An absorption band (often called $d$ band) appears at $\approx 1000 \text{ cm}^{-1}$ in the infrared spectra of many parent compounds of high critical temperature superconductors (HCTS) upon slight doping by either electrons or holes. The polaronic nature of the $d$ band has been established on sound arguments, which include the observation that this band is made of overtones of infrared active vibrational modes (IRAV's) induced by doping. The polaronic bands are common to all cuprates where the $\sigma$-band (often called $d$ band) appears at $\approx 1000 \text{ cm}^{-1}$ in the infrared spectra of many parent compounds of high critical temperature superconductors (HCTS) upon slight doping by either electrons or holes.

Recently, an increasing theoretical effort has been devoted to the investigation of many-polaron systems. An experimental study of the $d$ band through the whole phase diagram of a cuprate would provide a useful basis to the above theoretical efforts.

In the present paper the above task is pursued by following the evolution of the polaron band in ten Nd$_{2-x}$Ce$_x$CuO$_{4-y}$ (NCCO) single crystals. Their reflectivity $R(\omega, T)$ has been measured from 10 to 300 K and from 50 to 15000 cm$^{-1}$. Those measurements allowed us to follow with unprecedented detail the evolution of the $d$ band across the insulator-to-superconducting transition (IST) in a family of cuprates. This procedure also enables one to overcome the intrinsic difficulties in discriminating the $d$ band from the Drude term in the infrared spectrum of a single, metallic sample.

This investigation in the electron-doped NCCO should be relevant to HCTS, independently of the type of carriers involved. In fact, the well known equivalence between the optical properties of electron- and hole-doped HCTS (see, e.g., Refs. and ) has been recently extended to the anomalous transport properties.

The main results of the present work are summarized as follows: i) the average polaron energy softens with increasing doping and/or lowering temperature through the whole insulating phase, with an abrupt change of slope an intermediate doping; ii) this behavior persists in the metallic superconducting phase, where a polaron contribution peaked at a finite energy is still distinguishable, even at optimum doping; iii) no change in the polaron energy with doping is detected at IST; iv) a plain Drude behavior is observed in the overdoped, not superconducting regime. These results are discussed in connection with recent models of polaron-polaron interactions.

The NCCO single crystals investigated here were prepared as described in Ref. . Their doping concentrations are specified in Table I, together with that of a sample measured in Ref. . The Ce concentration was determined as the average of chemical microanalysis measurements at 4 to 7 positions on the crystal surface. The experimental apparatus has been described in detail in Ref. . The real part of the optical conductivity $\sigma(\omega, T)$ has been obtained from Kramers-Kronig transformations of $R(\omega, T)$ measured with the radiation electric field polarized in the Cu-O plane. $\sigma(\omega, T)$ is independent of the low- and high-energy extrapolations used to extract it, at least for $\omega \leq 5 \times 10^3 \text{ cm}^{-1}$.

$R(\omega, T)$, reported in Fig. 1, illustrates how the reflectivity evolves with doping for the most representative samples. The peak above $10^4 \text{ cm}^{-1}$ is due to the well known charge transfer (CT) band. A strong temperature dependence is observed in the $R(\omega, T)$ of the insulating samples $C$ ($x = 0; y < 0.01$), $F$ ($x = 0.04; y \sim 0$), and $H$ ($x = 0.12; y \sim 0$) for $\omega \lesssim 6 \times 10^3 \text{ cm}^{-1}$. This holds too for the superconducting sample $I$ ($x=0.17$), while no temperature dependence is observed in sample $J$ ($x=0.21$). The reflectivity of the other samples in Table I smoothly interpolates that of the samples shown in Fig. 1.
FIG. 1. \(R(\omega, T)\) spectra taken at 300 (dashed lines) and 20 K (full lines) but for the \(x = 0.17\) sample, which has been measured at low T both in the superconducting (T=10 K, full line) and in the metallic anomalous phase (T=40 K, dotted line).

The dependence of the polaron band on T and doping can be isolated from the plain effect of an increased carrier density by looking at the renormalized conductivity \(\sigma^*(\omega, T) = \sigma(\omega, T)/n^*\), where

\[
n^* = \frac{2mV}{\pi e^2} \int_0^{\omega^*} \sigma(\omega) d\omega
\]

is the spectral weight in the CT gap and is proportional to the number of carriers per unit cell. \(m\) is the carrier effective mass, assumed here equal to the free electron mass \(m_0\), \(V\) is the volume of the unit cell, and \(\omega^* = 10000\) cm\(^{-1}\), an approximate value for the CT energy gap. \(\sigma^*(\omega, T)\) is reported in Fig. 2 in a reduced infrared range for the same samples shown in Fig. 1.

For fixed T and increasing doping, the spectral weight shifts toward low energy and narrows until a Drude contribution appears above IST. The phonon peaks, increasingly screened, nearly vanish in sample \(H\).

For fixed doping, the spectral weight shifts toward low energy with decreasing T until a saturation temperature \(T_s\) is reached. Below \(T_s\), the far-infrared optical conductivity does not change sizably. An inspection to the sets of data taken for some samples at intermediate T’s suggests that \(T_s\) decreases with doping. It is equal or greater than room temperature in sample \(A\) (\(x=0; y < 0.005\)), on the order of 200 K in sample \(D\) (\(x=0; y < 0.04\)), quite lower in sample \(I\) (\(x=0.17; y < 0\)) where \(\sigma^*(\omega, T)\) still changes on going from 40 to 10 K, and finally is not relevant for sample \(J\) (\(x=0.21\)) where no appreciable dependence on T can be detected between 300 and 20 K. A finer tuning of the temperature sampling is required in order to get precise values of \(T_s\) and will be the object of further investigations. Since the spectral weight undergoes a “red shift” for decreasing T, the gap appearing at 300 K below \(\sim 250\) cm\(^{-1}\) in sample \(H\) is almost
completely filled at 20 K, indicating a low temperature “metallization” near IST. This “red shift” leads also to a dependence on T of the phonon line shapes (see the two low-doped samples C and F), which can be related to a Fano interaction with a polaron continuum shifting from high to low energy with decreasing T. [22]

Finally, for the most doped sample J, $\sigma^*(\omega, T)$ in Fig. 2 follows a conventional Drude behavior

$$n^*\sigma^* = \frac{\Gamma_D\omega_p^2}{\omega^2 + \Gamma_D^2},$$  \hspace{1cm} \text{(2)}$$

where $\omega_p = (ne^2/m)^{1/2}$ is the plasma frequency and $\Gamma_D$ is the inverse of the scattering rate, independent of $\omega$. In the same Fig. 2, a best fit of Eq. 2 to data is reported by dots ($\omega_p = 17500$ cm$^{-1}$, $\Gamma_D = 90$ cm$^{-1}$). On the other hand, the same type of fit is unsuccessful in sample I where one should add the $d$ band to the Drude term in order to satisfactorily fit $\sigma^*(\omega, T)$.

Let us now proceed to a quantitative analysis of $\sigma^*(\omega, T)$. The shift of the spectral weight between the insulating samples $C$ and $F$ is due to the “red shift” of the polaron $d$ band. [22] This analysis can be extended to more doped samples, where the peak energy of the $d$ band increasingly merges with the Drude term, by evaluating the first moment, $<\omega>$, of the polaronic contribution to $\sigma^*(\omega, T)$. In those highly doped samples the polaron band can be hardly isolated from the Drude and IRAV contributions, while both the mid-infrared (MIR) [22] and CT terms can easily be identified. Therefore, we actually estimate $<\omega(T)>$ by subtracting from $\sigma(\omega, T)$ the corresponding contributions $\sigma_{MIR}(\omega, T)$ and $\sigma_{CT}(\omega, T)$, which are determined from a standard fit to the $\sigma^*(\omega, T)$ data. [22] In conclusion, an approximate expression for the first moment of the polaron conductivity is given by

$$<\omega> \simeq \frac{\int_0^{\omega_p} \omega [\sigma - \sigma_{MIR} - \sigma_{CT}] d\omega}{\int_0^{\omega_p} [\sigma - \sigma_{MIR} - \sigma_{CT}] d\omega}. \hspace{1cm} \text{(3)}$$

This quantity, estimated at $T=300$ and 20 K, is plotted in Fig. 3 vs the spectral weight $n^*$ renormalized to $n_0$, the spectral weight in the CT gap of the less doped sample A. $<\omega(T)>$ has been estimated also for a sample with $x=0.15$ on the grounds of conductivity data at 10 K from Ref. [21] and is reported in Fig. 3.

A major softening of the $d$ band on going from room to low temperature is confirmed in all samples. As a function of doping, two different regimes can be identified. In the diluted polaron regime (samples A to D), where the intensity of the $d$ band $I_d$ increases [22] for $T \rightarrow 0$, $<\omega(T)>$ decreases at a much faster rate than at high doping. In the latter region, the determination of $I_d$ is affected by large errors. However, in a few samples [22] $I_d$ seems even to increase with $T$, as predicted in Ref. [24] for a system including polarons, free charges and impurities.

Quite surprisingly, no abrupt change in $<\omega(T)>$ is observed at IST and $<\omega(T)>$ is still finite in the superconducting phase, as confirmed from the value extrapolated from Ref. [21] (full triangle). $<\omega>$ vanishes, instead, at the superconducting-to-metal transition SMT, both at 300 and 20 K, in agreement with the plain Drude behavior of $\sigma^*(\omega, T)$ in sample J. It should also be mentioned that the polaron band narrows continuously for increasing doping, as observed when comparing sample F with sample H in Fig. 2.

The above results provide a verification for theoretical models recently proposed for describing a system of interacting polarons. Indeed, $<\omega>$ in Fig. 3 is closely related to the polaron energy $E_p$. In the limit of infinite polaron dilution ($n \rightarrow 0$) one observes [23] an almost symmetric polaron band and $<\omega> \simeq 2E_p/h$. At finite doping, both the polaron size and line shape are unknown and $<\omega>$ remains the best experimental estimate of $E_p$ presently available.

According to theoretical models accounting for polaron-polaron interaction, [8–10] an increase in the polaron density should reduce the electron-phonon coupling. This leads to a decrease of $E_p$, in qualitative agreement with present results. An explicit expression for the decrease of $E_p$ due to the dipole-dipole interaction in a liquid of large Feynman polarons has been recently derived: [1]

$$E_p^2 = E_{p0}^2 - 0.6(q/e)[1 + m_0/(m_{pol}^* - m_0)]h_{pol}^2. \hspace{1cm} \text{(4)}$$

Here, $E_{p0}$ is the polaron energy at infinite dilution, $(q/e) \sim (1 - 1/\epsilon_0)$, with $\epsilon_0$ the static dielectric constant,
$e$ is the free electron charge, $m_{pol}^*$ the polaron effective mass, and $\Omega_{pol}^2$ is equal to eight times the integral at the denominator of Eq. 3, namely, it is proportional to the polaron density. Equation (4) quantitatively accounts for the decrease of the polaron energy from sample A to sample D and predicts that $E_p$ vanishes at a doping just slightly higher than that of sample D, namely where the rate in the decrease of $<\omega>$ changes; see Fig. 3. This change of slope implies the insurgence of a new process, e.g., the formation of a polaron aggregate, not predicted by any of the above theoretical models. This process should account also for the persistence of polarons in the metallic superconducting phase with a collapse of $<\omega(T)>$ in the normal metal. The narrowing of the polaron band further supports the formation of polaron aggregates. These latter may be either polaron pairs, or clusters, or stripes.

The implications of a hypothetical superconducting polaron-pair aggregate have been discussed and compared to the properties of HCTS in a recent study of the tunneling dynamics of polarons in a two dimensional antiferromagnet. [13] This model also predicts a crossover (either sharp or continuous) from the polaron aggregate to a Fermi liquid for doping higher than the optimal one. On the other hand, evidence of stripes in certain HCTS clusters, or stripes. Moreover, it can be shown that the total energy of the system decreases if polarons dynamically self-aggregate in uni-dimensional arrays in the Cu-O plane, hereafter called wires, whose spacing decreases with increasing polaron density. [12] In this context, at the critical density IST, the Cu-O plane becomes unstable and strong fluctuations in the wire density together with the increasing interaction between wires give rise at low T to a crossover from an insulating phase to a superconducting polaron liquid. Therein, localized energy states, monitored by the sur-

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|       | A  | B  | C  | D  | E  | F  | G  | H  | I.  | J  | Homes |
|-------|----|----|----|----|----|----|----|----|-----|----|-------|
| $x$   | 0  | 0  | 0  | 0  | 0  | 0.04| 0.04| 0.10| 0.12 | 0.17| 0.21  | 0.15 |
| $y$   | $<0.005$ | $<0.005$ | $<0.01$ | $<0.04$ | $<0$ | $\sim0$ | $\sim0$ | $\sim0$ | $>0$ | $\sim0$ |

$^a$ $T_c = 21$ K
$^b$ $T_c = 23$ K, from Ref. 21