Optical properties of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$

C. C. Homes* and B. P. Clayman

Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

J. L. Peng and R. L. Greene

Center for Superconductivity Research, Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

(Received 26 March 1997)

The $ab$-plane reflectance of a Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ single crystal ($T_c$=23 K) has been measured from $\approx$35 to 9500 cm$^{-1}$ at temperatures above and below $T_c$, and the optical properties calculated from a Kramers-Kronig analysis. A rich phonon spectrum is observed, and there are a number of $c$-axis infrared and Raman modes that are observed at low temperature which are believed to be activated by disorder; several of these modes show evidence for electron-phonon coupling. The normal-state optical conductivity may be described by a Drude-like component and an overdamped midinfrared component. The Drude-like component narrows rapidly; at 30 K the mean free path is estimated to be $\approx$750 Å. Below $T_c$, the Drude carriers collapse into the condensate; the plasma frequency of the $\delta$ function is determined to be $\omega_p$=10 000 cm$^{-1}$. The small coherence length ($\xi_0$=70 Å) places this material into the clean limit ($\xi_0/l$<1). The London penetration depth is determined to be $\lambda_{ab}$=1600±100 Å, which places it well off the Uemura line. Estimates of the electron-phonon coupling from normal-state transport measurements of $\lambda_{ab}$<0.5, and the absence of Holstein sidebands below $T_c$, indicate that the carriers that participate in superconductivity are weakly coupled to the phonons. The small values for the penetration depth and the electron-phonon coupling constant suggest that the superconductivity in this material is not due to the electron-phonon mechanism, and is different than in other hole-doped superconducting cuprates. [S0163-1829(97)00434-7]

I. INTRODUCTION

In most high-temperature (high-$T_c$) superconducting cuprates, such as YBa$_2$Cu$_3$O$_{7-\delta}$ and La$_{2-x}$Sr$_x$CuO$_4$, the charge carriers are doped holes. However, in Nd$_{2-x}$Ce$_x$CuO$_4$, where superconductivity is induced by substituting Nd$^{3+}$ with Ce$^{4+}$, the CuO$_2$ planes are believed to be doped with electrons as well as holes. Another important difference between Nd$_{2-x}$Ce$_x$CuO$_4$ and other cuprate superconductors is the coordination of the planar copper atoms. In orthorhombic YBa$_2$Cu$_3$O$_{7-\delta}$ and tetragonal La$_{2-x}$Sr$_x$CuO$_4$ apical oxygen atoms sit above and below the copper atoms, yielding a nearly octahedral coordination. However, Nd$_{2-x}$Ce$_x$CuO$_4$ has a modified tetragonal ($D_{4h}$) structure which is composed of two-dimensional sheets of Cu-O layers with no apical oxygen atoms, resulting in copper atoms with square coordination. Within the Nd(Ce)O layers in between the CuO$_2$ planes, the Nd(Ce) and O atoms are not coplanar. The resistivity perpendicular to the CuO$_2$ planes is much higher than that in the planes ($\rho_{ab}$$\ll$\rho), and there is some evidence for an incipient metal-insulator transition along the $c$ axis in these materials at low temperature.

The Nd$_{2-x}$Ce$_x$CuO$_4$ system has attracted a great deal of interest because of its possible conventional BCS $s$-wave pairing in the superconducting state, as opposed to the unconventional $d$-wave behavior proposed for the hole-doped cuprates. The microwave surface impedance measurements on both thin films and single crystals have shown evidence for a conventional BCS $s$-wave behavior with a gap of $2\Delta$=4$K_B T_c$. Tunneling measurements have also shown a resemblance to conventional superconductors. However, the magnetic-field dependence of the specific-heat anomaly and thin-film transmission of Nd$_{2-x}$Ce$_x$CuO$_4$ both show a non-BCS-like behavior. Whether or not this system can be considered as a conventional BCS-type superconductor is an important question, given the strong evidence that the other hole-doped cuprates are not. Infrared techniques have long been acknowledged as a powerful method for probing the electronic properties of metals and superconductors, and may provide information about the nature of superconductivity in Nd$_{2-x}$Ce$_x$CuO$_4$. While there have been a number of reports on the infrared and Raman properties of ceramics, thin films, and single crystals of Nd$_{2-x}$Ce$_x$CuO$_4$, to date there has been no investigation of the far-infrared optical properties of single crystals.

In this paper we report on the optical properties of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ ($T_c$=23 K) over a wide frequency range, at temperatures above and below $T_c$. While the optical properties cannot make an absolute determination of the nature of the gap, they show a detailed phonon spectrum and they indicate that the coupling between the carriers that become superconducting and the phonons is very small, suggesting that the pairing mechanism is not phonon mediated. The small value for the penetration depth also separates this material from other cuprate superconductors.

II. EXPERIMENT AND SAMPLE PREPARATION

Large, single crystals of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ were grown from a CuO-based flux using a directional solidification technique. A mixture of high-purity (99.9%) starting materials of Nd$_2$O$_3$, CeO$_2$, and CuO were heated rapidly to just

0163-1829/97/56(9)/5525(10)/$10.00 5525 © 1997 The American Physical Society
above the melting point (1270°C for this Ce concentration). After a soak of several hours at the maximum temperature, the materials were cooled slowly to room temperature. During the course of the growth, the flux was allowed to flow out of the crucible at the end of the growth process, so that free-standing crystals are left in the bottom of the crucible that do not need to be mechanically separated from the flux. To induce superconductivity, the crystals were annealed in an inert gas atmosphere.

The reflectance of a single crystal of Nd1.85Ce0.15CuO4 has been measured for the radiation polarized parallel to the ab plane from ~30 to 9500 cm−1, at temperatures above and below Tc, on a Bruker IFS113V Fourier-transform interferometer, using a sensitive overtaking technique. The crystal examined in this case was ~2×2 mm in the ab plane, but was quite thin along the c axis (~50 μm). The crystal had a flat, mirrorlike surface that was free of flux. Both resistivity and magnetization showed a sharp superconducting transition at 23 K, with a width of ~1 K.

The optical properties (i.e., the complex conductivity ωσ = σ1 + iσ2) have been calculated from a Kramers-Kronig analysis of the reflectance, which requires extrapolations at high and low frequencies. At low frequency, the reflectance was extrapolated to zero frequency by assuming a Hagen-Rubens 1−R×√ω dependence above Tc, and a superconducting 1−R×ω2 dependence below Tc. The reflectance has been extended to high frequency using the data of Zhang et al. for Nd1.80Ce0.2CuO4 (~6 eV), and Uchida et al. for La2CuO4 (~35 eV), above which a free-electron (R ∝ω−4) behavior was assumed.

III. RESULTS AND ANALYSIS

The ab plane reflectance for Nd1.85Ce0.15CuO4 (Tc = 23 K) is shown in Fig. 1 from ~30 to 15000 cm−1 at several temperatures above Tc (295, 180, 100, and 30 K), and below Tc at 10 K. The inset shows the reflectance at 295 and 10 K over a much wider frequency range.

The real part of the optical conductivity σ1(ω) for Nd1.85Ce0.15CuO4 (Tc = 23 K) for E⊥c from ~30 to 800 cm−1 at several temperatures above Tc (295, 220, 180, 100, and 30 K) in the normal state. In the normal state, the conductivity may be approximated by a Drude component (dashed line) and a mid-infrared band (dash-dot line), which have been drawn for the 30 K data. The extrapolated value for σdc at 295 K is ~7000 Ω−1 cm−1, while at low temperature just above Tc, the Drude component has narrowed considerably and σdc≈5×104 Ω−1 cm−1. The downward pointing arrows denote vibrations which are present at 295 K. The arrow pointing left indicates that satisfactory fits may also be obtained using overdamped midinfrared oscillators at very low (ω→0) frequencies.

over a much wider frequency range. The reflectance of Nd1.85Ce0.15CuO4 displays a strong “metallic” character, and is over 90% for ω<1000 cm−1 at 295 K. There is a substantial temperature dependence in the reflectance, which increases quickly with decreasing temperature until at 30 K it is over 95% in the same frequency range. The high values of the reflectance contrasts with a the lower reflectance of a similar hole-doped material La1.85Sr0.15CuO4 material. Also, the characteristic “ledge” in the reflectance at ~450 cm−1 that is observed in many of the hole-doped cuprates is absent in this material. Despite the high values for the reflectance, there is a great deal of fine structure below ~600 cm−1 visible at 295 K; this structure becomes sharper as the temperature is lowered and a number of new features are observed as well.

The real part of the optical conductivity [σ1(ω)] has been calculated from a Kramers-Kronig analysis of the reflectance curves in Fig. 1. The normal-state conductivity (T>Tc) is shown in Fig. 2 from ~30 to 800 cm−1 at 295, 220, 180, 100 K, and just above Tc, at 30 K. The normal-state conductivity can be described in general terms as a Lorentzian centered at zero frequency and an overdamped midinfrared component. At room temperature the conductivity associated with the zero-frequency Lorentzian is quite broad. However, as the temperature is lowered there is a rapid narrowing of this feature as spectral weight is transferred from high to low frequencies, while the conductivity at high frequency shows little change with temperature.

Figure 3 shows σ1(ω) over the same frequency range just above Tc at 30 K, and below Tc at 10 K; the inset in Fig. 3
shown in Fig. 2. Figure 4 shows the
\[ \frac{1}{\tau(\omega)} = \frac{\omega_p^2}{4\pi^2} \text{Re} \left[ \frac{1}{\sigma(\omega)} \right] \]
and
\[ \frac{m^*(\omega)}{m} = 1 + \lambda(\omega) = \frac{\omega_p^2}{4\pi^2} \text{Im} \left[ \frac{1}{\sigma(\omega)} \right]. \]

The plasma frequency may be determined experimentally from the optical conductivity sum rule,
\[ I(\omega) = (120/\pi) \int_0^\infty \sigma_i(\omega') d\omega'. \] (Note that this normalization is due to the fact that the optical conductivity is in units of $\Omega^{-1} \text{cm}^{-1}$.) If the conductivity is due purely to a free-carrier response, then $I(\omega \to \infty) = \omega_p^2$. Figure 4 shows the value of this integral as a function of frequency in the normal state as well as below $T_c$. Regardless of whether the one- or two-component model is adopted, the low-frequency behavior is associated with the free-carrier response and the high-frequency component of $\sigma_i(\omega)$ is generally considered to be due to bound excitations which show low temperature de-
TABLE I. The fitted phonon parameters for the infrared active modes in the ab plane of Nd_{1.85}Ce_{0.15}CuO_{4} at 295, 100, and 10 K. In Nd_{2}CuO_{4} the four E_{u} and two E_{g} infrared modes are expected to be active in the ab plane, while the three A_{2u} infrared modes, and the A_{1g} and B_{1g} Raman modes are expected along the c axis only. The ‘obs’ column refers to modes previously observed in ceramic materials. (All units are in cm^{-1}).

<table>
<thead>
<tr>
<th>Mode</th>
<th>(obs)</th>
<th>ω_{TO,1} (ω_{LO,1})</th>
<th>γ_{1}</th>
<th>ω_{pl}</th>
<th>ω_{TO,1}</th>
<th>ω_{pl}</th>
<th>γ_{1}</th>
<th>ω_{pl}</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_{g}</td>
<td>(516)</td>
<td>564.1 (596)</td>
<td>16.9</td>
<td>420</td>
<td>561.3</td>
<td>15.9</td>
<td>630</td>
<td>562.3</td>
</tr>
<tr>
<td>A_{2u}</td>
<td></td>
<td>521.6</td>
<td>7.6</td>
<td>254</td>
<td>519.9</td>
<td>8.7</td>
<td>256</td>
<td></td>
</tr>
<tr>
<td>E_{u}</td>
<td>(344)</td>
<td>439.8 (506)</td>
<td>15.7</td>
<td>544</td>
<td>434.2</td>
<td>4.2</td>
<td>508</td>
<td>434.1</td>
</tr>
<tr>
<td>A_{2g}</td>
<td>(304)</td>
<td>303.2 (490)</td>
<td>10.2</td>
<td>837</td>
<td>304.8</td>
<td>4.8</td>
<td>855</td>
<td>304.3</td>
</tr>
<tr>
<td>A_{2u}</td>
<td>(225)</td>
<td>~220</td>
<td>~30</td>
<td>~1300</td>
<td>~216</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A_{2a}</td>
<td>(134)</td>
<td>146.4</td>
<td>~10</td>
<td>~1500</td>
<td>145.0</td>
<td>~8</td>
<td>~900</td>
<td>130.8</td>
</tr>
<tr>
<td>A_{1g}</td>
<td>(132)</td>
<td>130.8</td>
<td>~8</td>
<td>~900</td>
<td>~112.5</td>
<td></td>
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<td></td>
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<tr>
<td>E_{u}</td>
<td></td>
<td>78</td>
<td>~8</td>
<td>~990</td>
<td>74</td>
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</table>

*The frequency of the longitudinal optic modes have been calculated from ω_{LO,1} = ω_{TO,1} = ω_{pl}/ε_{o}.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd_{1.85}Ce_{0.15}CuO_{4} ceramic at 10 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ae(1500 cm^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ae(3000 cm^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ae(5000 cm^{-1})</td>
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</table>

FIG. 4. The value of the conductivity sum rule integral \( I(\omega) = (120/\pi) \int_{0}^{\omega} \sigma_{1}(\omega')d\omega' \) for Nd_{1.85}Ce_{0.15}CuO_{4} in the infrared frequency range at 295, 180, 30, and 10 K. In the normal state, all the curves have converged by \( \approx 2500 \) cm^{-1} indicating that the temperature-dependent free carriers have been completely integrated, yielding \( \omega_{p} = 16 \) 000 \pm 800 cm^{-1}. Below \( T_{c} \) at 2500 cm^{-1} the sum rule is significantly lower; this decrease is estimated by \( \omega_{p}^{2} - \omega_{pS}^{2} \), where \( \omega_{pS} = 10 \) 000 cm^{-1} is the estimated plasma frequency of the condensate.

FIG. 4. The value of the conductivity sum rule integral \( I(\omega) = (120/\pi) \int_{0}^{\omega} \sigma_{1}(\omega')d\omega' \) for Nd_{1.85}Ce_{0.15}CuO_{4} in the infrared frequency range at 295, 180, 30, and 10 K. In the normal state, all the curves have converged by \( \approx 2500 \) cm^{-1} indicating that the temperature-dependent free carriers have been completely integrated, yielding \( \omega_{p} = 16 \) 000 \pm 800 cm^{-1}. Below \( T_{c} \) at 2500 cm^{-1} the sum rule is significantly lower; this decrease is estimated by \( \omega_{p}^{2} - \omega_{pS}^{2} \), where \( \omega_{pS} = 10 \) 000 cm^{-1} is the estimated plasma frequency of the condensate.

The frequency of the longitudinal optic modes have been calculated from \( \omega_{LO,1} = \omega_{TO,1} = \omega_{pl}/\epsilon_{o} \), where \( \epsilon_{o} = 4.7 \).

Ref. 17 (Nd_{1.85}Ce_{0.15}CuO_{4} ceramic at 10 K).

Ref. 24 (Nd_{1.85}Ce_{0.15}CuO_{4} ceramic at 10 K).

CF refers to a possible low-lying electronic transition due to crystal-field excitations, as discussed in Ref. 28.

The uncertainty in the background does not allow the widths and strengths to be reliably fitted below \( T_{c} \) for these modes.

should be \( \approx \omega_{p}^{2} \). As Fig. 4 illustrates, the normal-state curves have all merged by \( \approx 2500 \) cm^{-1}, yielding a value for \( \omega_{p} = 16 \) 000 \pm 800 cm^{-1}. The conductivity sum rule also provides a good estimate for the plasma frequency of the condensate, \( \omega_{pS}^{2} = (120/\pi) \int_{0}^{\omega} [\sigma_{1}(\omega) - \sigma_{1}(\omega)]d\omega \), where \( \sigma_{1}(\omega) \) and \( \sigma_{1}(\omega) \) the are frequency-dependent conductivities for \( T = T_{c} \) and \( T < T_{c} \), respectively. This sum rule yields \( \omega_{pS} = 10 \) 000 \pm 800 cm^{-1}. This missing spectral weight from the sum rule at 2500 cm^{-1} is indicated by two solid dots in Fig. 4 (the upper point corresponds to \( \omega_{p}^{2} \) and the lower point to \( \omega_{p}^{2} - \omega_{pS}^{2} \)). The plasma frequency of the condensate is related to the strength of the \( \delta \) function by \( \delta \approx \omega_{pS}^{2} \), and \( \omega_{pS}^{2} = 4 \pi n_{s}e^{2}/m^{*} \), where \( n_{s} \) is the density of superconducting carriers, and \( m^{*} \) is their effective mass.

The value of \( \omega_{p} = 16 \) 000 cm^{-1} is used to calculate \( m^{*}(\omega)/m \) and \( 1/\tau(\omega) \), which are shown in the upper and lower panels in Fig. 5, respectively. For \( T < T_{c} \), \( \sigma_{1}(\omega) \) is suppressed at low frequency (as shown in Fig. 3) so that the complex conductivity will be dominated by the imaginary term \( \sigma_{2}(\omega) = \omega_{pS}^{2}/(4\pi \omega) \). In this case the low-frequency mass enhancement gives the ratio of \( \omega_{p}^{2} / \omega_{pS}^{2} \), \( 1 + \lambda(\omega) = \omega_{pS}^{4}/\omega_{p}^{2} \). In Fig. 5(a), \( 1 + \lambda(\omega = 0) \approx 2.5 \) at 10 K, indicating that \( \approx 40\% \) of the free carriers have condensed, in good agreement with the existing values for \( \omega_{p} \) and \( \omega_{pS} \) determined from sum rules.

The frequency-dependent penetration depth \( \lambda_{ab}(\omega) = 2\pi \sqrt{\omega \sigma_{2}(\omega)} \) at 10 K is shown in the inset in Fig. 5(a). The extrapolated zero-frequency value is \( \approx 1600 \) Å. The penetration depth is related to the plasma frequency of the condensate, \( \lambda_{ab} = 2\pi \omega_{pS} \), so that a \( \lambda_{ab} (\omega = 0) = 1600 \) Å yields \( \omega_{pS} \approx 10 \) 000 cm^{-1}, again in good agreement with the sum-rule value. The fact that \( \lambda_{ab}(\omega) \) shows some frequency de-
FIG. 5. (a) The frequency-dependent mass enhancement \( m^*(\omega)/m = 1 + \lambda(\omega) \) for Nd\(_{1.85}\)Ce\(_{0.15}\)CuO\(_4\) from \( \omega = 50 \) cm\(^{-1}\) to 3000 cm\(^{-1}\) at 295, 140, and 10 K (using \( \omega_p = 16,000 \) cm\(^{-1}\)). At 10 K, \( m^*(\omega \rightarrow 0)/m = \omega^2/\omega_p^2 \) is extrapolated to \( \approx 2.5 \). This indicates that \( \approx 40\% \) of the free carriers have condensed into the \( \delta \) function, and gives \( \omega_p \approx 10,000 \) cm\(^{-1}\). Inset: the frequency-dependent penetration depth \( \lambda_{ab}(\omega \rightarrow 0) \approx 1600 \) Å. (b) The unrenormalized frequency-dependent scattering rate at 295, 220, 140, 30, and 10 K. While \( 1/\tau(\omega) \) is linear at high frequency, a “knee” develops at low temperature \( \approx 1500 \) cm\(^{-1}\), below which \( 1/\tau(\omega) \) remains linear until developing a quadratic behavior and saturating to a finite value at low frequency. The rapid suppression of \( 1/\tau(\omega) \) at low frequency in the normal state is similar to the “pseudogap” observed in other cuprates.

Dependence below \( \approx 300 \) cm\(^{-1}\) is an indication that not all of the free carriers have condensed into the \( \delta \) function, and that there is some low-frequency residual conductivity. The frequency-dependent scattering rate is shown in Fig. 5(b) for several temperatures above and below \( T_c \). While \( 1/\tau(\omega) \) is linear at high frequency, a “knee” develops at low temperature \( \approx 1500 \) cm\(^{-1}\), below which \( 1/\tau(\omega) \) remains linear until taking on a quadratic behavior and saturates to a finite value at low frequency. The rapid suppression of \( 1/\tau(\omega) \) at low frequency in the normal state is similar to the “pseudogap” observed in other cuprates. However, the energy scale over which this suppression occurs is quite large (\( \approx 1500 \) cm\(^{-1}\)), when compared to other hole-doped cuprates, which typically show a suppression only at low frequency (\( \approx 500 \) cm\(^{-1}\)). Fitting the temperature-dependent linear part of \( 1/\tau(\omega) \) (500 cm\(^{-1}\) \( \leq \omega \leq 1500 \) cm\(^{-1}\)) to the form \( \alpha \omega + \beta \) gives \( \alpha = 0.39 \) (0.57) and \( \beta = 482 \) (38) cm\(^{-1}\) at 295 K (30 K). The small value of \( \alpha \), and the negative intercept of \( \beta \) for \( T \geq T_c \), is similar to the behavior of some “overdoped” cuprates. In the one-component model, \( \Gamma(\omega \rightarrow 0) = \Gamma_D \), which provides a useful connection with the two-component model and allows a comparison with transport data. The temperature-dependent damping obtained in this manner is shown in Fig. 6.

The damping varies quadratically at low temperatures, but displays a linear trend at high temperature. This behavior has been naively modeled using \( \Gamma_D(T) = \Gamma_D(0) + a(T - T^*) \Theta(T) + b T^2 [1 - \Theta(T)] \), where \( \Theta(T) = 1/[1 + \exp(T^*/T)] \) is a broadened step function. A good agreement with the data is obtained using \( \Gamma_D(0) \approx 100 \) cm\(^{-1}\), \( a = 2.6 \) cm\(^{-1}\) K\(^{-1}\), and \( b = 7.8 \times 10^{-3} \) cm\(^{-1}\) K\(^{-2}\). The crossover temperature from quadratic to linear behavior is taken to be \( T^* \approx 110 \) K, and \( \Gamma_D = 30 \) K. Using these parameters and \( \omega_p \approx 16,000 \) cm\(^{-1}\), the dc resistivity may be calculated (\( \rho = 60 \Gamma_D / \omega_p^2 \), in units of \( \Omega \text{cm} \)), and is shown in the inset in Fig. 6. A comparison of the dc resistivity deduced in this way from the optical measurements is in good qualitative agreement with transport measurements on single crystals, in particular with regard to the linear behavior observed at high temperature. It is interesting to note that for \( T < T^* \), a new phonon structure also appears, although it is uncertain if this is related to the behavior of the damping or the frequency-dependent scattering rate.

The real part of the dielectric function at several temperatures above and below \( T_c \) is shown below 1000 cm\(^{-1}\) in Fig. 7. The rapid decrease of \( \varepsilon_r(\omega) \) at low frequency with decreasing temperature is an indication of the suppression of the quasiparticle scattering rate. In a purely Drude system, the zero crossing corresponds to the location of the screened plasma frequency, \( \omega_{p0} \approx \omega_p^2 / \varepsilon_{\infty} \). The observed zero crossing at \( \approx 6600 \) cm\(^{-1}\) would require that \( \varepsilon_{\infty} \approx 3.5 \). However, the presence of a number of excitations in the midinfrared will tend to shift the zero crossing to a higher frequency, leading to an underestimate of \( \varepsilon_{\infty} \). As a result, a value of \( \varepsilon_{\infty} = 4.7 \) has been determined by fitting the reflectance at high frequency. In a system where all of the normal-state carriers collapse into the superconducting \( \delta \) function, then the real part of the dielectric function in Eq. (1) becomes...
disagreement with other single-crystal work, 20,22–24 which four E_u assigned as such. This assignment of the vibrations are observed at 130, 314, 352, and 514 cm\(^{-1}\) and the Cu-O stretching modes.

As well, the general reduction of symmetry may also result in the mixing of the infrared and Raman modes, and as a result the Raman modes may become infrared active. As well, the general reduction of symmetry may also result in more general selection rules, so that vibrations in the undoped material which are active only along one polarization may become active in several in the doped material. In this way, infrared-active A_{2u} c-axis modes may appear in the ab plane. A total of four Raman-active modes are expected; the A_{1g} and B_{1g} modes are active along the c axis, while the two E_g modes are active in the ab plane. By considering that c-axis modes may be active in the ab plane, many of the assignments that we make are similar to some previous assignments made in ceramics. 25

In previous studies 23–25 at 30 K the B_{1g} and A_{2u} modes have been observed at 344 cm\(^{-1}\) and 516 cm\(^{-1}\), respectively. These frequencies are quite close to the two features that are activated at low temperature at 349 and 521 cm\(^{-1}\), and strongly suggests that these two modes are the c-axis B_{1g} and A_{2u} modes, activated by disorder. Indeed, both the B_{1g} and A_{2u} modes involve the Nd(Ce)-O bonds. 24

The A_{1g} mode is observed in Nd_2CuO_4 at 228 cm\(^{-1}\). 23,24 Although the A_{1g} mode involves displacements of the Nd atoms, this mode has been observed in the same location in a variety of Nd_{2−x}M_xCuO_4 (M=Ce, Th, and Sr) materials, 23 despite the different masses of the dopant ions. This suggests that the broad feature at \(\approx 220\) cm\(^{-1}\) may be the A_{1g} mode. While the A_{1g} mode, which like the B_{1g} and A_{2u} modes, involves the Nd(Ce)-O bonds, may be activated by disorder, it appears to be quite strong in Figs. 2 and 3 (see Table I). Typically, modes activated by disorder are expected to be weak. It may be possible that the oscillator strength of the A_{1g} mode is enhanced by coupling to a charge-transfer mechanism. The Nd_{2−x}Ce_xCuO_4 materials are strongly anisotropic, and there is some evidence to suggest that the behavior along the c axis may be insulating at low temperatures. 26 It may be the case that the Nd(Ce)O planes are isolated, and that charge segregation occurs within the Nd(Ce)O planes. Typically, the charge associated with an atomic cluster is very sensitive to the configuration, or bond lengths. The effective charge is an important quantity when discussing the bonding ionicity. However, the evaluation of the effective charge is difficult for more than two kinds of atoms. For a ternary compound the extended effective charge Z_k is defined as
\[
\sum_i \left[ \omega_{LO,i}^2 - \omega_{TO,i}^2 \right] = \frac{1}{e_x} \sum_i \omega_{ni}^2 = \frac{4\pi}{V_e} \sum_k (Z_k e)^2 / M_k, \tag{5}
\]
where \(\Sigma_i Z_k = 0; j\) denotes the phonon mode, \(V_e\) is the unit-cell volume, and k is the sum over all atoms with mass \(M_k\) and effective average charge \(Z_k e\), and \(\omega_{ni}\) is the effective plasma frequency of the ith phonon. In Nd_{1.85}Ce_{0.15}CuO_4 the constituent elements are all much heavier than the oxygen mass (\(M_O\), so the right-hand side of Eq. (5) may be approximated by \(16\pi(Z_{pe})^2/(V_e M_O)\). At 295 K the oxygen effective charge is \(Z_O = -1.3\), which is similar to the values of \(Z_O\) in the hole-doped cuprates 35 where \(|Z_O| \approx 1–1.3\). However, below 100 K a number of new phonon features are observed, as indicated in Fig. 3. Because the oscillator strengths of the phonons below \(\approx 300\) cm\(^{-1}\) cannot be unambiguously determined, only the phonons above 300 cm\(^{-1}\) have been considered; this treatment gives \(Z_O \approx -2\), which is the full valence for the oxygen atom in this system and indicates a substantial increase at low temperature in the average oxygen bonding. Because there is no shift in any of
the Cu-O vibrations associated with the CuO$_2$ planes, this suggests that there is a large degree of ionicity in the Nd(Ce)O planes. If the A$_{1g}$ mode in neighboring unit cells are π out of phase, then the change in the local charge density may create a local dipole moment in the ab plane that is modulated at the same frequency as the A$_{1g}$ mode, leading to enhanced oscillator strengths. This is also an alternate mechanism (that does not depend on disorder) by which c-axis vibrations may become active in the ab plane. This mechanism has also been proposed to explain the activity of the A$_{1g}$ modes in lightly doped La$_{2-x}$Sr$_x$CuO$_4$ and is commonly observed in quasi-one-dimensional molecular crystals where the totally symmetric modes are not only observed in directions transverse to their polarization but also display greatly enhanced oscillator strengths due to this charge-transfer mechanism.\(^{37,38}\)

The low-frequency conductivity is dominated by the appearance of four strong vibrations at $\approx$ 78, 118, 129, and 147 cm$^{-1}$ (the mode at 78 cm$^{-1}$ is visible most clearly below $T_c$). Both the A$_{2u}$ c-axis and E$_u$ in-plane mode are observed at $\approx$ 130 cm$^{-1}$.\(^{32}\) The E$_u$ mode is doubly degenerate; in the presence of a symmetry-breaking process such as disorder, this degeneracy may be lifted, resulting in a doublet. Because the 118, 129, and 147 cm$^{-1}$ vibrations are closely spaced, it is difficult to make definite assignments. Although the E$_u$ Raman mode is observed at $\approx$ 122 cm$^{-1}$,\(^{24}\) which is close to the observed modes, it is quite weak and is normally not observed. Because this mode would have to be activated by disorder to become infrared active, it would likely be much weaker than any of the observed vibrations. The mode at 78 cm$^{-1}$ falls well below the estimated phonon frequencies, and does not readily suggest an assignment. However, because this mode is visible in $\sigma_1(\omega)$ above $T_c$ at 30 K, it is not related to the superconductivity in this material. There is also a possibility that this mode (and perhaps others) may be a low-lying electronic transition due to crystal-field excitations.\(^{28}\) A similar quartet of lines has also been observed at slightly higher frequency ($\approx$ 150–170 cm$^{-1}$ region) in lightly doped La$_{2-x}$Sr$_x$CuO$_4$,\(^{36}\) where it was proposed that the observed tilting of the CuO$_6$ octahedra\(^{39}\) at low temperature was responsible for the quartet. Thus, while doping-induced disorder may be responsible for the splitting of the low-frequency modes, it may also be the case that a similar distortion of the CuO$_2$ planes may lead to a splitting of the E$_u$ mode. While the oscillator strengths of these modes are difficult to determine because of the rapidly changing backgrounds above and below $T_c$ (as may be seen in Fig. 3), they appear to be much larger than in the lightly doped La$_{2-x}$Sr$_x$CuO$_4$ material. If this structure is due to phonons, then these large oscillator strengths may be an indication of electron-phonon coupling.

**B. Electronic properties**

The optical conductivity in the normal state in Fig. 2 shows a rapidly narrowing Drude-like component. The temperature-dependent damping $\Gamma_0 = \Gamma(\omega \rightarrow 0)$ shown in Fig. 6 indicates that at low temperature $\Gamma_0$ saturates to a value of $\approx$ 100 cm$^{-1}$. An estimate of the Fermi velocity in the CuO$_2$ planes of $v_F \approx 2.2 \times 10^7$ cm/s may be obtained from band-structure calculations,\(^{40}\) which yields a mean free path (l = $v_F / \Gamma_0$) of $\approx$ 750 Å at 30 K. This large value for the mean free path at low temperature indicates that the doping-induced disorder in the Nd(Ce) layers does not lead to strong scattering in the CuO$_2$ planes.

The observation that there is relatively little scattering in the CuO$_2$ planes is consistent with the description of a “clean-limit” system \([\epsilon_{ab} \ll \epsilon_{\alpha \beta}]\), where the coherence length is $\xi_0 \approx 70$–80 Å (Ref. 9). In the BCS theory,\(^{14}\) the determination of the penetration depth at $T=0$ is described by $\lambda_{ab} \approx (1 + \xi_0/l)$; the local clean-limit approximation ($\xi_0/l \ll 1$) implies that $\lambda_{ab} \approx \lambda_L$, thus the measured penetration depth is essentially the London penetration depth.

In a clean-limit system, most of the normal-state carriers are expected to collapse into the δ function below $T_c$. However, estimates of the strength of the condensate indicate that only $\approx$ 40% of the normal-state carriers have condensed at $T_c/2$. In a variation of the two-component model, it has been suggested that the carriers responsible for much of the mid-infrared component may be centered at very low frequency (ω → 0);\(^{41}\) essentially creating another distinct “free-carrier” component. In this picture, there are now two separate types of carriers in the normal state; (i) a narrow Drude component (Γ $\approx$ 100 cm$^{-1}$ at 30 K), all of which collapses into the δ function below $T_c$, and (ii) heavily damped carriers (Γ $\approx$ 1000 cm$^{-1}$) whose properties do not change below $T_c$. If $\omega_D$ is the plasma frequency of the Drude component, and $\omega_{p,\alpha}$ is the plasma frequency of the overdamped carriers, then it must be true that $\omega_D^2 + \omega_{p,\alpha}^2 = \omega_p^2$, where $\omega_p$ is the plasma frequency of both types of carriers, as determined by optical conductivity sum rules. Thus, the requirement that $\omega_D^2 \approx \omega_{p,\alpha}^2 (\approx \delta^{1/2})$ satisfies the clean-limit condition. This estimate works reasonably well, as $\omega_D$ $\approx$ 10 000 cm$^{-1}$ for the Drude component, and the resulting value for $\omega_{p,\alpha} \approx 12$ 500 cm$^{-1}$ can fit the 30 K conductivity out to $\approx$ 1000 cm$^{-1}$ nearly as well as the midinfrared excitations, which are shown in Fig. 2.

While the hope-doped cuprates, such as YBa$_2$Cu$_3$O$_{6+x}$, all show a general depression of the conductivity in the far infrared for $T < T_c$, at low frequency there is a considerable amount of residual conductivity\(^{42}\) (absorption\(^{43}\)). This residual conductivity is usually taken as one of the indications that the energy gap is not a BCS-like gap. While there is a substantial reduction of the low-frequency conductivity below $T_c$, in Fig. 3, and the conductivity appears to be decreasing down to the lowest measured frequency, there is a rather large error associated with the low-frequency conductivity due to the high value of the reflectance. Thus, the uncertain nature of the conductivity in this region makes it difficult to draw conclusions about the nature of the gap, BCS or otherwise.

In ordinary metals where there is strong coupling between electrons and phonons, the conduction electrons may be scattered inelastically by phonons. In the normal state, this process has a definite threshold at the frequency of the phonon $\Omega_0$ (at T = 0). As a result, a sideband starting at $\Omega_0$ appears in the conductivity. The spectral weight of this feature (normalized to the free-carrier contribution) is equal to the electron-phonon coupling constant $\lambda_{tt,44}$ appropriate for transport but thought to be closely related to the $\lambda$ in the Eliashberg strong-coupling theory of superconductivity.\(^{45}\)
Below $T_c$, the development of an isotropic gap of $2\Delta$ at the Fermi surface requires an energy of $2\Delta$ to break the quasiparticle pairs; as a result the threshold for quasiparticle scattering now shifts to a higher frequency $\Omega_0 + 2\Delta$. The mechanism is referred to as the Holstein emission process.\(^\text{46}\) In conventional strong-coupling metals, such as lead, a Holstein sideband due to electron-phonon coupling has been observed in the superconducting state.\(^\text{47}\)

To achieve high $T_c$'s in strongly coupled metals requires $\lambda \approx 1$,\(^\text{38,4}\) and estimates of the electron-phonon spectral density in cuprate systems yield similar values for $\lambda$.\(^\text{50}\) Thus, it was expected that the Holstein structure would be strong in this material. However, as Fig. 3 and the phonon parameters listed in Table I indicate, for $T \approx T_c$ and $T \ll T_c$, there are no anomalies, as the changes in the phonon parameters (in particular the frequencies) are very small and no new spectral features are observed. This implies that the phonons are almost totally decoupled from the electronic continuum, and that $\lambda$ is very small ($\lambda < 1$).

An estimate of strength of the electron-phonon coupling constant for the free carriers may also be calculated from the frequency-dependent scattering rate\(^\text{51}\)

$$\frac{\hbar}{\tau} = 2\pi\lambda nkT, \quad (T \gg \theta_D).$$

(It is important to note that this is a high-temperature expression.) An examination of the scattering rate in Fig. 6 in the linear region ($T \approx 150$ K) yields $\lambda_{nr} = 0.59 \pm 0.1$, which places this material in the weak-coupling limit; the value for $\lambda_{nr}$ will scale depending upon the choice of $\omega_p$. This value for $\lambda_{nr}$ is larger than a previously measured value ($\lambda_{nr} = 0.15 \pm 0.01$) for Nd$_{1.85}$Ce$_{0.15}$CuO$_4$,\(^\text{36}\) but is similar to results obtained for hole-doped cuprates.\(^\text{15}\) The generally small value for $\lambda_{nr}$ for the superconducting carriers does not preclude the possibility of strong electron-phonon coupling with those normal-state carriers that have not condensed.\(^\text{41}\) Because these carriers are overdamped, a Holstein sideband in the normal state would be broadened,\(^\text{52}\) and below $T_c$ no additional structure would be expected, as these carriers do not condense. The likelihood that the Holstein sidebands are absent and the small value for $\lambda_{nr}$ suggests that the superconductivity in this material is not phonon mediated. However, by itself this is no evidence of a non-BCS mechanism; the BCS mechanism simply requires an attractive interaction.

A recent study of Ba$_{0.6}$K$_{0.4}$BiO$_3$ ($T_c \approx 30$ K) (Ref. 54) concluded that despite reports of a large value for the electron-phonon coupling constant $\lambda = 1$, and behavior which demonstrated an order parameter with an $s$-wave symmetry,\(^\text{53}\) the electron-phonon coupling in Ba$_{0.6}$K$_{0.4}$BiO$_3$ must necessarily be small, $\lambda = 0.2$. This led to the conclusion that Ba$_{1-x}$K$_x$BiO$_3$ was an $s$-wave superconductor that is not driven by the electron-phonon interaction.

It has been observed that in many underdoped and optimally doped cuprates, the strength of the condensate $\delta$ varies monotonically with $T_c$.\(^\text{35}\) This relationship is depicted in Fig. 8 for several cuprates (La$_{2-x}$Sr$_x$CuO$_4$, YBa$_2$Cu$_3$O$_{6+x}$, and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$); the dashed line upon which these points lie is generally referred to as the Uemura line. A point has also been included for a superconducting oxide that is not based on CuO$_2$ planes and that is also believed to be an electron-doped material, Ba$_{0.6}$K$_{0.4}$BiO$_3$;\(^\text{41}\) this material falls somewhat below the Uemura line. However, the value of the condensate ($\delta_{\Omega_0^0} = 10^{640}$ cm$^{-1}$) obtained for the cuprate Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ lies nowhere near the other points. This is surprising in view of the fact that this material is nearly optimally doped and that other “disordered alloy” systems such as La$_{2-x}$Sr$_x$CuO$_4$, in the underdoped and optimally doped regions, are well described by the Uemura relationship. It is unlikely that this behavior is due to the material being overdoped, as the condensate in materials which lack chains is observed to decrease in the overdoped regime.\(^\text{56}\) This suggests that the superconductivity in this material is fundamentally different that other hole-doped cuprate superconductors.

**V. CONCLUSIONS**

The reflectance of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ has been measured over a wide frequency range above and below $T_c$, and the optical properties determined. In addition to the expected four infrared-active $E_u$ modes, a number of $c$-axis infrared and Raman modes are activated by doping-induced disorder, and are observed at low temperature in the $ab$ plane. Several of the activated features have very large oscillator strengths, which may be an indication of electron-phonon coupling. Strong electron-phonon coupling may suggest a distortion of the Nd(Ce)O and CuO$_2$ layers. There is also the possibility that some of these features may be due to low-lying electronic transitions due to crystal-field excitations.

In the normal state the optical conductivity consists of a narrow Drude-like feature that narrows rapidly with decreasing temperature, and a midinfrared component that can be described by overdamped oscillators; there is some evidence...
that part of the midinfrared band may be due to very lowfrequency excitations ($\omega \to 0$), which may essentially behave like a second “free-carrier” component. Below $T_c$, only the Drude carriers collapse into the $\delta$ function. The plasma frequency of the condensate is $\omega_p \approx 10000 \pm 600 \text{ cm}^{-1}$, giving a (London) penetration depth of $\lambda_\text{D} \approx 1600 \pm 100 \text{ Å}$ at 10 K. From transport measurements, $\lambda_\text{D} \approx 0.5$; as well, no Holstein sidebands are observed below $T_c$. This indicates that the carriers that participate in superconductivity are only weakly coupled to the phonons, suggesting that if the superconductivity in this material can be described by the BCS model, then the pairing is not due to the electron-phonon mechanism. While optical techniques cannot unambiguously determine the symmetry of the superconducting energy gap, the strength of the condensate in Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ is much larger than in other cuprate materials with similar $T_c$'s, indicating that the superconductivity in this material is different than in other cuprate superconductors.

ACKNOWLEDGMENTS

The authors would like to acknowledge many useful discussions with D. N. Basov, D. A. Bonn, A. V. Puchkov, and T. Timusk. We are grateful to A. W. McConnell for assistance in the laboratory. This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Linville Institute, and Simon Fraser University. Work at Maryland is supported by the NSF under Contract No. DMR-9510475.

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31. For a fit to $\sigma_1(\omega)$ at 30 K the Drude component in Fig. 2 consists of $\omega_p = 1100 \text{ cm}^{-1}$ and $\Gamma_D = 48 \text{ cm}^{-1}$, while the midinfrared band has been generated using four (arbitrary) Lorenzian oscillators: (i) $\omega_1 = 130$, $\gamma_1 = 160$, $\omega_2 = 5500$, (ii) $\omega_1 = 240$, $\gamma_2 = 550$, $\omega_2 = 7000$, (iii) $\omega_3 = 800$, $\gamma_3 = 2050$, $\omega_3 = 8000$, and, (iv) $\omega_4 = 2800$, $\gamma_4 = 4600$, $\omega_4 = 14000$. (All units are in cm$^{-1}$.)


