \) increases approximately linearly with frequency. For frequencies close to the value of the scattering rate, \( \sigma_1 \) starts to decrease and \( \sigma_2 \) shows a maximum, \( \nu_{max} \approx 1/2\pi\tau \). The gray solid line in Fig. 2 provides a good description of the conductivity at \( T = 50 \) K and demonstrates the validity of the Drude model for LCCO. Substantial devia-
A similar maximum at correspondingly higher frequencies has been observed in infrared experiments on hole-doped cuprates [27]. Assuming a spin-fluctuation scenario of superconductivity, the frequency of the conductivity peak can be ascribed to the quadrupled frequency of the superconducting gap $4\Delta_0$. Compared to an s-wave superconductor with the conductivity onset at $2\Delta_0$, an additional shift by $2\Delta_0$ arises due to a four-particle final state. The d-wave pairing in connection with a spin-fluctuation mechanism may lead to another characteristic energy scale of the optical conductivity [29]. In that case the residual attraction in a d-wave superconductor binds a particle and hole in a spin exciton at an energy $\Delta_{spin}$. As a result the characteristic feature in the conductivity is shifted to $2\Delta_0 + \Delta_{spin}$ [29]. These mechanisms possibly explain the origin of the conductivity peak shown in Fig. 3.

Although the optical spectroscopy is not sensitive to a sign change of the superconducting order parameter, the conductivity data in Fig. 3 provide strong experimental evidence for a highly anisotropic (and, possibly, d-wave) energy gap in underdoped LCCO: according to d-wave model calculations including spin-fluctuation scattering, a gap with nodes gives rise to a residual Drude-like peak [20], and a peak at finite frequencies resulting from inelastic scattering processes [28, 29].

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Due to the suppression of the conductivity at far-infrared frequencies, substantial spectral weight is removed from this frequency range and is transferred to the
delta-function at zero frequency (superconducting condensate). This transfer leads to the dramatic increase of \( \sigma_2(\nu) \) at low frequencies, \( \sigma_2(\nu) = A/\nu \). The spectral weight of the superconducting condensate can easily be obtained as the pre-factor of this proportionality \( A = n_e^2/m = 1.7 \times 10^6 \Omega^{-1} \text{cm}^{-2} \). The missing spectral weight (partial sum rule \( \sigma_1 \)) can be calculated by direct integration

\[
\Delta N(\omega) = \frac{2}{\pi} \int_0^{\infty} [\sigma_{1,n} - \sigma_{1,s}](\omega) d\omega .
\]

The result is shown in the inset of Fig. 4. \( \sigma = \Delta N \) indicates the conservation of the spectral weight. The change of spectral weight, \( \Delta N \), saturates only around \( \nu \sim 400 \text{ cm}^{-1} \), i.e. for frequencies well above the characteristic gap frequency. In LCCO the far-infrared saturation gives \( \Delta N = 1.9 \times 10^6 \Omega^{-1} \text{cm}^{-2} \) and is \( \sim 20\% \) higher than the measured weight of the condensate. This difference probably indicates that some amount of the spectral weight remains in the superconducting state at frequencies below the range of the present experiment.

At frequencies below \( 10 \text{ cm}^{-1} \) and in the superconducting state, \( \sigma_1 \) shows a wing of the low-frequency excitations (upper panel of Fig. 4) which probably corresponds to a Drude-like quasiparticle peak \( \omega_0^q \). The rate of the quasiparticle scattering is strongly suppressed compared to the normal-state \( (1/2\pi\tau) \approx 100 \text{ cm}^{-1} \) at \( T = 50 \text{ K} \) and attains values around 10 cm\(^{-1} \).

Fig. 4 shows the temperature dependence of the quasiparticle scattering of LCCO. The effective scattering rate has been obtained solely from the submillimeter-wave conductivity using a two-fluid analysis \( [17] \)

\[
\sigma^*(\omega) = \frac{\varepsilon_0 \omega^2 \tau}{1 - i\omega\tau} + A[\frac{\pi}{2} \delta(0) + \frac{i}{\omega}] .
\]

Here \( \omega_p^q, \tau, \) and \( A \) represent the plasma frequency, the scattering rate of quasiparticles, and the spectral weight of the superconducting condensate. In this equation the delta function \( \delta(0) \) obviously does not influence the calculations at finite frequencies and the parameter \( A \) is obtained as low-frequency limit of \( \sigma_2 \).

The most prominent feature of Fig. 4 is the suppression of the effective scattering rate directly at \( T_c \). This is similar to the temperature dependence of the scattering rate in optimally-doped YBa\(_2\)Cu\(_3\)O\(_7-\delta\), where a drop in \( 1/\tau \) has been observed, e.g. using microwave resonator technique \( [28] \) or submillimeter transmission spectroscopy \( [17] \). However, in case of YBa\(_2\)Cu\(_3\)O\(_7-\delta\) the scattering rate revealed a linear temperature dependence above \( T_c \), in contrast to LCCO where the scattering rate levels off for temperatures below \( \sim 100 \text{ K} \).

IV. CONCLUSIONS

In conclusion, combining two experimental techniques we obtained the far-infrared conductivity of underdoped \( \text{La}_{2-x}\text{Ce}_x\text{CuO}_4 \) in the frequency range above and below the gap frequency. No characteristic onset of absorption is observed in the superconducting state, which is inconsistent with the conventional BCS scenario. At low temperatures a maximum of infrared conductivity is observed at frequencies close to \( 100 \text{ cm}^{-1} \) which is qualitatively similar to the properties of the hole-doped cuprates. The quasiparticle scattering rate is suppressed upon entering the superconducting state. These results provide experimental evidence for a d-wave or highly anisotropic s-wave gap in underdoped LCCO.

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