Far-infrared transmission study on $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ thin films

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Far-infrared transmission of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ thin films ($T_c=19$ K) has been measured in the frequency range of $15\sim150$ cm^{-1}. An energy-gap-like peak is observed in T_s/T_n at 40 cm^{-1} ($\equiv E_p$), corresponding to $E_p\sim3.0kT_c$, which is reminiscent of the BCS-type superconductors. On the other hand, both the temperature and magnetic-field dependence of the peak show a non-BCS-like behavior. Also, reducing T_c to 12 K by oxygen depletion does not affect the peak energy, for which $E_p=4.8kT_c$ is extracted. The similarities of these observations to the case of $YBa_2Cu_3O_{7-x}$ are discussed.

Several peculiar properties of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (NCCO) make it of particular interest among high-temperature cuprate superconductors: There is no Cu-O chain,[1] the temperature dependence of the in-plane normal state dc-resistivity ρ_{a-b}(T) is quadratic instead of linear,[2] and both electrons and holes appear to contribute to the transport in the Cu-O plane.[3] Especially interesting is that conventional (BCS) s-wave-like behavior has been reported by several groups: Microwave surface impedance measurements on both thin film and single crystals by Wu *et al.* have shown evidence for s-wave-BCS-like behavior in the temperature dependence with an energy gap of $2\Delta\sim4.1kT_c$.[4] Tunneling measurements have also shown a resemblence to conventional superconductors, with a gap-like feature at $2\Delta\sim3.9kT_c$.[5] On the other hand, there have been several observations indicating strong similarities between NCCO and other high-temperature cuprate superconductors which are non-BCS-like: Normal-state infrared reflectance exhibits many of the features (linear frequency dependence of the reflectance in midinfrared and a ledge at 420 cm^{-1}) common to the hole doped high-T_c cuprates such as $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_8$, and $Tl_2Ba_2CaCu_2O_8$.[6] In addition, the specific-heat anomaly observed in ceramic NCCO shows significant similarities to $YBa_2Cu_3O_{7-\delta}$ (YBCO) in its magnetic-field dependence.[7] Whether NCCO can be considered as a BCS-type superconductor or not is an important, but yet unresolved, issue and should be addressed for furthur study. One of the most direct methods to answer this question is to probe frequency-dependent conductivity using far-infrared (FIR) transmission spectroscopy. FIR transmission measurements have provided clear information about the energy gap, including its temperature dependence, not only in the conventional superconductors,[8] but also in conducting oxides such as $Ba_{1-x}K_xBiO_3$ (BKBO).[9]

In this work, we present far-infrared (FIR) transmission data on NCCO thin films, focusing on the temperature and magnetic-field dependence in the superconducting and normal states. c-axis oriented thin films (thickness $\sim$ 1500 Å) were epitaxially grown on (100) $LaAlO_3$ substrates (substrate temperature $\sim$800 °C) in $\sim$200 mtorr of N_2O gas by a pulsed laser ablation technique. X-ray diffraction and TEM studies have shown a high-quality morphology and microstructure in these films.[12] Two samples were measured in our transmission study and the results were reproducible. ac-susceptibility measurements showed $T_c\sim$ 19 K, defined as the middle point of the transition curve, and transition width $\sim$ 1.5 K for both samples. Temperature-dependent transmission data were taken at temperatures from 5 to 25 K using a step-scan Fourier transform spectrometer over 15 $\sim$150 cm^{-1} spectral range with a 4-K Si bolometric detector. The sample and a $LaAlO_3$ reference, both wedged by 4° to avoid multiple reflections of the FIR radiation, were mounted in such a way that they could be switched in and out of the FIR beam path. At each temperature, transmission of the sample was ratioed to that of the reference, generating a relative transmission T_r. In the thin-film approximation ($\lambda\gg\lambda_p\gg d$, where λ is the radiation wavelength, λ_p is the penetration depth, and d is the film thickness), the transmittance through the sample is given by, including the multiple reflection inside the substrate,

$$T=\frac{4n}{|1+N+y|^2}\left[\frac{T_s e^{-\alpha t}}{1-R_sR_f e^{-2\alpha t}}\right], \qquad (1)$$

where $N=n+ik$ is the optical constant of the substrate, $y=(4\pi\sigma d/c)$ with σ being the complex ac conductivity of the film, $\alpha=4\pi\omega k$ is the substrate absorption coefficient, and t is the substrate thickness. $T_s=(4n/|1+N|^2)$ and $R_s=(|1-N|^2/|1+N|^2)$ are the transmittance and reflectivity at the substrate-vacuum boundary and $R_f=(|N-1-y|^2/|N+1+y|^2)$ is the reflectivity of the thin film. The transmittance of the reference is given by setting $d=0$ in Eq. (1). Then the relative transmission T_r is

$$T_r=\frac{1}{\left|1+\dfrac{y}{1+N}\right|^2}\left[\frac{1-R_s^2 e^{-2\alpha t}}{1-R_sR_f e^{-2\alpha t}}\right]. \qquad (2)$$

In interpreting the frequency and temperature dependence of T_r, we considered possible contributions from the substrate (N) in addition to the effect from the film (σ). $LaAlO_3$ has an IR-active phonon at ω = 180 cm^{-1} (Ref. 13) near which N is expected to be strongly frequency dependent. We have done a series of measurements on the substrates to characterize N (Ref. 14) and found that, *for* $\omega<100$ cm^{-1}, (i) $n\gg k$, (ii) n increases quadratically with

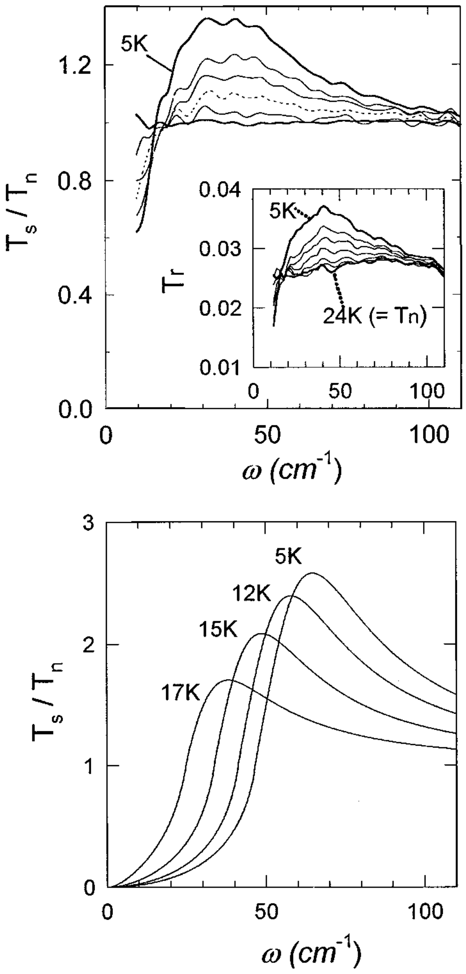

FIG. 1. Temperature dependence of FIR transmission of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ thin film with $T_c = 19$ K. Upper panel: The inset shows T_r (the relative transmission) for 5 (thick line), 12, 15, 17, 19, 21, and 24 K (thick line) from the top curve (at ω=40 cm^{-1}). The main panel shows T_s/T_n, where $T_n = T_r$ in the normal state (24 K) and $T_s = T_r$ from 5 to 21 K. Lower panel: BCS prediction for T_s/T_n, calculated from the temperature-dependent Mattis-Bardeen equations for the conductivity (T_n is for 24 K, T_s is for 5, 12, 15, 17 K).

ω between $n = 4.6 \pm 0.1$ (ω=20 cm^{-1}) and $n = 5.0 \pm 0.1$ (ω=100 cm^{-1}), (iii) there is no measurable temperature dependence of n and k between 5 and 24 K. From (i), N in Eq. (1) can be approximated as n. Also our model calculations show that (ii) has very little effect on the frequency dependence of T_r. In other words, for the frequency range of these measurements, the substrate behaves like a simple dielectric material. Therefore, the frequency and temperature dependence of T_r results from σ.

In the inset of Fig. 1 (upper panel) we show T_r for different sample temperatures. At 5 K, the transmission approaches zero at zero frequency due to the superfluid screening. At high frequency, the transmission approaches the normal-state value. The peak of the transmission, which possibly could be a manifestation of an energy gap as is the case in BCS superconductors,[8,9] is located at ~40 cm^{-1} (5 meV $= 3.0kT_c$). As temperature is increased, the peak gradually decreases in height (accompanied by the decreasing superfluid screening below the peak) and eventually disappears at T_c, while the peak position does not show any noticeable shift. For the convenience of comparison with the field dependence data to be presented below, we normalize T_r with the normal state T_r at 24 K, $[T_r/T_r(24\text{ K})]$, as shown in the main panel. Let us call it T_s/T_n, which means the superconducting to normal-state transmission ratio. The bottom panel shows the BCS prediction of T_s/T_n which we will discuss later.

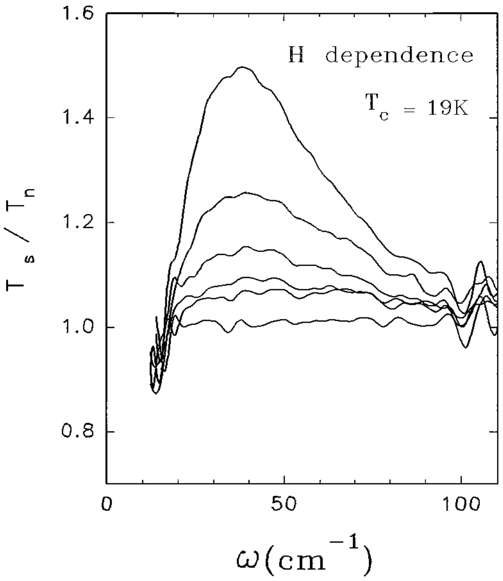

FIG. 2. Magnetic-field dependence of the transmission ratio T_s/T_n when T_c =19 K. Magnetic field was applied normal to the *a-b* plane and the sample temperature was fixed at 2 K. T_n is taken at 12 T while T_s are for 0, 0.75, 1.5, 2.5, 4, and 8 T from the top curve (at ω=40 cm^{-1}).

We also have studied the magnetic-field dependence of transmission at a fixed temperature (2 K). The magnetic field plays a similar role as temperature in that it breaks the superconducting condensates into the normal carriers above H_{c2}. The normal state driven by magnetic field H ($\geqslant H_{c2}$) will be nearly identical as the state for $T \geqslant T_c$ and one should observe the energy gap in the field dependence of transmission as well as in the temperature dependence.[15] The sample was cooled in zero field and then the magnetic field was applied normal to the *a-b* plane of the film. Transmission through the sample was taken by a rapid scan Fourier transform spectrometer with a 2-K bolometric detector. In Fig. 2 we present the normalized transmission T_s/T_n, where T_n is taken at H=12 T and T_s are for different magnetic fields at $0 \leqslant H \leqslant 12$ T. The same gap-like feature as in Fig. 1 is observed. The peak, located at the same frequency as in Fig. 1, rapidly decreases up to 2.5 T and then gradually flattens out. The field dependence terminates at ~ 8 T, indicating the system is entering the normal state, consistent with H_{c2} = 7 ~ 8 T at 4 K reported from dc transport measurements.[16] The field dependence offers further evidence that the feature is an intrinsic property of charge carriers in the superconducting state.

We now describe the transmission on the same sample after its T_c has been reduced by oxygen annealing. Anneal-

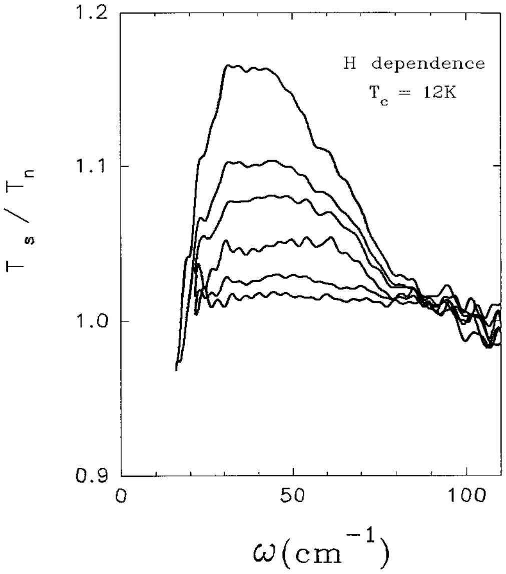

FIG. 3. Magnetic-field dependence of the transmission ratio T_s/T_n after the T_c has been reduced to 12 K. T_n is taken at 12 T. T_s's are for 0, 0.5, 0.75, 1.5, 2.5, and 3.5 T from the top curve.

ing the sample in O_2 gas (400 torr) at 500 °C for 20 min resulted in a reduction of T_c to 12 K with a broadening of transition width (3 K). Details of the T_c dependence on the annealing process are found in Ref. 3. In Fig. 3, we show the magnetic-field dependence of the transmission under the same conditions as before the annealing. The height of the peak is reduced by about $\frac{1}{3}$ in T_s/T_n, while the peak position remains the same as for the $T_c=19$ K case. The peak position in this case corresponds to $4.8kT_c$ instead of $3.0kT_c$. The peak is quenched at $H\sim 3.5$ T, compared with 8 T before the annealing, indicating a reduction of H_{c2} as well.

The overall observations of both temperature and magnetic-field dependence of transmission consistently suggest that the peak at $\sim 40\ \mathrm{cm}^{-1}$ is a manifestation of the electronic property of the superconducting phase of NCCO which we are naturally led to associate with an energy gap. Though we do not attempt to extract out the exact value of the gap, it is clearly smaller and more BCS-like compared with, for example, YBCO. This aspect is comparable with the results of microwave surface impedance and tunneling measurements, reporting evidence of an energy gap at $2\Delta\sim 3.9kT_c$ and $4.1kT_c$, respectively.[4,5] On the other hand, the temperature and field dependences, together with the observation at reduced T_c film, are highly non-BCS-like. This aspect, in contrast to the former, has a strong qualitative similarity with an observation on YBCO: Though there are still a lot of controversies on the experimental data and even more on their interpretations about the optical studies regarding the energy gap in YBCO,[10] it is interesting to compare our NCCO data with the pure *a*-*b* plane conductivity of YBCO single crystals obtained by the polarized infrared reflectivity measurements in Ref. 11. There it is shown that a development of a gap feature takes place at $\hbar\omega\sim 8kT_c$ and it remains essentially at the same frequency at all temperatures below T_c. (Little temperature dependence of the gap has also been reported in $Bi_2Sr_2CaCu_2O_8$ single crystals.[17]) In addition, for the underdoped samples with reduced T_c, a substantial weakening in the strength of the feature results but there is no shift in the gap energy, which is the same as our observation seen in Fig. 3. In contrast, for a BCS-type superconductor, for example BKBO, infrared transmission measurements have found that the peak gradually shifts to lower frequency and reduces in height as the temperature is increased. Also for samples with lower T_c, the gap feature shifts proportionally to lower frequency.[9] To compare our data with the BCS theory, we show the BCS prediction for T_s/T_n in the lower panel in Fig. 1. The curves were calculated from the temperature-dependent Mattis-Bardeen equations for the conductivity.[18] The parameters such as film thickness, T_c, and the optical indices of the substrate were taken from our samples. The normal-state resistivity was assumed to be 80 $\mu\Omega$ cm which was measured on similar NCCO films at 25 K. A value of 0.3 electrons per unit cell[6] for the electron density gives a scattering rate of $1/\tau = 190\ \mathrm{cm}^{-1}$. First of all, the peak height in the calculated curve is significantly larger than that of the corresponding data for each temperature. Also, contrary to the measurement, the calculation predicts a clear shift of the peak of the curve as the temperature is increased due to the decrease of the energy gap.

One could question whether the lack of temperature dependence of the gap energy is intrinsic, since the samples in our study are relatively thin and inhomogeneities such as defects or impurity phases, if present, could affect the optical response. Although extensive characterizations have confirmed that these films are highly homogeneous,[12] we tried to see if it is a possibile scenario that (i) the superconducting state is BCS-like, (ii) the absence of a shift of the gap energy is caused by the hypothetical inhomogeneities in the film. As a simple way to model the imperfections, we assume some amount of Drude-type normal charge carriers in the sample that could be caused when the superconducting order parameter is locally suppressed around the inhomogeneous regions. Then the superconducting carriers are assumed to follow the Mattis-Bardeen prediction and the total conductivity of the film $[=\sigma(\omega)]$ is written as a sum of the two components,

$$\sigma(\omega)=f\sigma_S(\omega)+(1-f)\sigma_D(\omega), \tag{3}$$

where f is the fraction of the superconducting carrier, $\sigma_S(\omega)$ and $\sigma_D(\omega)$ are the conductivity functions for the superconducting and the normal carriers respectively. The simulated result shows that the shift in the temperature dependence of T_s/T_n becomes smaller and the peak height is reduced due to the normal carriers. However, in order to make the calculated curve look rather similar to the data in Fig. 1, an unreasonably large amount of normal carriers must be assumed ($\sim$ 75% of total charge carriers) and even then the shape of the simulated curve shows qualitative disagreements with the data. The disagreement becomes even more pronounced when a Lorentz-oscillator-type conductivity is assumed for the inhomogeneity-induced normal carriers. Thus the simulations allow us to reject inhomogeneities as the cause of the observed behavior of the peak.

To summarize, we have performed temperature and magnetic-field dependent FIR transmission measurements of NCCO thin films. In both measurements, a peak is observed in T_s/T_n at $\sim$40 cm^{-1} (5 meV) which could be associated with a BCS-type energy gap. On the other hand, its dependences on temperature and T_c are similar to YBCO which is highly non-BCS-like. This means that the ground state of superconducting NCCO is very subtle and can not be simply classified as a conventional BCS-type.

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[15] A few differences could be expected in the detailed behavior of the gap feature. (i) In the magnetic field dependence, an energy dissipation is caused by the response of vortices to the FIR radiation. As a result, an extra contribution to the optical conductivity could be exhibited below 2Δ. (ii) Unlike in the temperature dependence, the (bulk) gap energy 2Δ is field independent in the first order. Field-dependent FIR absorption measurement on a conventional superconductor (Pb film) is found in W.S. Martin and M. Tinkham, Phys. Rev. **167**, 421 (1968).

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