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Pseudo-gap and superconducting condensate energies in the infrared spectra of Pr-doped $YBa_2Cu_3O_7$

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Abstract. – The (a, b)-plane infrared and visible conductivity (30–30000 cm^{-1}) of a 40% praseodymium-substituting yttrium $YBa_2Cu_3O_7$ film displays a loss of spectral weight over two separate energy ranges when lowering the temperature. A first loss of spectral weight is present in the range 300–800 cm^{-1} from room temperature down to 40 K ($T_c = 35$ K). A further distinct spectral weight diminution appears in the superconducting phase at frequencies below 200 cm^{-1}. This diminution can be observed due to the high signal-to-noise ratio allowed by the large area of the thin film. We propose that the lower energy loss of spectral weight reflects the formation and the properties of the superconducting condensate.

Introduction. – The microscopic interpretation of the infrared response of the normal and superconducting states in high-T_c cuprates is still highly debated. The far infrared reflectivity of superconducting oxides increases at low temperatures, although not reaching 100%. In the superconducting state, the expected loss of spectral weight in the real part of the optical conductivity $\sigma_1(\omega)$ —transferred to a zero-centered δ-function to warrant both infinite DC conductivity and charge conservation of the system— is clearly observed in optimally doped samples [1]. However, as the reflectivity never achieves unambiguously unity, there is a non-vanishing real part of the optical conductivity down to the lowest available energy. Such a residual conductivity suggests unpaired quasi-particles, in agreement with a *d*-wave symmetry for the order parameter. The existence of nodes allows pair breaking at all temperatures, yielding a (non–$\boldsymbol{k}$-sensitive) infrared response of quasi-particles at energies below the maximum gap value.

More recently it was noticed that the loss of spectral weight in the infrared (IR) conductivity, while occurring close to the superconducting transition in optimally doped compounds, seems to take place well above T_c in underdoped materials [2]. The surprising fact is that

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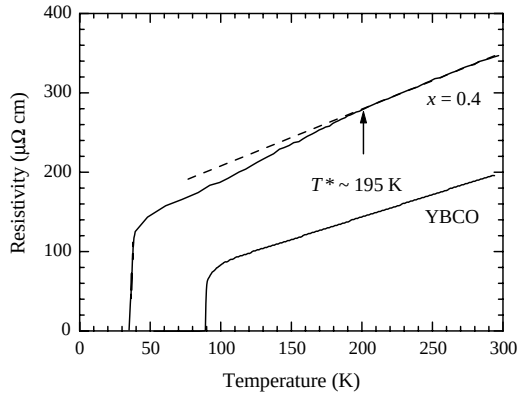

Fig. 1 – Temperature dependence of the DC resistivity of Pr-YBCO films on YSZ. The temperature where the resistivity no longer shows a linear thermal dependence in the $x = 0.4$ sample is indicated by T^*.

the energy scale below which this IR "normal-state gap seems" to develop does not change with doping (within the accuracy of this technique). Although commonly referred to as the pseudo-gap [2], the characteristic energy scale of this "normal-state gap" does not increase with underdoping as observed by other techniques, *e.g.* tunnelling [3]. The loss of spectral weight in the optical conductivity due to the pair condensation at T_c seems to occur over the same energy scale as the "normal-state gap", a feature similarly observed in STM spectroscopy [4]. These considerations suggest that non-coherent Cooper pairs are at the origin of the pseudo-gap. Models involving pairing above T_c have been discussed in different frameworks, including those in which an explicit distinction is made between an excitation gap and a coherence gap [5]. Several authors argue that phase fluctuations play an important role in these under-doped materials due to the small carrier density [6].

DC transport also provides a hint of the occurrence of a pseudo-gap. In optimally doped cuprates, the (a, b)-plane electrical resistivity is linear from T_c up to above room temperature, whereas in underdoped compounds deviations from linearity occur below $T^* > T_c$ [7]. The depression observed in the resistivity curves has been related to the spin-gap (or pseudo-gap) determined from NMR data [8].

Optical [9, 10] and coherent THz [11] studies on Pr-YBCO point towards localization effects. The superconducting IR response of these compounds was not analyzed in detail, though. In this paper we study the optical (a, b)-plane response of a $Y_{1-x}Pr_xBa_2Cu_3O_7$ (Pr-YBCO: $x = 0.4$) thin film as a function of temperature. We find an optical conductivity of Pr-YBCO characterized by two energy scales: i) a "normal state gap" below 800 cm^{-1} and ii) an energy scale that we suggest is characteristic of the superconducting condensate below 200 cm^{-1}. We argue that this scale is detectable because the Pr doped film is in the dirty limit. The small amplitude of the effect is measurable because of the high signal-to-noise level achieved due to the large area of the samples. The loss of spectral weight at this scale appears only below T_c.

Experimental. – Thin films of Pr-YBCO ($x = 0.4$) and YBCO (as a reference sample) were grown by sputtering on stabilized zirconia (YSZ) substrates. The samples are c-axis oriented and typically 5000 Å thick. The electrical DC resistivity shown in fig. 1 was measured by standard four-point methods. Table I summarizes our samples' critical temperatures. The

optimally doped YBCO film shows a linear temperature behavior almost all the way down to T_c. The dashed straight line on the top of the $x = 0.4$ data helps to locate approximately the pseudo-gap opening temperature T^* indicated by the arrow. The Pr-doped film has a depleted resistivity below $T^* \sim 195$ K. A detailed investigation [12] of the whole phase diagram (T_c *vs.* oxygen concentration) for various amounts of Pr (from $x = 0$ to 0.6) confirms that our samples, according to their critical temperatures, are fully oxidized. The Pr substituted sample can be considered as underdoped even though the physics and chemistry of this compound is evidently more complex. A similar T^* can be seen in under-doped YBCO films [7], albeit with $T_c = 70$ K. In other words, Pr-induced disorder possibly decreases T_c.

Our IR reflectivity spectra were obtained with a Bruker IFS 66v interferometer between 30 and 7000 cm^{-1}. Near-infrared and visible data between 4000 and 30000 cm^{-1} were measured in a Cary 4000 grating spectrometer. In the overlapping spectral range, measurements from both spectrometers agree within 0.5%. Reference mirrors are gold for measurements in the Bruker spectrometer and silver in the Cary. The spectra were collected between 6 K and room temperature in the whole frequency range with a He gas flow cryostat. The stability of temperature during the measurements was better than 0.5 K. With our 1 cm^2 samples we can resolve the spectra (relative to each other) within 0.2%, what is difficult to achieve in typical small size single crystals.

Data analysis and results. – The spectral functions were determined for our samples by Kramers-Kronig transform. At low frequencies (below 30 cm^{-1}) a Hagen-Rubens extrapolation was used at all temperatures, including the superconducting state. Above the highest measured frequency (30000 cm^{-1}) the reflectivity was assumed constant up to 10^6 cm^{-1} and a ω^{-4} termination was used up to infinity. Below 150 K our films are opaque enough to avoid a significant contribution from the substrate to the Kramers-Kronig obtained functions. To verify this, we simulated the optical reflectivity of a substrate-film system using the known complex refraction index of the substrate and fitting a phenomenological Drude-Lorentz dielectric function to the film. For pure YBCO, the reflectivity obtained from our simulated dielectric function agrees with that measured for single crystals. The Kramers-Kronig calculated optical conductivity agrees with that obtained from our simulations within 3% for all samples below 150 K.

It is useful to define a plasma frequency $\Omega_p^2 = 10^{-4} ne^2/(2\pi c)^2 \epsilon_0 m$, n being the charge density, m the bare electron mass, c the speed of light and ϵ_0 the vacuum permittivity. One can estimate the plasma frequency from optical data using the classical sum rule, neglecting all interband and localized states transitions:

$$\Omega_p^2 = \frac{Z_0}{\pi^2} \int_0^\infty \sigma_1(\omega)\ \mathrm{d}\omega\,. \tag{1}$$

$Z_0 = 377\ \Omega$ is the vacuum impedance. Everything else being in SI units, the above definitions give Ω_p and σ_1 in cm^{-1} and $\Omega^{-1}cm^{-1}$, respectively. Because electronic transitions *do* occur at high energy, it is fairly common to introduce a cutoff energy (1–2 eV) in order to restrict the integration to the free carrier contribution (believed to be confined below this energy). In this case, the bare electron mass must be replaced by its effective mass m^*. This plasma frequency estimation should yield an effective ratio N_{eff}/m^* for the carriers (whether mobile or localized).

It is worthwhile to recall that such a sum rule is generally valid for a standard Fermi liquid, within a single band approximation, and provided that the band structure does not change with temperature. Conversely, the sum rule may not hold if a single-band model is inappropriate to describe our materials implying, for instance: i) possible carrier density

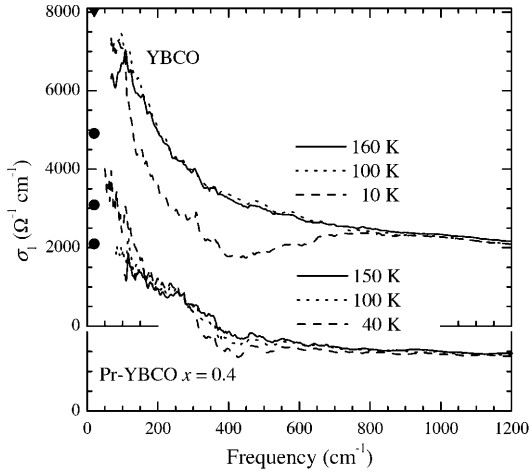

Fig. 2 – Optical conductivity σ_1 of Pr-YBCO films on YSZ. The solid symbols are obtained from the DC resistivity for the corresponding temperatures in the normal state. A loss of spectral weight is observed below 800 cm^{-1} in both $x = 0$ and 0.4 samples. For the former it is observed in the superconducting state only. For the latter it is already present far above T_c. Note that the set of axes for $x = 0.4$ is shifted by 2000 Ω^{-1}cm^{-1} with respect to YBCO.

transfer from one band to the other as the temperature changes [13] or ii) strong singularities (like Van Hove singularities) present in the density of states at the Fermi level [14]. Because there is no general agreement on the correct microscopic description of the normal state of cuprates, we assume, as commonly done in the literature and despite these restrictions, that the sum rule described by eq. (1) is valid.

Figure 2 shows the real part of the optical conductivity for our samples. The normal-state low-frequency conductivity extrapolates consistently at various temperatures to the measured DC conductivity (solid symbols). The normal-state spectral response of the YBCO film does not change with temperature, and is dominated by a Drude-like peak down to T_c. Below T_c a loss of spectral weight is observed in the low-frequency conductivity (below ~ 800 cm^{-1}). Note that in this sample grown on YSZ (not the most suitable substrate for epitaxy) the residual low-temperature conductivity is higher (~ 1500 Ω^{-1}cm^{-1}) than the one commonly reported in the literature ($\sim$ 500–1000 Ω^{-1}cm^{-1}) [15–17]. Despite this higher residual conductivity, no extra features or bumps are present in our film when compared to better samples. The response of our system is qualitatively the same.

In the $x = 0.4$ film the free carrier response is still the major contribution to the normal-

Table I – Pr-YBCO *characteristic parameters.* T_c, ΔT_c *(in parentheses) and* T^* *are directly obtained from the resistivity in fig.* 1. Ω_p *and* $N_{\rm eff}$ *are calculated at room temperature with eq.* (1) *integrated up to* 1.5 eV. $N_{\rm eff}$ *uses the bare-electron mass as* m^*.

x	T_c (K)	T^* (K)	Ω_p (cm^{-1})	$N_{\rm eff}$ (cm^{-3})
0	89(1)		22000	5.1×10^{21}
0.4	35(2.5)	195	19200	4.1×10^{21}

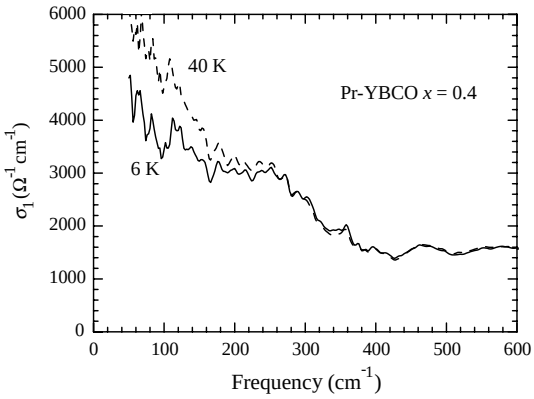

Fig. 3 – Far-infrared conductivity of the 40% Pr sample ($T_c = 35$ K). The superconducting transition is marked by a loss of spectral weight below 200 cm^{-1}.

state conductivity. A loss of spectral weight develops progressively below about 800 cm^{-1} as the temperature is lowered from room temperature. This loss is small but clearly present. It is difficult to ascertain exactly below which temperature it occurs. It is clearly visible at 100 K. In any case, it starts to develop well above $T_c = 40$ K. Figure 3 shows that upon cooling down into the superconducting state (below T_c) a further loss of spectral weight takes place below about 200 cm^{-1}. Table I shows absolute values for $N_{\rm eff}$ and Ω_p estimated with eq. (1) integrated up to 1.5 eV at $T = 300$ K. We used the bare-electron mass to obtain $N_{\rm eff}$. As noticed previously, the numbers may be off due to the arbitrary choice of the high-frequency limit, but except for a failure of the sum rule, the relative change with temperature and between samples is meaningful.

In fig. 4, we display the thermal evolution of $N_{\rm eff}$ for each sample normalized by its value at 300 K. The estimated error in $N_{\rm eff}$ is about twice the symbol size. The arrows indicate the measured T_c. Both samples exhibit a decrease of the carrier density when crossing T_c, associated to the spectral weight transferred to the zero-centered δ-function. Note that the

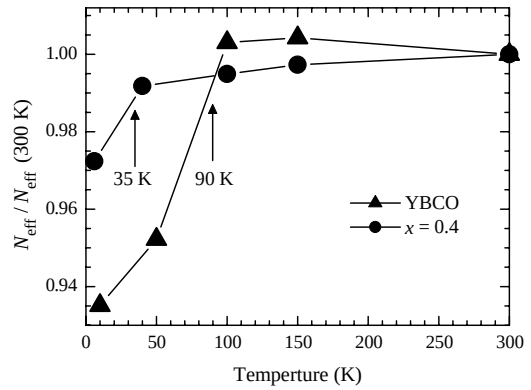

Fig. 4 – Effective charge density of the $x = 0$ and 0.4 samples. The data are normalized by each sample's value at 300 K. The error bars are about twice the symbols size. The arrows indicate the critical temperatures.

smaller loss of spectral weight in the $x = 0.4$ sample is a common feature of underdoped materials.

Discussion. – Our YBCO film shows no detectable loss of spectral weight above T_c. We can compare our $x = 0.4$ sample ($T_c = 35$ K) with Orenstein *et al.* underdoped ($T_c = 30$ K) YBCO [18]. For this comparison only, we restrict the integration limits in eq. (1) to the 200–2000 cm^{-1} range, where Orenstein's results are independent of Kramers-Kronig extrapolations. Cooling from 150 K to 100 K, the charge lost in our $x = 0.4$ sample is about 8% of the charge condensed between 100 K and 10 K in our YBCO film. The same calculation for the $T_c = 30$ K and $T_c = 90$ K samples of ref. [18] yields 7%. Thus, the effect of underdoping YBCO by Pr is equivalent to the effect of underdoping by oxygen deficiency in terms of apparent spectral weight loss.

The new feature in the $x = 0.4$ sample is the fact that an additional loss occurs in the superconducting phase ($T < T_c$) below ~ 200 cm^{-1}, and not over the entire spectrum below 800 cm^{-1} as reported for other cuprates [16, 19]. Part of this loss may be related to the evolution of a localization band clearly present in the $x = 0.5$ compound [20]. This band is seen as a shoulder in fig. 3 around 200 cm^{-1}. However, relying on the $x = 0.5$ data, we estimate that it cannot account for more than 30% of the lost area. Actually, we have checked that the loss of spectral weight below T_c is consistent with the superfluid density expected for a 40 K sample, according to the Uemura plot [21].

We thus conclude that the low-temperature IR data of the $x = 0.4$ shows a condensation of carriers into a superfluid below T_c, in an energy range of the order of 200 cm^{-1}. This implies that there exists in this sample a superconducting energy scale distinct from and smaller than that of the pseudo-gap. If we identify this scale with 2Δ we have $\Delta \sim 10$ meV. The existence of an energy scale characteristic of the condensate, which follows the same doping dependence as T_c, has already been seen by Andreev spectroscopy [5]. In fact we find a $2\Delta/kT_c$ ratio of about 6 in accordance to ref. [5].

So why would the gap be visible here? It is well accepted that the gap is usually not visible in the IR spectra of high-T_c superconductors because they are in the clean limit. But the coherence length of the Pr-doped sample may be as large as 50 Å [22]. We calculate a mean free path of 66 Å, using a scattering rate of 1000 cm^{-1} (determined from the optical data) and a Fermi velocity of 2×10^7 cm/s. Therefore, Pr-YBCO is rather in the dirty limit making it possible to see the superconducting gap by IR spectroscopy.

Summary. – The optical response of superconducting (Y, Pr)$Ba_2Cu_3O_7$ shows a low-frequency loss of spectral weight below $T_c = 35$ K in the $x = 0.4$ Pr sample at an energy scale of 200 cm^{-1}. This scale relates to the formation of the superconducting condensate. It suggests a superconducting gap ~ 10 meV, corresponding to $2\Delta/kT_c \sim 6$. Our data suggest that highly accurate measurements in other strongly underdoped cuprates in the dirty limit could possibly show a similar effect.

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