Transitions at $T>T_c$ in underdoped crystals of $YBa_2Cu_3O_{7-x}$ observed by resonant Raman scattering

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It has been shown that under a particular resonant condition it is possible to observe Raman interband electronic scattering between quasidegenerate bands associated with the apical oxygen around the S point of the Brillouin zone in $YBa_2Cu_3O_{7-x}$ (1-2-3). The identification of the near-IR (1.16 eV) excited Raman-scattering structure observed between 200 and 700 cm^{-1} with the transition between these quasidegenerate bands at the Fermi level, which have neither CuO_2 nor chain character, and the vicinity of the energy of this transition with the value of the superconducting gap, has caused us to investigate the temperature dependence of the Raman electronic scattering. We have analyzed two single crystals underdoped with different T_c. The integrated intensity of the electronic background versus temperature shows a similar behavior for both samples. Singularities are observed not only at T_c but also at two temperatures higher than T_c at $T^*=1.6\ T_c$ and T_D that correspond to the appearance of a pseudogap for underdoped 1-2-3 with the same T_c.
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I. INTRODUCTION

Raman scattering has been intensively used in characterization of high-T_c superconducting materials, providing information about the phonon spectra and about electron-phonon interaction width of the superconducting gap, etc.[1] Moreover because of the large number of electronic levels around E_F in these materials, by changing the laser excitation energy it is possible to probe different resonant conditions for the Raman scattering. In this way it is possible to emphasize, for example, different aspects of the crystal[2] or of the electronic structures.[3–5]

We have already shown that the most pronounced difference between IR (1.16 eV) and visible (2.51 eV) excited spectra in $z(yy)\bar{z}$ of an untwined $YBa_2Cu_3O_{7-x}$ (1-2-3) single crystal is the absence in the latter one of a broad feature between 200 and 700 cm^{-1}. Similar broad features, but with relative different shape and intensity, have been observed also in the ceramic samples with $x>0.5$. By comparison of ceramic samples with same oxygen content but different oxygen isotopes we have observed no energy shift of this background (see Ref. 3, Fig. 6.3) indicating that the nature of this peak is clearly nonphononic.

As mentioned before, such a background is not observed in the visible excited Raman, moreover, nobody has observed by visible Raman excitation any similar structure in 1-2-3 at any oxygen content at room temperature [similarities can be found with the broad peak in the electronic background that develops below T_c (Ref. 6)]. On the contrary, reflectance measurements on ^{18}O-substituted samples have shown the existence of some features in the $\varepsilon_2(\omega)$ spectra of 1-2-3 below 800 cm^{-1}, also independent of the isotope substitution.[7] These structures have been interpreted by Mazin *et al.*[3,4] as related to low-energy electronic interband transitions on the base of accurate local-density approximation (LDA) energy bands calculations. In particular one of these has been assigned to interband transition between two quasidegenerate bands with prevalently O(4) (p) character at the S point in the Brillouin zone. One of these two bands crosses the E_F. In accordance with LDA calculations,[3,4] such a transition should be observed in resonant conditions also by Raman scattering at excitation energy smaller than 1.9 eV. Within this framework, we have assigned the background we observe exciting at 1.16 eV to the interband electronic scattering between the two O(4) (p) bands around the S point.[5]

If the background we observe in metallic 1-2-3 is really related to such an interband transition it will be interesting to study what happens to it when the transition to the superconducting state occurs considering that these electronic states belong neither to the CuO_2 plane nor to the CuO chain and that the energy of such a transition is of the order of the superconducting gap. In order to answer to these questions we have studied the Raman scattering of two different single crystals with different T_c's as a function of temperature.

II. EXPERIMENT

IR Raman-scattering measurements were performed in a backscattering configuration by means of an IFS 88 Bruker interferometer at resolution 6 cm^{-1}. A diode pumped cw Nd-YAG laser was used for excitation (1.16 eV). In order to avoid local heating of the sample due to absorption of the incident laser radiation, we kept the laser power as low as possible (80 mW within a spot larger than 0.3 mm in diameter; by increasing the laser power up to 150 mW no detectable increase in the anti-Stokes intensity has been observed). The samples were bonded by indium to the cold finger of liquid-He flow optical cryostat and the temperature was controlled by a ITC4 Oxford controller and monitored by a second temperature detector placed nearby the crystal (once the thermal equilibrium was reached the temperature was stable within half a degree of Kelvin). More than 14 h of accumulation for each spectrum were needed in order to obtain a reasonable signal-to-noise ratio. Both the crystals we have

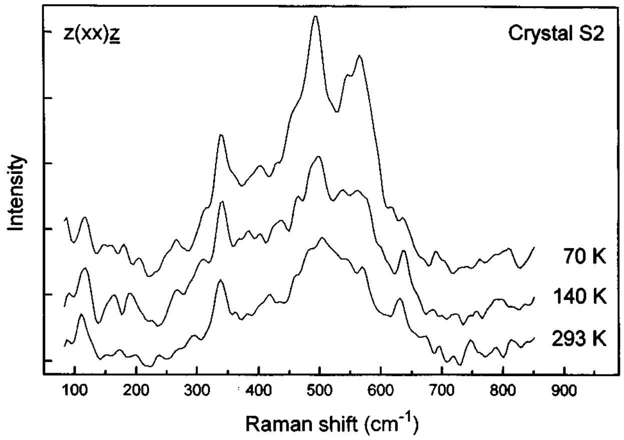

FIG. 1. Raman scattering of a twinned $YBa_2Cu_3O_{7-x}$ single crystal $S2$ at different temperatures.

studied were twinned crystals, and the spectra reported here have been performed with the polarization parallel to the CuO_2 plane in A_{1g} scattering geometry. Because of this we will refer now to the Raman-scattering geometry we have used as $z(xx)\bar{z}$, meaning both indistinguishable components of the Raman tensor $z(xx)\bar{z}$ and $z(yy)\bar{z}$. The two crystals, both grown by flux methods, indicated as $S1$ and $S2$, show a superconducting critical temperature T_c of 73 and 84 K, respectively.

III. RESULTS AND DISCUSSION

As already mentioned before, the Raman-scattering background of a twinned single crystal in $z(xx)\bar{z}$ obtained by exciting at 1.16 eV show a broad peak between 200 and 700 cm^{-1} superimposed to the phonon structure (Fig. 1). The most pronounced phonon peaks are at 340 and at about 500 cm^{-1}; these correspond to the out-of-phase O(2)-O(3) and the O(4) A_g modes, respectively.[8] Examples of Raman spectra of one of the two crystals analyzed are reported in Fig. 1. The absolute intensity of the spectra and the relative intensity of the different features show a strong temperature dependence. The observation of intensity anomalies of some Raman modes in the superconducting states of the 1-2-3 system at different laser energy excitations has already been reported.[9] They have shown a singularity at T_c of the temperature dependence of the Raman efficiency of the A_g phonons of 1-2-3. The amplitude of this anomaly is strongly dependent on the phonon and on the excitation energy. In our spectra, obtained by exciting at 1.16 eV, a change in the temperature dependence of the phonons intensity is clearly observed for the apical oxygen phonon mode around 500 cm^{-1} but in the case of the mode at 340 cm^{-1} the error bars are too large to judge if there is a singularity or not at T_c [see Figs. 2(a) and 2(b) for sample $S2$; similar behavior has been observed for sample $S1$]. The Raman intensity of the former phonon mode increases as T is decreased up to T_c and then decreases lowering further the temperature.

In Fig. 3 the temperature dependence of the broad peak integrated intensity of sample $S2$ is reported. The intensity change with temperature is more pronounced and complex in the case of the electronic background than for the phonon modes. By lowering the temperature down to a certain temperature we indicate as T_D the intensity of the broad feature between 200 and 700 cm^{-1} remains almost constant. Below this temperature the peak abruptly increases about 25% in intensity, and it remains almost constant till reaching a temperature T^*. At T^* the intensity starts to increase again reaching a maximum at T_c and then decreases monotonically. By plotting the integrated intensity of the background times temperature versus temperature these discontinuities can be emphasized by the displacement from the linear be-

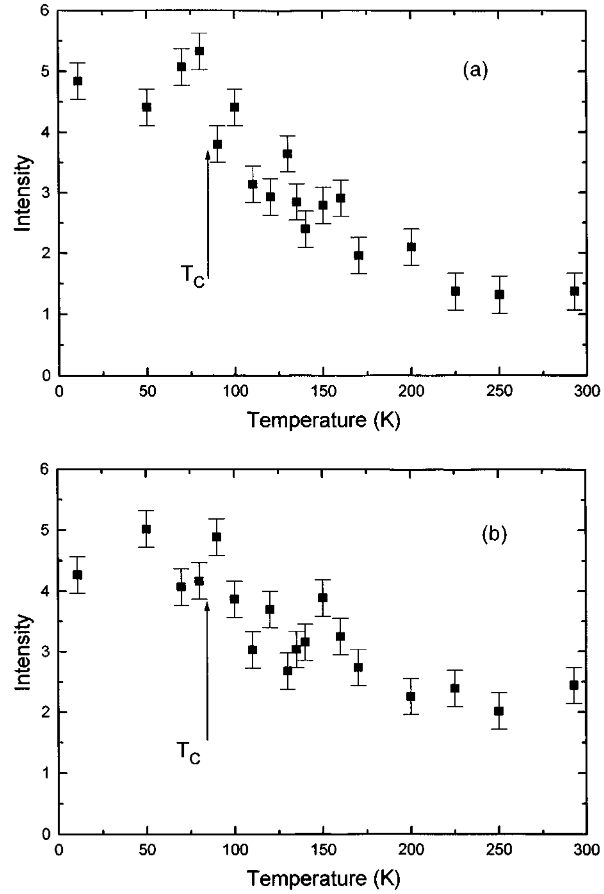

FIG. 2. Temperature dependence of the intensity of the apical oxygen A_g mode around 500 cm^{-1} (a) and of the O(2)-O(3) A_f dimpling mode at 340 cm^{-1} (b) in crystal $S2$.

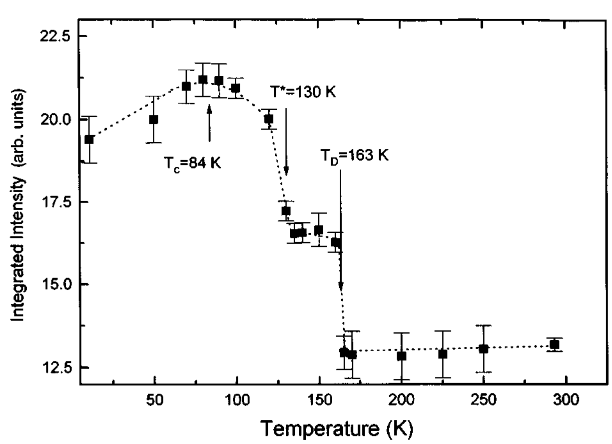

FIG. 3. Temperature dependence of the integrated intensity of the electronic Raman broad peak in crystal $S2$.

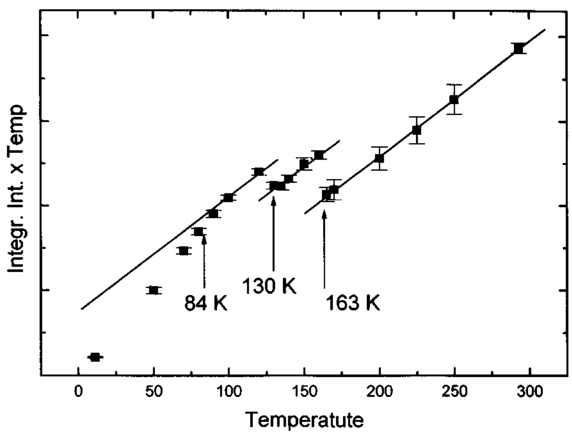

FIG. 4. Temperature dependence of the integrated intensity of the electronic Raman broad peak times temperature in crystal $S2$.

havior (Fig. 4). The same temperature dependence has been observed for the crystal $S1$. The difference is in the temperature at which singularities appear (see Table I). While T^* is increasing linearly with T_c, T_D is lower in the sample with higher T_c.

We want to concentrate our discussion on the temperature dependence of the electronic background. Change in the electronic Raman background intensity can be induced by several factors (change of resonance conditions, of density of states, etc.). The effect of the opening of the superconducting gap on the electronic Raman scattering has been extensively studied by different authors (see Ref. 10 and references therein). Across-the-gap excitation in superconducting high-T_c have been observed by several groups. All data show a peak in the electronic background in the superconducting phase around 400 cm^{-1} which would correspond to $2\Delta/kT=7$. The nonzero intensity below this value has been interpreted as a distribution of gaps. The decrease in intensity of the background we observe applies to the range from 200 to 700 cm^{-1}; this would correspond to a value of $2\Delta/kT$, extremely large for a gap opening in the associated electronic band, indicating that the decrease is probably not the direct effect of the gap opening but can be interpreted as evidence that the excitation is coupled to the superconducting order parameter. Another possible explanation is that the change in intensity is due to a change in the resonant condition. Dewing *et al.* have shown the existence in the 1-2-3 system of a broad peak in absorption with a maximum at 0.7 eV, whose intensity changes with T and shows a maximum at T_c.[11] In fact, in this case the electronic transition is the one that mainly contributes to the resonant enhancement of the broad peak in the electronic background. Observed with IR excitation the Raman intensity should, in a first approximation, follow the temperature dependence of the electronic absorption itself.

TABLE I. Temperatures of the singularities (T_c,T^*,T_D) in the background intensity observed in crystals $S1$ and $S2$.

	T_c (K)	T^* (K)	T_D (K)
$S1$	73	102	245
$S2$	84	130	163

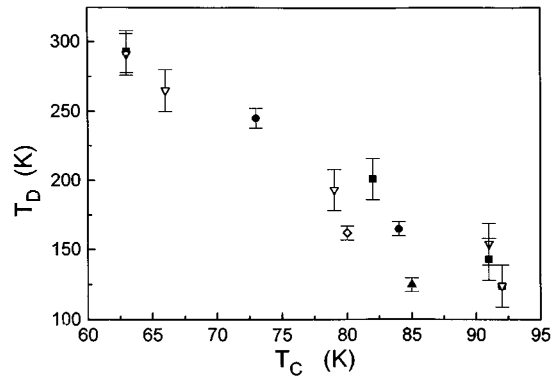

FIG. 5. Dependence of the temperature of pseudogap opening from T_c in $YBa_2Cu_3O_{7-x}$. Data is derived from different experimental techniques; points indicated with open diamonds, solid squares, solid triangles, and open triangles are obtained from Refs. 14, 15, 16, and 17, respectively. Solid circles refer to the T_D obtained in this work for $S1$ and $S2$ crystals.

Anomalies at temperature T^* greater than T_c that scale as proportionally with T_c has been observed by extended x-ray-absorption fine structure in high-T_c materials like $La_{1.85}Sr_{0.15}CuO_4$ (Ref. 12) and $Bi_2Sr_2CaCu_2O_{8+y}$ (Bi2212),[13] in particular at 1.6 T_c and 1.4 T_c, respectively. They have observed that the Cu sites are frozen at $T<T^*$ in two well-defined conformations characterized by two Cu-O (apical) bond lengths. A local structural change such as the one observed by Bianconi *et al.*[12,13] can account for the change in intensity of the electronic background we are studying. In fact a structural change can induce a change in the electronic structure of the system and consequently a change either in the resonant condition or in the density of states of the electronic band involved in the scattering.

As T_c increases from sample $S1$ to $S2$ the temperature of the second singularity, indicated as T_D, decreases. By plotting the value of T_D we have obtained for the two crystals versus T_c, and comparing these values with the data of the opening of a pseudogap reported in literature[14–17] for the 1-2-3 system (Fig. 5), it results that the value obtained by us falls nicely in this curve. The existence in the normal state of a pseudogap (in the density of states or in the spin spectrum) in underdoped high-T_c superconductors have been discussed extensively in the literature.[18–24] The results we report are not sufficient to allow choosing between these models, but we want to briefly discuss the possible agreement of our data with two of these.[19–21]

In a spin-bipolaron model such as the one discussed by Alexandrov and Mott,[19] the spin gap corresponds to a singlet-triplet bipolaron exchange energy. The low-energy band structure is formed by two singlet and triplet bosonic bands separated by an exchange energy J of the order of magnitude of about 15 meV and a half width of the same order of magnitude which sets an upper limit to the singlet-triplet transition energy at about 50 meV. These values almost coincide with the energy of the background we observed. Within this framework this background will be due to singlet-triplet scattering of spin bipolarons and the resonant state is due to optical absorption of intersite bipolarons. Within this model the pseudogap is associated with the singlet-triplet exchange energy and the pseudogap is associated with the thermal excitation of singlet-to-triplet bipolarons. Moreover the observation of the change of the oscillator strength $YBa_2Cu_3O_{7-\delta}$ with temperature, reported in Ref. 25, has been interpreted in terms of Bose-Einstein condensation of small bipolarons by using the spin-bipolaron model proposed by Alexandrov and Mott.[19] The temperature dependence of the Raman phonon modes reported in Fig. 2 shows strong similarities to the temperature dependence of the absorption band between 2000 and 10 000 cm^{-1} in $YBa_2Cu_3O_{7-\delta}$ as reported in Ref. 25. Such a change in the electronic absorption with temperature can induce, because of the variation of the resonant condition, an analog change in the Raman intensity when exciting, as in our experiment, within the same spectral range.

The appearance of a pseudogap in the fermionic density of states is predicted to appear at $T>T_c$ in the boson-fermion model for high-T_c superconductors proposed by Ranninger and Robin.[20] In this model bosons are bonded carriers $(2e)$ of polaronic origin and fermions are mobile holes (e) in the CuO_2 conducting planes; assuming a common potential for both species an exchange of one boson with two fermions is allowed. A pseudogap at temperature well above T_c opens up and evolves in a true gap at T_c, and within this temperature interval the appearance of strong non-Fermi-liquid behavior is predicted. The dependence on temperature of the optical conductivity in the normal state has been studied.[26] These calculations have shown a large redistribution of the oscillator strength from the spectral range $\omega\leqslant\omega_D\sim 2T_D$ to $\omega\geqslant\omega_D$ by lowering the temperature from the T_D down to T_c. Such an increase of the optical conductivity at high energy would be consistent with an increase of the intensity of the electronic Raman background we observed in our measurement.

IV. CONCLUSIONS

We have reported on the temperature behavior of the low-energy electronic background observed in Raman scattering by exciting with near-IR excitation. This background, probably associated with an interband transition between quasidegenerate electronic levels around the Fermi energy associated with the apical oxygen, shows three transitions with temperature. One of these transitions coincides with the appearance of the superconductivity in the system. This indicates that even if the opening of the gap in these states is not clearly observed this excitation is coupled to the superconducting order parameter. The other two transitions occur at temperature greater than T_c. One transition proportional to T_c coincides probably with structural transformations observed in other high-T_c material families.[13] The latter transition occurs at a temperature T_D that coincides with the pseudogap opening detected by several experimental techniques in the underdoped 1-2-3 system. The comparison of such an observation with the theoretical models shows a qualitative agreement with two of these,[19–21] nevertheless, the data we have at the moment does not allow us to chose between these two and other models.

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