Three energy scales in the superconducting state of hole-doped cuprates detected by electronic Raman scattering

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We explored by electronic Raman scattering the superconducting state of Bi2Sr2CaCu2O8+δ (Bi-2212) crystal by performing a fine tuned doping study. We found three distinct energy scales in A1g, B1g and B2g symmetries which show three distinct doping dependencies. Above p=0.22 the three energies merge, below p=0.12, the A1g scale is no more detectable while the B1g and B2g scales become constant in energy. In between, the A1g and B1g scales increase monotonically with underdoping while the B2g one exhibits a maximum at p=0.16. The three superconducting energy scales appear to be an universal feature of hole-doped cuprates. We propose that the non trivial doping dependencies of the three scales originate from the Fermi surface changes and reveal competing orders inside the superconducting dome.

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INTRODUCTION

Conventional superconductors are characterized by a single energy scale, the superconducting gap, which is proportional to the critical temperature Tc. The existence of more than one energy scale in the superconducting state of hole-doped cuprates has stirred many debates since several years [2–9] and has raised the question of the existence of more than one gap in the superconducting state of cuprates [10–14]. To move toward an understanding of high-temperature superconductivity, one of the most challenging issue is the identification of the energy scales associated with the onset of coherent excitations in the superconducting state. The electronic Raman spectroscopy is an efficient probe for this task. Depending on the symmetries (A1g, B1g or B2g) related to the quasi-tetragonal structure of the cuprates, the energy scales can be explored in different regions of the Brillouin zone by electronic Raman scattering. Usually, the B1g and B2g energy scales are respectively assigned to the maximum amplitude of the d-wave 2∆ pairing gap in the region near (±π, 0) and (0, ±π) (called the antinodal region) and the weaker amplitude in the region near (±π/2, ±π/2) (called the nodal region) [15, 16]. A priori these two scales have the same origin (the 2∆ pairing gap) and have to follow each other. In fact, they exhibit distinct doping dependencies and are responsible for the two gaps issue in the superconducting state of hole-doped cuprates. Several distinct scenarios are still debated [5–7, 10–12, 16–22]. One of them has been to associate the nodal energy scale to the superconducting state while the anti-nodal one is associated with the pseudogap [23, 24]. Although the origin and significance of these two scales are not yet explained a common thread is emerging: at least two electronic orders compete inside the superconducting dome of hole-doped cuprates and make distinct the doping evolutions of B1g and B2g energy scales.

Competing orders are the necessary ingredients to induce Fermi surface changes [25, 26]. In hole-doped cuprates angular photoemission spectroscopy (ARPES) revealed above Tc a disconnected Fermi surface with “Fermi arcs” centered around the nodes in underdoped Bi-2212 compound [27]. More recently, quantum oscillations measurements under high magnetic field and low temperature have shown that Fermi surface undergoes a reconstruction into pockets in underdoped YBa2Cu3O7−δ (Y-123) compound [28–31].

On the other hand, there exists a third energy scale detected in A1g symmetry whose origin is still mysterious although it has been detected for a long time [32–35]. In Y-123 compound, the A1g energy peak was found to follow the inelastic neutron scattering resonance with nickel and zinc substitutions [36–39]. In the very beginning of the cuprates Raman studies, the A1g peak was assigned to the 2∆ pairing gap, but later considerations showed that long range Coulomb screening washes out the gap effects in the A1g geometry [15, 42] and recent investigations advocate rather in favor of a collective mode [16, 43, 44]. However, no thorough doping evolution of the A1g energy scale has been yet established.

In this study, our purpose is to accurately determine the actual doping dependencies of these three energy scales on a large range of doping p to get a better understanding of their origins. In particular, we are interested in finding the specific range of doping levels for which the energy scales present drastic changes and how they can be connected to the doping evolution of the Fermi surface and competing orders mentioned above.

In order to reach this goal we have performed light polarized electronic Raman scattering on Bi-2212 single crystals which can be associated to the 1/4mmm-D17h space group [45]. We have got the Raman spectra in A1g,
$B_{1g}$ and $B_{2g}$ symmetries. In particular special care has been devoted to extract the pure $A_{1g}$ spectrum from well controlled subtractions of the Raman spectra. Importantly, the doping level was solely controlled by oxygen insertion to avoid cationic substitutions which can dramatically change the electronic Raman spectra [46]. The large range of doping levels from $p=0.06$ to $p=0.23$ was successfully obtained from specific annealing treatments described in the experimental procedure. This allows us to follow simultaneously in an unique system the doping evolution of the $A_{1g}$, $B_{1g}$ and $B_{2g}$ energy scales and track them even for from very low and high doping levels.

We show that the $A_{1g}$, $B_{1g}$ and $B_{2g}$ energy scales in Bi-2212 merge together above $p=0.22$ and decrease with doping. This corresponds to a huge enhancement of the antinodal Bogoliubov quasiparticles spectral weight related to a Lifshitz transition where the hole like Fermi surface transforms into an electron like. On the other hand, the difference between the $B_{1g}$ and $B_{2g}$ energy scales is abnormally large below $p=0.12$ and the $B_{1g}$ and $B_{2g}$ scales are almost constant with doping. This corresponds to a significant loss of the antinodal Bogoliubov quasiparticles spectral weight where charge ordering settled. Between these two doping levels the $A_{1g}$ and $B_{1g}$ scales increase monotonically while the $B_{2g}$ scale is non monotonic and it is peaked at $p=0.16$ for which $T_c$ is maximum.

**DETAILS OF THE EXPERIMENTAL PROCEDURE**

**A. Raman Experimental Set Up**

Electronic Raman experiments have been carried out using a triple grating spectrometer (JY-T64000) equipped with a liquid-nitrogen-cooled CCD detector. Raman spectra above and below $T_c$ were obtained using an ARS closed-cycle He cryostat. The laser excitation line used was the 532 nm of a diode pump solid state laser. The laser power at the entrance of the cryostat was maintained below 2 mW to avoid over heating of the crystal estimated to 3 K/mW at 10 K. The $B_{1g}+A_{2g}$ and $B_{2g}+A_{2g}$ symmetries have been obtained from cross linear polarizations at 45° from the Cu-O bond directions and along them respectively [47]. The change between these both symmetries was obtained by keeping fixed the orientations of the analyzer and the polarizer and by rotating the crystal with an Attocube piezo-driven rotator. We got an accuracy on the crystallographic axes orientation with respect to the polarizers close to 2°. The $A_{1g}+B_{2g}$ and $A_{1g}+B_{1g}$ symmetries were obtained from linear parallel polarizations at 45° from the Cu-O bond directions and along them respectively. In practice we measure the $B_{1g}+A_{2g}$ and $A_{1g}+B_{2g}$ responses and then rotate the crystal to get the $B_{2g}+A_{2g}$ and $A_{1g}+B_{1g}$ ones. In the following we have made the assumption that the $A_{2g}$ electronic Raman scattering contribution is negligible i.e. the Raman vertices $\gamma_{xy} - \gamma_{yz} \approx 0$. This is supported by the very weak Raman contribution at low energy (below 1000 cm$^{-1}$) in pure $A_{2g}$ extracted from a combination of linear and circular polarizations spectra [48].

All the spectra have been corrected for the Bose factor and the instrumental spectral response. They are thus proportional to the imaginary part of the Raman response function $\chi''_\nu(\omega, T)$ where $\nu$ refers to the vertex symmetry $A_{1g}$, $B_{1g}$ or $B_{2g}$.

**B. Crystal Growth and Characterization**

The Bi-2212 single crystals were grown by using a floating zone method. The optimal doped sample with $T_c = 90$ K was grown at a velocity of 0.2 mm per hour in air [49]. In order to get overdoped samples down to $T_c = 65$ K, the as-grown single crystal was put into a high oxygen pressure cell between 1000 and 2000 bars and then was annealed from 350°C to 500°C during 3 days [50]. The overdoped samples below $T_c = 60$ K was obtained from as-grown Bi-2212 single crystals put into a pressure cell (Autoclave France) with 100 bars oxygen pressure and annealed from 9 to 12 days at 350 °C. Then the samples were rapidly cooled down to room temperature by maintaining a pressure of 100 bars. In order to get the underdoped sample down to $T_c = 50$ K, the optimal doping crystal was annealed between 350 °C and 550 °C during 3 days under vacuum of 1.3 10$^{-6}$ mbar.

The critical temperature $T_c$ for each crystal has been determined from magnetization susceptibility measurements at a 10 Gauss field parallel to the c-axis of the crystal. More than 30 crystals have been measured among 60 tested. The selected crystals exhibit a quality factor of $T_c/\Delta T_c$ larger than 7. $\Delta T_c$ is the full width of $T_c$ transition measured. A complementary estimate of $T_c$ was achieved from electronic Raman scattering measurements by defining the temperature from which the $B_{1g}$ superconducting pair breaking peak collapses. The level of doping $p$ was defined from $T_c$ using Presland and Tallon’s equation [51]: $1 - T_c/T_c^{max} = 82.6(p - 0.16)^2$. $T_c$ versus $p$ is reported in fig.3 (a).

**EXPERIMENTAL RESULTS**

In figure 1 (a-d) are displayed the Raman responses of an over-doped (OD) Bi-2212 single crystal with a $T_c = 60$ K. The (red/grey) and (black) curves were measured below and above $T_c$ in the $A_{1q} + B_{1g}$, $A_{1q} + B_{2g}$, $B_{1g}$ and $B_{2g}$ symmetries. The sharp peaks located at 127, 297, 327, 359 and 474 cm$^{-1}$ are phonon lines that will be discussed in a next article. A comparison between (c) and (d) panels shows that the $B_{1g}$ electronic contribution is preponderant compared to the $B_{2g}$ one. It manifests itself as an intensive 2$\Delta$ pair breaking whose maximum is peaked at 244 cm$^{-1}$ (see inset of panel (c)).
The $B_{2g}$ electronic peak although much lower in intensity is centered around the same energy ($\approx 254 \text{ cm}^{-1}$).

In $A_{1g} + B_{1g}$ symmetry (panel (a)), the $B_{1g}$ electronic contribution is dominant such that the $A_{1g}$ electronic peak can only be observed in the $A_{1g} + B_{2g}$ response (panel (b)) since the $B_{2g}$ contribution is weak. The $A_{1g}$ electronic continuum (detectable in panel (b)) is maximum around 250 cm$^{-1}$ nearby the energies of the $B_{1g}$ and $B_{2g}$ peaks.

The Raman responses in fig.1 (e-h) and (i-l) correspond respectively to the optimally doped crystal (OP) ($T_c = 90$ K), $p=0.16$ and the under-doped crystal (UD) ($T_c = 70$ K), $p=0.11$. Examining the $B_{1g}$ and $B_{2g}$ Raman responses of the OP90 crystal (g,h), we can notice that the $B_{1g}$ electronic contribution remains predominant compared to the $B_{2g}$ one although the $B_{1g}$ Raman response is significantly reduced in intensity with respect to OD 60 compound. The energies of the $B_{1g}$ and $B_{2g}$ superconducting peaks (see insets of panels (g-h)) are still close to each other. Interestingly the energy of the $A_{1g}$ peak is observable in $A_{1g} + B_{2g}$ symmetry (panel (f)) and its energy is clearly distinct ($\approx 350 \text{ cm}^{-1}$) from those of $B_{1g}$ and $B_{2g}$ peaks rather located around 500 cm$^{-1}$. Concerning the UD 70 Bi-2212 single crystal, the $B_{1g}$ and $B_{2g}$ superconducting peaks are clearly distinct in energy and respectively located at 560 cm$^{-1}$ and 390 cm$^{-1}$ (see insets of panels (k-l)). The weak fingerprints of these two peaks are indicated by black arrows in the $A_{1g} + B_{1g}$ and $A_{1g} + B_{2g}$ spectra (panels (i-j)). On the other hand the $A_{1g}$ electronic peak is no more detectable in UD Bi-2212 single crystal.

Importantly, we cannot easily extract the pure $A_{1g}$ electronic spectrum by subtracting the $B_{1g}$ spectrum from the $A_{1g} + B_{1g}$ one (or the $B_{2g}$ spectrum from the $A_{1g} + B_{2g}$). There are two reasons for this: (i) the $B_{1g}$ and $A_{1g} + B_{1g}$ spectra (or the $B_{2g}$ and $A_{1g} + B_{2g}$ spectra) were obtained from two distinct crystal orientations (by rotating the crystal), this potentially introduces change in the Raman responses intensity; (ii) an additional half-wave plate for measuring the $B_{1g}$ ($B_{2g}$) spectrum was used to keep the same polarization at the entrance of the spectrometer than the $A_{1g} + B_{1g}$ ($A_{1g} + B_{2g}$) spectrum.

In order to circumvent these difficulties and extract the pure $A_{1g}$ electronic contribution we made two distinct subtractions:

$$
\chi''_{A_{1g}} = \chi''_{A_{1g} + B_{1g}} - \alpha \beta \chi''_{B_{1g}} \quad (1)
$$

$$
\chi''_{A_{1g} + B_{2g}} = \beta \chi''_{A_{1g} + B_{2g}} - \alpha \chi''_{B_{2g}} \quad (2)
$$

$\alpha$ is the intensity correction factor corresponding to the half-wave plate absorption used in $B_{2g}$ and $B_{1g}$ symmetries, $\alpha=1.2$ and $\beta$ is the intensity correction factor linked to the change of the crystal orientation between $B_{1g}$ and $A_{1g} + B_{1g}$ symmetries (or the $B_{2g}$ and $A_{1g} + B_{2g}$ symmetries).

In order to fix $\beta$ we defined two sums [52]:

$$
\chi''_{S1} = \chi''_{A_{1g} + B_{1g}} + \alpha \chi''_{B_{2g}} \quad (2)
$$

$$
\chi''_{S2} = \chi''_{A_{1g} + B_{2g}} + \alpha \chi''_{B_{1g}} \quad (3)
$$

The $\chi''_{S1}$ and $\chi''_{S2}$ responses were successively obtained after a crystal rotation (see experimental procedure). The $\beta$ factor is then defined such as $\chi''_{S1} = \beta \chi''_{S2}$. The $\chi''_{S1}$ (solid line) and $\beta \chi''_{S2}$ (dashed line) responses in the normal and superconducting state are displayed in fig. 2 (c,f,i). They merge perfectly in the normal and superconducting states which allows us to estimate $\beta$ precisely for each doping level. $\beta$ is close to 1 with a variation less than 10 %.

In fig.2 (a-b), (d-e) and (g-h) are displayed the pure $A_{1g}$ Raman spectra extracted in two distinct manners ($A'_{1g}$ and $A''_{1g}$) in the normal and superconducting states for the OD60, OP90 and UD70 Bi-2212 single crystals. In the insets, the $A_{1g}$ electronic superconducting peak is revealed by subtracting the normal $A_{1g}$ contribution from the superconducting one. We find well defined $A_{1g}$ superconducting peaks consistent each other in the both cases of extraction which makes reliable our findings. Interestingly the energy of the $A'_{1g}$ superconducting peak (see inset) increases with under-doping ($\approx 265 \text{ cm}^{-1}$ to $\approx 370 \text{ cm}^{-1}$) while the intensity of the $A'_{1g}$ peak decreases before disappearing below $p=0.12$ (see insets of panels (a,d)).

In order to get a global view of the doping evolution
of the three superconducting peaks detected in the $A_{1g}$, $B_{1g}$ and $B_{2g}$ symmetries. The energy of each superconducting peak as a function of doping is plotted in fig.3 (a).

Firstly, we find that the three energies merge above $p=0.22$. Below $p=0.22$, the $A_{1g}$ energy moves away from the $B_{1g}$ and $B_{2g}$ scales. This is confirmed from the both extractions ($A_{1g}'$ or $A_{1g}''$). The $A_{1g}$ scale is no more detected below $p=0.12$ while the $B_{1g}$ and $B_{2g}$ scales are detected until low doping level (0.07). The $B_{1g}$ energy scale monotonically increases with under-doping and seems to saturate below $p=0.12$.

The $B_{2g}$ scale is non monotonic and exhibits a maximum close to the optimal doping $p=0.16$. Above $p=0.16$ the $B_{2g}$ decreases and it becomes constant in energy below $p=0.12$. Our study of the $B_{2g}$ and $B_{1g}$ energy scales at low and high doping levels is a refinement of earlier works on Bi-2212 [4, 20, 46, 53–58]. Here we show that the $B_{1g}$ and $B_{2g}$ energy scales vary very slowly below $p=0.12$ down to $p=0.06$. The saturation of the $B_{1g}$ superconducting peak in energy was previously reported down to $p \approx 0.11$ and interpreted as a pseudo resonance mode stemming from a strong fermionic self-energy due to the interaction with spin fluctuations [59].

Our extended work to low and high levels of doping reveals two particular ranges: (i) above $p=0.22$ (blue/grey) zone in fig 3 (a) where $A_{1g}$, $B_{1g}$ and $B_{2g}$ superconducting peaks merge and (ii) below $p=0.12$ (red/grey) zone in fig.3(a) where the $B_{1g}$ and $B_{2g}$ peaks are almost constant in energy.

This is illustrated in figs. 4 and 5. In fig.4 are displayed the $B_{1g}$, $B_{2g}$ and $A_{1g}$ Raman responses of two Bi-2212 single crystals in the superconducting and normal states for $p \geq 0.22$. The subtracted Raman responses at 10 K from the one at 110 K show that for OD50 and OD63 compounds, the energies of the $B_{1g}$ and $B_{2g}$ and $A_{1g}$ peaks coincide with each other (see panels (d-f) and (i-k)).

On the other hand, in fig. 5 are reported selected $B_{1g}$ and $B_{2g}$ Raman responses of under-doped Bi-2212 crystals (below $p=0.12$) in the superconducting and normal states. The Raman responses measured at 10 K subtracted from the one at 110 K (see insets of the panels (a-f)) show that the $B_{1g}$ energy scale saturates and the $B_{2g}$ scale is almost constant in energy.

FIG. 2. (Color online) $A_{1g}$ extracted electronic Raman responses in the superconducting state (10 K) and normal state (110 K) for selected doping levels of Bi-2212 single crystals. Here are shown the distinct extractions of the $A_{1g}$ Raman responses: $A_{1g}'$ and $A_{1g}''$ associated respectively with equations (1) and (2). In the insets are displayed the subtracted Raman responses at 10 K from those at 110 K. The Raman responses in panels (c,f,i) show the sums $\chi''_{51}$ and $\beta \chi''_{52}$ related to the equations (1) and (2). $\beta$ was defined to make the sums merging.

FIG. 3. (Color online) (a) Doping evolutions of the $A_{1g}$, $B_{1g}$ and $B_{2g}$ energy scales in the superconducting state. The arrows pinpoint the three special doping levels: Above $p=0.22$ (blue/grey) zone, all the energies scales merge, at $p=0.16$ the $B_{2g}$ scale is maximum and below $p=0.12$, the $B_{2g}$ and $B_{1g}$ scales are almost constant in energy while the $A_{1g}$ one is no more detectable. Open circles describe the superconducting transition $T_c$ versus $p$ following the Presland-Tallon law [51]; (b) asymmetric coefficient extracted from $A_{1g}'$ and $A_{1g}''$ superconducting peaks by a standard fit (see equation (4)).
B2g scale is peaked and reaches a maximum. We suspect that at least two of these particular doping levels arise from Fermi surface evolution. It is surprising to find that above p=0.22 the three energy scales merge. We rather expect for a d-wave superconducting gap that the A1g, B1g and B2g scales have quite distinct energies. Considering a full hole-like cylindrical Fermi surface the energy ratios between the three scales should be $15$: $\omega_{B1g}/\omega_{B2g} \approx 1.3$ and $\omega_{A1g}/\omega_{B1g} \approx 3$ instead of $\omega_{B1g}/\omega_{B2g} \approx \omega_{A1g}/\omega_{B1g} \approx 1$. Such a discrepancy have also been reported in strongly overdoped Tl2Ba2CuO6+δ (Tl-2201) and Y-123 cation-substituted compounds. This has been interpreted as a change of the d-wave gap symmetry into a mixing of a d-wave gap with a s-wave component $60$, $61$. However, the thermal conductivity measurements in strongly overdoped Tl-2201 showed that nodes are still there $62$. Consequently, we rather believe in a strong alteration of the quasiparticles spectral weight in the antinodal Raman response which modifies the A1g, B1g and B2g electronic peaks positions. This is indeed the case, in ARPES measurements on Tl-2201 in the superconducting state, a quasiparticles anisotropy reversal between the nodes and the antinodes was reported. At high doping level the low energy antinodal Bogoliubov quasiparticle spectral weight is strongly enhanced with respect to the nodal one $63$.

In the specific case of Bi-2212 case, the doping level p=0.22 corresponds to the Lifshitz transition wherein, as a van Hove singularity crosses the chemical potential with underdoping, the electron-like anti-bonding Fermi surface at high doping level transforms into hole-like. A such a change in the Fermi surface topology considerably increases the antinodal quasiparticles spectral weight and can make the three energy scales merge above p=0.22. Preliminary calculations advocate for this scenario but more deeper theoretical investigations are still required and will be developed in a near future. The Lifshitz transition in overdoped Bi-2212 has been first observed by ARPES in Bi-2212 $64$ and recently detected by the analysis of the integrated Raman intensity as a function of doping level in Bi-2212 $65$. We found that p=0.22 is the starting point of the pseudogap as the doping decreases. The occurrence of a Lifshitz transition at the doping level for which the pseudogap collapses has also been reported in other cuprates $66$, $67$.

On the other hand, when approaching the doping level p=0.12, the Raman intensities of the B1g and A1g peaks are drastically reduced in a such a way that the A1g peak is no more detectable in the Raman spectra (see fig.1 (a,c,i) and fig.2 (a,d,g) (b,e,h) for the B1g and A1g peaks respectively). The decrease of the B1g peak intensity implies that one of the A1g peak is also altered because the A1g peak is considered as a bound state of the B1g pairing peak $43$, $44$. We interpret this significant drop of the peak intensity as a loss of coherent Bogoliubov quasiparticles spectral weight at the antinodes while the nodal region is protected in the underdoped side of the cuprate phase diagram $16$, $20$, $68$. This has been corroborated

![FIG. 4. (Color online) B1g and B2g and A1g Raman responses in the superconducting (red/grey) and normal (black) states of over-doped Bi-2212 single crystals. (a-c) for p=0.23, (g-i) for p=0.22. (d-f) and (j-l) correspond respectively to the subtracted Raman responses at 10 K from the one at 110 K for p=0.23 and p=0.22. The dashed line show that the locations in energy of the B1g , B2g and A1g merge for each doping level above p=0.22.](image-url)

![FIG. 5. (Color online) B1g and B2g Raman responses ($\chi''(\omega,T)$) in the superconducting (red/grey) and normal (black) states of selected underdoped Bi-2212 single crystals below p=0.12. The inset in each panel corresponds to the subtracted Raman response ($\Delta \chi''(\omega)$) obtained from measurements at 10 K and 110 K. We can notice that both B1g , B2g electronic peak are almost constant in energy below p=0.12. Note that the Raman spectra of UD 50 compound was obtained with a 600 g/mm diffraction grating instead of 1800 g/mm one in order to improve the signal/noise ratio and detect the B1g and B2g superconducting peaks which become weaker in intensity with underdoping. As a consequence, the energy resolution of UD90 compound is lower than the other doping.](image-url)
by (i) ARPES measurements \cite{14} \cite{69} and by (ii) scanning tunneling spectroscopy (STS) which show that Bogoliubov quasiparticles occupy only a restricted region in the k-space around the nodes \cite{70}. We also infer that the Fermi arcs detected in the normal state by ARPES \cite{27} extend into the superconducting state and correspond to a loss of Bogoliubov quasiparticles spectral weight at the antinodes. The antinodal quasiparticles are no more available for the superconducting state because they are involved in a distinct electronic order. The loss of antinodal quasiparticles spectral weight starts below the pseudogap temperature $T^*$ and it is strongly accentuated by the emergence of the charge ordering as the temperature decreases.

Charge ordering was first proposed from STS measurements in underdoped Bi-2212 \cite{71} \cite{73} and then revealed by nuclear magnetic resonance \cite{74} \cite{75}, resonant X-ray scattering \cite{76} \cite{78} and recently confirmed by tunneling \cite{79}. Interestingly, the temperature onset of the Fermi surface reconstruction defined as the temperature for which the Hall coefficient towards negative values in Y-123 \cite{50} \cite{82} is also peaked at $p=0.12$. The observation of a sign change in the Hall coefficient at low temperatures hints that Fermi surface undergoes a reconstruction into pockets induced by some form of (short-range) charge ordering under high magnetic field \cite{83}.

The loss of antinodal spectral weight in the electronic Raman spectra has a clear impact on the $B_{1g}$ and $B_{2g}$ peak energies as showed in previous works \cite{18} \cite{20} \cite{21} \cite{68}. When quasiparticles spectral weight is mostly concentrated around the nodal regions, this pushes back the $B_{2g}$ peak to lower energy and makes larger the $B_{1g}/B_{2g}$ energy ratio with respect to this expected value close to 1.3. This can be seen in Fig.3 (a). Below $p=0.12$ the $B_{1g}/B_{2g}$ ratio is $\approx 1.6$ higher than the one expected. The saturation of the pairing gap energy at the antinodes ($B_{1g}$ scale) can then be interpreted as a competition between superconductivity and charge ordering which prevents an increase of $T_c$ in agreement with recent investigations \cite{82} \cite{84}.

Finally $p=0.16$ corresponds to the doping level for which the superconducting transition $T_c$ is maximum. This could be the best compromise to enhance superconductivity in a complex medium where several electronic phases compete.

Interestingly the line shape of the $A_{1g}$ superconducting peak becomes more asymmetric with under doping. See for instance its change in the inset of fig.2(d) (OP90) in comparison with the line shape of fig.2(a) (OD60). We can estimate the line shape asymmetry as a function of doping by fitting the subtracted Raman responses $\Delta \chi''_{A_{1g}, A_{1g}}(\omega) = \chi''_{A_{1g}, A_{1g}}(\omega, 10K) - \chi''_{A_{1g}, A_{1g}}(\omega, 110K)$ by a standard line shape equation :

$$\Delta \chi''_{A_{1g}, A_{1g}}(\omega) = \frac{A}{\gamma q^2} \frac{(\omega - \omega_0)/\gamma + q^2}{1 + ((\omega - \omega_0)/\gamma)^2}$$

where $A$ is a renormalization factor, $q$ the asymmetric coefficient. $q$ tends to infinity for a Lorentzian shape and to a finite value otherwise. $\gamma$ is the full width at half maximum and $\omega_0$ is defined such as the $A_{1g}$ peak takes a maximum value at $\omega_m = \omega_0 + \frac{\gamma}{2}$. We chose to report the $\frac{\gamma}{q}$ ratio as the strength of the asymmetric line shape.

The $\frac{\gamma}{q}$ ratio versus doping is plotted in fig. 3 (b). It has been calculated from both $\Delta \chi''_{A_{1g}, A_{1g}}(\omega)$ and $\Delta \chi''_{A_{1g}, A_{1g}}(\omega)$ subtracted responses. We find in both cases an increasing of the asymmetric line shape with under-doping. We suspect this asymmetry comes from the additional contribution $2\Delta$ pairing peak to the $A_{1g}$ peak as already reported in our previous study \cite{30}. The asymmetric line shape is then enhanced by the increase of the distance in energy between the $A_{1g}$ peak and the $2\Delta$ pairing peak as the doping level is reduced (see fig.3 (a)).

In conclusion, we have succeeded to extract from electronic Raman scattering study in a reliable manner, the $A_{1g}$, $B_{1g}$ and $B_{2g}$ Raman responses. We find three electronic peaks distinct in energy related to the three symmetries in the superconducting state of Bi-2212. We report a finely tuned doping evolution of these three electronic peaks by oxygen insertion only into the Bi-2212 structure without cationic substitution. The $B_{1g}$ and $A_{1g}$ increase monotonically as the doping level is reduced whereas the $B_{2g}$ exhibits a non monotonic behavior with a maximum near the optimal doping level. We identify three special doping levels. Above $p=0.22$ all the peaks merge in energy (see blue zone in fig.3(a)). Below, $p=0.12$ the $A_{1g}$ is no more detected whereas the $B_{1g}$ and $B_{2g}$ scales exhibit two ”plateau” at distinct energies (see red zone in fig.3 (a)). Between $p=0.22$ and $p=0.12$, the $A_{1g}$ peak and $B_{1g}$ scales increases monotonically while the $B_{2g}$ scale is non monotonic and exhibits a maximum in energy at $p=0.16$. We suspect that at least the $p=0.22$ and 0.12 doping levels are directly connected to the doping evolution of the antinodal Bogoliubov quasiparticles spectral weight at low energy. $p=0.22$ corresponds to the doping level for which a Lifshitz transition occurs \cite{61} \cite{65} and the antinodal quasiparticles spectral weight is strongly increased. On the other hand, $p=0.12$ corresponds to the doping level for which the charge ordering is well settled \cite{71} \cite{77} and the antinodal quasiparticles spectral weight is strongly reduced. Finally, $p=0.16$ corresponds to the maximum of $T_c$ where probably the Fermi surface is still disturbed. The $B_{1g}$, $B_{2g}$ and $A_{1g}$ peaks all disappear above $T_c$. The $B_{1g}$ and $B_{2g}$ peaks are two pieces of the $2\Delta$ pairing gap depending on the the part of the Fermi surface probed and the $A_{1g}$ peak is a collective mode related to the $2\Delta$ pairing gap, probably a bound state located below $2\Delta$ threshold of the particle-hole continuum \cite{43}. Remarkably, these three superconducting energy scales although partially detected in other cuprates such as HgBa$_2$CuO$_{6+x}$ (Hg-1201), Y-123 and TI-1201 are an universal feature to all the cuprates and reveal competing orders inside the superconducting dome.

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