Far-infrared c-axis conductivity of flux-grown $Y_{1-x}Pr_xBa_2Cu_3O_7$ single crystals studied by spectral ellipsometry

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The far-infrared c-axis conductivity of flux-grown $Y_{1-x}Pr_xBa_2Cu_3O_7$ single crystals with $0.2 \leq x \leq 0.5$ has been studied by spectral ellipsometry. We find that the c-axis response exhibits spectral features similar to deoxygenated underdoped $YBa_2Cu_3O_{7-\delta}$, i.e., a pseudogap develops in the normal state, the phonon mode at 320 cm^{-1} exhibits an anomalous T dependence, and an additional absorption peak forms at low temperature. This suggests that the T_c suppression in flux grown Pr-substituted crystals is caused by a decrease of the hole content and/or by carrier localization rather than by pair breaking.

Superconductivity above the liquification temperature of nitrogen was first discovered in 1987 in the cuprate high-T_c compound $YBa_2Cu_3O_{7-\delta}$ (Y-123) with a critical temperature of $T_c = 92$ K.[1] It was subsequently shown that chemical substitution of Y by most rare-earth elements leaves T_c almost unaffected with $T_c > 90$ K.[2] Ever since, the reason why Pr-123 does not become superconducting (SC) has been a puzzle.[3] A number of models have been proposed which explain the absence of SC in Pr-123 either in terms of pair breaking by the magnetic Pr moments,[4] a hole depletion of the CuO_2 planes caused by a mixed valency of $Pr^{3+/4+}$ (Ref. 5) or a partial substitution of Pr^{3+} for Ba^{2+} (Ref. 6), a modification of the charge transfer between CuO chains and CuO_2 planes,[7] or a hole redistribution and localization due to a strong hybridization of the Pr $4f$ and O $2p$ orbitals.[8] Recently, it has been reported that Pr-123 can also be made SC with $T_c > 90$ K.[9] This finding has led to renewed interest in the electronic properties of the Pr-123 compound. Yet the essential mechanism which decides whether Pr-123 is a superconductor with $T_c > 90$ K or a non SC insulator is still unknown.

In this paper we report ellipsometric measurements of the far-infrared (FIR) c-axis conductivity of partially Pr-substituted flux grown $Y_{1-x}Pr_xBa_2Cu_3O_7$ crystals with $0.2 \leq x \leq 0.5$. We show that the c-axis conductivity of the Pr-substituted crystals exhibits virtually the same spectral features as deoxygenated and thus underdoped $YBa_2Cu_3O_{7-\delta}$ crystals, i.e., a spectral pseudogap forms in the normal state, the oxygen bond-bending phonon mode at 320 cm^{-1} exhibits its anomalous T dependence, and an additional broad absorption peak forms at low T. This finding implies that a similar effect causes the T_c suppression in flux grown Pr substituted and deoxygenated Y-123 crystals, namely, a depletion and/or a localization of the Zhang-Rice-type hole carriers of the CuO_2 planes. From our measurements we do not obtain any decisive information about the hole depletion mechanism in Pr-substituted samples.

Pr-substituted $Y_{1-x}Pr_xBa_2Cu_3O_7$ crystals have been grown by a flux-method[10] using Y-stabilized Zr_2O crucibles. Farily large crystals with a typical size of the ac face of 3 by $0.5-1$ mm^2 have been used. They have been annealed in an O_2 gas stream for 1 day (d) at 600°C then cooled within 1 d to 400 °C and further annealed for 10 d at 400 °C. A Zn-substituted $YBa_2Cu_{2.94}Zn_{0.06}O_{6.9}$ crystal has been annealed under similar conditions but with the final step at 500 °C for 5 d. The midpoint SC transition temperature T_c and the 10 to 90 % halfwidth ΔT_c have been determined by dc-SQUID magnetization measurements at 5 Oe. The Pr content and the Zn content have been determined by EDX analysis. For the Pr-substituted crystals we obtained $T_c = 81(3)$ K for $x \approx 0.2$, $T_c = 64(3)$ K for $x \approx 0.3$, $T_c = 48(4)$ K for $x \approx 0.4$, and $T_c = 24(5)$ K for $x \approx 0.5$. For the Zn-substituted crystal we obtained $T_c = 76(3)$ K for $z \approx 0.06$.

The ellipsometric measurements have been performed at the National Synchrotron Light Source (NSLS) using a home-built ellipsometer attached to a Nicolet Fast-Fourier spectrometer at the U4IR beamline.[11] Some experiments have been done with the ellipsometer attached to a Bruker 113V using a conventional Hg arc light source. The optical measurements have been performed on the as grown clean ac surfaces (with the c axis in the plane of incidence). The technique of ellipsometry provides significant advantages over conventional reflection methods in that (a) it is self-normalizing and does not require reference measurements and (b) the real and the imaginary parts of the dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ are obtained directly without a Kramers-Kronig transformation. Since only relative intensities of the reflected light are required, the ellipsometric measurements are more accurate and reproducible than conventional reflection measurements.

Figure 1 shows the spectra of the FIR c-axis conductivity σ_{1c} of the $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$ crystal with $T_c = 81(3)$ K in the normal and in the superconducting state. The room temperature spectrum is composed of an almost frequency independent electronic background on which five infrared active phonon modes are superimposed. The phonon modes correspond to those of fully oxygenated $YBa_2Cu_3O_7$.[12] It has been previously shown for deoxygenated $YBa_2Cu_3O_{7-\delta}$ that the strength of the phonon mode at 630 cm^{-1}, which corresponds to the vibration of apical oxygen neighboring an empty chain fragment, is a good indicator for the oxygen deficiency of a given sample. The absence of the 630 cm^{-1} phonon mode thus confirms the fully oxidized state of our present crystal. With decreasing T the electronic background
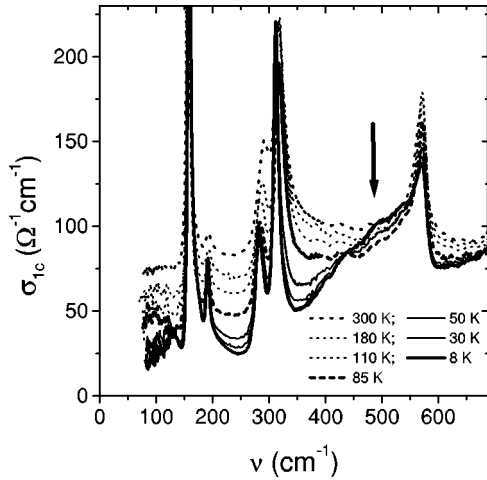
FIG. 1. Spectra of the real part of the FIR c-axis conductivity of $Pr_{0.2}Y_{0.8}Ba_2Cu_3O_7$ with $T_c = 81(3)$ K in the normal and the superconducting state. The position of the additional low-temperature peak is indicated by the solid arrow.

FIG. 2. Optical FIR c-axis conductivity of Zn-substituted $YBa_2Cu_{2.94}Zn_{0.06}O_{6.9}$ with $T_c = 76(3)$ K at different temperatures in the normal- and the superconducting state. The arrow indicates the onset of the spectral gap in the superconducting state.

can be seen to develop a spectral gap in the normal state already well above T_c. The characteristic features of this normal state spectral gap are identical to those of the pseudogap which has been observed in an underdoped deoxygenated $YBa_2Cu_3O_{6.75}$ crystal with similar T_c.[13,14] In both crystals the normal state pseudogap has a similar size of $\omega_{NG} \sim 700$–800 cm^{-1} (defined as the onset of the suppression of the conductivity with decreasing temperature) and its onset temperature T_{NG} is around 200 K. Even the spectral shape of the pseudogaps compares very well. Close to T_c, the in-plane oxygen bond-bending mode at 320 cm^{-1} becomes strongly renormalized, its spectral weight decreases and its position is shifted by about 10 cm^{-1} towards lower energies. Simultaneously, an additional broad peak appears around 500 cm^{-1} which is indicated by the arrow. Once more, the same spectral features have been observed in the FIR c-axis response of underdoped deoxygenated Y-123.[13,14] The broad low-T peak and the related strong anomaly of the 320 cm^{-1} phonon mode have been successfully explained in terms of a model where the bilayer cuprate compounds like Y-123 are treated as a superlattice of intra- and interbilayer Josephson junctions.[15,16] Within this model, the broad low-T peak corresponds to the transverse optical Josephson plasmon which arises from the out of phase oscillation of the intrabilayer and interbilayer longitudinal plasmon modes. The strong anomaly of the 320 cm^{-1} phonon mode is explained as due to the drastic changes of the local electric fields acting on the in-plane oxygens as the Josephson currents set in the SC state.[15] Overall, this close analogy implies that the T_c suppression upon Pr substitution is caused by a depletion and/or a localization of the mobile holes of the CuO_2 planes rather than by pair breaking.

For comparison, we also investigated a $YBa_2Cu_{2.94}Zn_{0.04}O_{6.9}$ crystal whose T_c is suppressed by a similar amount to $T_c = 76(3)$ K. Meanwhile, it is well established that the T_c suppression in Zn-substituted samples is caused by strong pair breaking due to impurity scattering in the unitarity limit on the Zn impurities while the hole content of the CuO_2 plane is hardly affected.[17] Figure 2 displays σ_{1c} at different temperatures between room temperature and 10
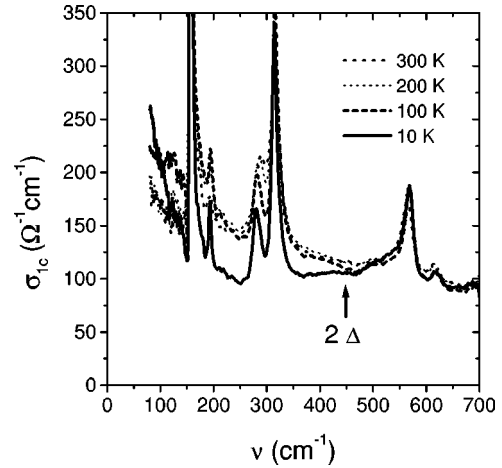
K. It is evident that no sign of a pseudogap in the normal state c-axis conductivity occurs, despite the fact that the T_c value is severely suppressed. The c-axis conductivity instead hardly changes in the normal state. If anything, it rather exhibits a very weak Drude-like behavior since σ_{1c}^{el} increases slightly with decreasing T and towards low frequency. Note that a similar behavior has been observed in a Zn-free $YBa_2Cu_3O_{6.9}$ crystal which was annealed under the same conditions being almost optimally doped with $T_c = 92$ K.[13,18] Also the anomaly of the 320 cm^{-1} phonon mode is much weaker for the Zn-substituted crystal than for the 20% Pr-substituted crystal and there is no clear evidence for the additional low-T peak. For the Zn-substituted crystal a spectral gap forms only in the superconducting state below $T_c = 76$ K. Then the pair breaking effect due to the Zn-impurities is clearly evident. Firstly, the size of the spectral gap is significantly reduced to $2\Delta_{SC} \approx 450$ cm^{-1} as compared to $2\Delta_{SC} \approx 650$ cm^{-1} in pure optimally doped $YBa_2Cu_3O_{6.9}$.[13] Secondly, the residual conductivity remains very large even at the lowest temperature of 10 K. This indicates that a large number of quasiparticles remain unpaired in the SC state due to the strong pair-breaking effect of the Zn impurities. No such characterstic signature of the pair-breaking effect is observed for the Pr-substituted crystals.

Figure 3 shows the T dependence of the FIR c-axis conductivity of the $Pr_{0.3}Y_{0.7}Ba_2Cu_3O_7$ crystal with $T_c = 64(3)$ K which is more strongly Pr-substituted than the previous one. The normal state spectra are shown in Fig. 3(a). Once more a spectral pseudogap can be seen to develop in the normal state. The pseudogap now already starts to form around room temperature and its size clearly exceeds the measured spectral range, i.e., $\omega_{NG} > 700$ cm^{-1}. A corresponding increase of the onset temperature and of the size of the pseudogap with increasing underdoping of the CuO_2 planes has been previously observed for strongly deoxygenated Y-123 crystals.[13,14,18] All the characteristic spectral features are very similar to those in a deoxygenated Y-123 crystal with comparable $T_c \sim 60$ K. On the other hand, the absolute value of the σ_{el}^{1c} is significantly higher in the Pr-substituted crystal. This effect can be understood to be due to
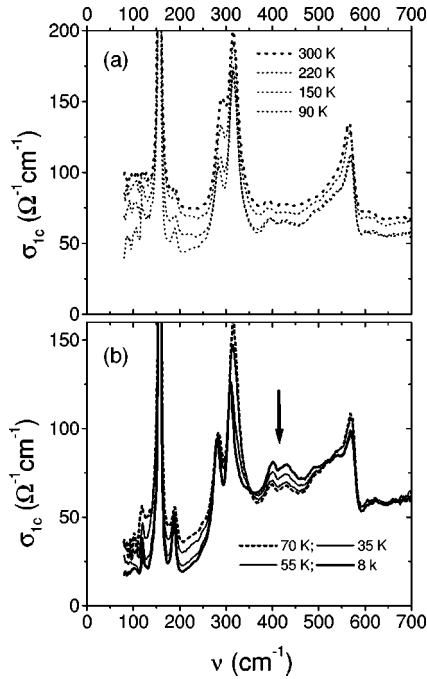
FIG. 3. Temperature dependence of the real part of the FIR c-axis conductivity of $Pr_{0.3}Y_{0.7}Ba_2Cu_3O_7$ with $T_c = 64(3)$ K, (a) in the normal state and (b) in the superconducting state. The solid arrow marks the position of the additional low-temperature absorption peak.

the presence of the fully oxygenated and thus metallic CuO chains. Evidence for metallic CuO chains has been obtained even in pure Pr-123.[19] A similar chain-related effect on σ_{el}^{1c} has previously been observed for Ca-substituted $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ crystals for which the absolute value depends on the oxygen content and thus the metallicity of the CuO chains while the characteristic frequency and T dependence is determined mainly by the hole doping of the CuO_2 planes.[13,18] Another difference as compared to the deoxygenated Y-123 crystals is the observation of two weak defect modes in the spectral range of 400 to 450 cm^{-1}. These modes are present already at room temperature but become more pronounced at low T. These defect modes possibly originate from oxygen defects within the CuO chain layer other than the usual O(1) oxygen defects in Y-123. Alternatively, they might correspond to crystal field excitations of the magnetic Pr^{3+} ions. Figure 3(b) shows the low-temperature data in the SC state. It can be seen that the 320 cm^{-1} phonon mode becomes strongly renormalized and that an additional peak develops around 420 cm^{-1} again in close analogy to deoxygenated underdoped $YBa_2Cu_3O_{6.6}$ with $T_c \sim 60$ K.[20,14] The additional peak is not quite as pronounced as for the Pr-free underdoped Y-123 crystals. In the context of the Josephson-plasmon superlattice model this difference can be explained as due to the larger quasiparticle conductivity of the Pr-substituted crystal which leads to a stronger damping of the transversal Josephson plasmon mode.[15] As was noted above, this difference can be attributed to the metallic conductivity of the CuO chains and the subsequently higher normal state c-axis conductivity of the Pr-substituted crystals. Also due to the presence of the fully oxygenated metallic CuO chains, the interbilayer Josephson plasmon frequency, as deduced from the zero crossing of ε_1
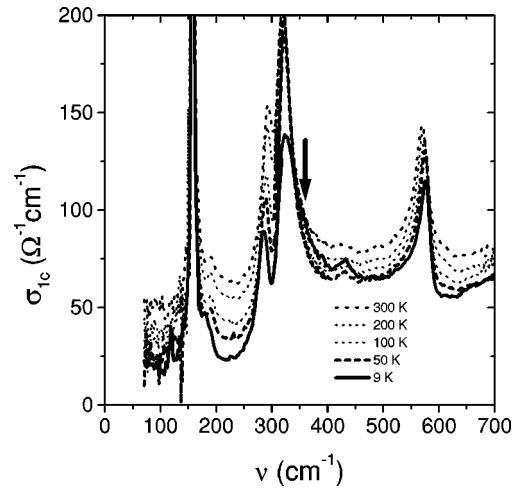

FIG. 4. Real part of the FIR c-axis conductivity of $Pr_{0.4}Y_{0.6}Ba_2Cu_3O_7$ with $T_c = 48(4)$ K. The arrow indicates the position of the low temperature absorption peak which merges with the phonon mode at 320 cm^{-1}.

and/or from the low frequency slope of ε_1, appears to be somewhat higher in the Pr-substituted crystals compared to deoxygenated Y-123 with similar T_c. More details about the dependence of the interbilayer and intrabilayer Josephson plasmons on the presence of the metallic CuO chains, including fits with the model given in Ref. 15, will be presented in a forthcoming publication.

Figures 4 and 5 show the FIR c-axis conductivity of $Pr_{0.4}Y_{0.6}Ba_2Cu_3O_7$ with $T_c = 48(4)$ K and $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_7$ with $T_c = 24(5)$ K, respectively. The absolute values σ_{1c}^{el} once more are significantly higher for the fully oxygenated Pr-substituted crystals than for comparably underdoped deoxygenated Y-123. This circumstance allows us to see more clearly the characteristic features of the normal state pseudogap in such strongly underdoped 123-type samples. For the $x = 0.4$ crystal it is evident that the size of the normal state pseudogap exceeds the measured spectral range by far, i.e., $\omega_{NG} \gg 700$ cm^{-1}. This finding confirms our previous report that the size of the pseudogap of deoxygenated Y-123 crystals increases continuously on the under-
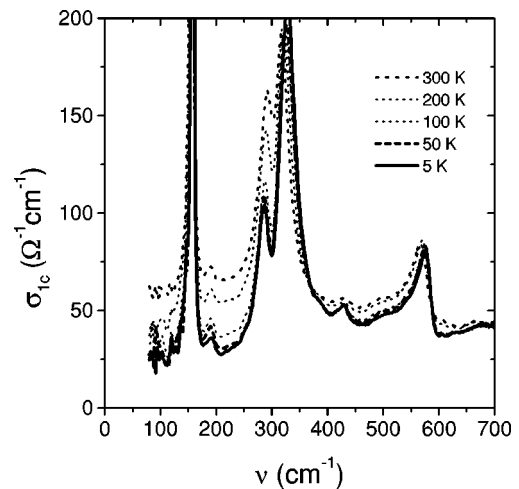

FIG. 5. Temperature dependence of the real part of the FIR c-axis conductivity of $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_7$ with $T_c = 24(5)$ K.

doped side.[13,14] The pseudogap forms around room temperature and it is not related to the formation of the additional low-T peak nor to the anomaly of the 320 cm^{-1} phonon mode. Notably, the characteristic shape of the anomaly of the 320 cm^{-1} phonon mode and the additional peak, which both merge for the present sample, indicate that the size of the intrabilayer Josephson plasmon is somewhat smaller for this 40% Pr-substituted crystal than for a comparably underdoped pure $YBa_2Cu_3O_{6.5}$ crystal with $T_c = 52$ K. Instead the spectral shape of the anomalous 320 phonon mode and the additional peak resemble that of a more strongly underdoped $YBa_2Cu_3O_{6.45}$ crystal with $T_c = 25$ K.[15] It worth noting that this effect is expected within the Josephson superlattice model since the separation of the CuO_2 planes is somewhat larger in the Pr-substituted crystal than in the pure Y-123 resulting in a smaller intrabilayer Josephson plasma frequency for the Pr-substituted sample. In contrast, as noted above, the interbilayer plasma frequency appears to be larger in the Pr-substituted crystals due to the presence of the metallic CuO chains. Figure 5 shows the FIR c-axis conductivity of our most heavily Pr-substituted $Pr_{0.45}Y_{0.55}Ba_2Cu_3O_7$ crystal with $T_c = 24(5)$ K. It is remarkable that for this crystal, which is located close to the metal insulator transition around $x = 0.55$, the normal state pseudogap suddenly is less pronounced and its size has decreased. This finding seems to indicate that the pseudogap disappears around the metal insulator transition. Note that it has not been possible to follow the evolution of the electronic c-axis conductivity in such detail in correspondingly underdoped deoxygenated Y-123 crystals for which the absolute values of σ_{1c}^{el} are much lower.[15,20]

Finally, we comment on the question whether our FIR c-axis conductivity data provide any information about the mechanism which causes the hole depletion of the CuO_2 planes upon Pr substitution. Recent x-ray diffraction measurements revealed that flux-grown Pr-123 crystals are Cu deficient on the Cu(1) site and/or exhibit a partial substitution of Pr on the Ba site.[21] It was argued that these effects may be responsible for the hole depletion. The only anomalous features in the FIR phonon modes of our Y,Pr-123 crystals which may be indicative of structural disorder within the CuO chain layer are the weak defect mode at 420 cm^{-1},

whose origin is yet unknown, and a broadening of the phonon mode at 280 cm^{-1} due to vibration of chain oxygen[11] which is more pronounced for the Pr-substituted crystals than for deoxygenated crystals with similar T_c.[13,14] However, a similar defect mode around 400–450 cm^{-1} and an even stronger broadening of the Cu(1) mode at 280 cm^{-1} have recently been observed in Nd-123 which is superconducting with $T_c = 93$ K.[22] Therefore, while these features may be related to a deficiency on the Cu(1) site, it is unlikely that they are responsible for the strong T_c suppression which occurs only for the Pr-substituted crystal but not for Nd substituted one. In our spectra we do not observe any anomalous broadening or shift for example of the phonon mode at 155 cm^{-1} to which mainly Ba and Cu(1) contribute.[11] While the masses of Ba and Pr are very similar one still expects this mode to be broadened if Ba^{2+} is substituted by Pr^{3+} since their electronic environment should be rather different.[21] To conclude, we do not observe any anomalous changes of the FIR active phonon modes which could be used as an indication that the decrease of the hole doping of the CuO_2 planes can be explained as a chemical doping effect. Our data rather favor the model of Fehrenbacher and Rice where the charge carriers of the CuO_2 planes are redistributed and localized in hybridized Pr $4f$ and O $2p$ orbitals.[8] Note that this model is supported by recent x-ray absorption measurements.[23]

In summary, by spectral ellipsometry we have studied the far-infrared c-axis conductivity of Pr-substituted $Pr_xY_{1-x}Ba_2Cu_2O_7$ crystals with $0.2 \leq x \leq 0.5$. We have shown that the c-axis conductivity of these crystals exhibits spectral features similar to deoxygenated and thus underdoped $YBa_2Cu_3O_{7-\delta}$. A spectral pseudogap already forms in the normal state, the oxygen bond-bending phonon mode at 320 cm^{-1} exhibits an anomalous T dependence and an additional broad absorption peak forms at low T. This finding suggests that the T_c suppression in the Pr-substituted samples is caused by a decrease in the concentration or a localization of the mobile hole carriers of the CuO_2 planes.

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