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Raman study of carrier-overdoping effects on the gap in high-T_c superconducting cuprates

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Raman scattering in the heavily overdoped $(Y,Ca)Ba_2Cu_3O_{7-\delta}$ ($T_c=65$ K) and $Bi_2Sr_2CaCu_2O_{8+\delta}$ ($T_c=55$ K) crystals has been investigated. For both the crystals, the electronic pair-breaking peaks in the A_{1g} and B_{1g} polarizations were largely shifted to the low energies close to a half of $2\Delta_0$, Δ_0 being the maximum gap. It strongly suggests *s*-wave mixing into the *d*-wave superconducting order parameter and the consequent manifestation of the Coulomb screening effect in the B_{1g} channel. Gradual mixing of *s*-wave component with overdoping is not due to the change of crystal structure symmetry but a generic feature in all high-T_c superconducting cuprates.

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In spite of a tremendous amount of studies on the electronic phase diagram of high-T_c superconducting cuprates (HTSC), there are many unresolved problems. One of the remaining problems is the electronic state in the overdoped regime, where the transition temperature T_c decreases with carrier doping. A naive picture is that the T_c suppression is due to the weakening of pair interaction such as electron correlation and thus the gap decreases in scale with T_c. However, the experimental results do not support such a simple picture. The recent scanning tunneling microscope (STM) study demonstrated a phase-separated state in the overdoped regime, consisting of the superconducting and the normal metallic phase.[1] This accounts for the anomalous increase in unpaired carriers[2] and/or the decrease in superfluid density[3,4] with overdoping. In this phase-separation model, the nature of superconducting gap would be maintained. On the other hand, in the model assuming the quantum critical point at hole concentration $p\sim0.19$,[5] it is expected that a gap nature radically changes in the heavily overdoped state where the pseudogap disappears. Therefore, the study of superconducting gap properties in the overdoped regime, such as a gap magnitude and symmetry, is of great importance to discuss the model for the electronic state as well as the pairing mechanism of HTSC.

Most of the previous gap studies in the overdoped regime are on $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) by tunneling and Raman-scattering spectroscopies.[6–9] Although it is almost established that the gap magnitude decreases with doping, the values are still controversial. For example, the pair-breaking peak energy (26 meV) observed in the Raman-scattering spectrum of overdoped Bi-2212 with $T_c=57$ K (Ref. 7) is much smaller than the value ($2\Delta_0=42$ meV) obtained from the tunneling experiment for nearly the same T_c sample.[6] It has also been suggested by the Raman study that the gap-T_c ratio, $2\Delta/k_BT_c$, radically decreases with overdoping. For example, in $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201), it changes from $2\Delta/k_BT_c=8$ at the optimum doping down to less than 3 at the heavy overdoping with $T_c/T_{c,max}=0.4$.[10]

Another problem is of the gap symmetry, which is crucially important to discuss the pairing mechanism. Raman scattering has been playing an important role in establishing the *d*-wave symmetry of HTSC.[11] However, in some of the overdoped HTSC, the pair-breaking peak in Raman spectra seems to change its polarization dependence that is characteristic to *d*-wave superconductor.[8] Although in most cases it has been attributed to the *s*-wave component mixing due to orthorhombicity,[12–14] it is necessary to examine whether it can be a more generic nature in HTSC or not.

Motivated by these problems, we have investigated the Raman-scattering spectra of overdoped HTSC. In this work, we present Raman-scattering spectra of heavily overdoped $(Y,Ca)Ba_2Cu_3O_{7-\delta}$ (Y/Ca-123) and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212), focusing on the pair-breaking peaks. It was found that for these heavily overdoped crystals the electronic pair-breaking peaks for all polarizations are located at much lower energy than $2\Delta_0$. These Raman data are well explained by the *s*-wave mixing with overdoping, accompanied by the change of the screening effect, as proposed by Nemetschek *et al.*[15]

The Y/Ca-123 crystals were grown by a crystal pulling technique[16] and detwinned under uniaxial pressure. By annealing further in high-pressure (800 atm) oxygen at 450 °C, we prepared heavily overdoped crystals with $T_c=65$ K. The Ca content (12%) and the oxygen content ($7-\delta=6.87$) were determined by an inductively coupled plasma analysis and iodometric titration, respectively. The Ca-free Y-123 crystal with $T_c=93$ K was also prepared for a reference of optimally doped sample. The Bi-2212 crystals were grown by a KCl flux technique. T_c for the as-grown crystals was about 90 K, close to the values reported for optimally doped Bi-2212. Heavily overdoped crystals with $T_c=55$ K were prepared by postannealing of the as-grown crystals at 450 °C for 100 h under oxygen gas pressure of 900 atm.

The Raman-scattering spectra were measured in the pseudo-backscattering configuration with a T64000 Jobin-Yvon triple spectrometer equipped with a liquid-nitrogen cooled charge-coupled device (CCD) detector. A typical spectral resolution was 3 cm^{-1}. The Ar^+-Kr^+ laser line of 2.54 eV was used for Y/Ca-123, while several excitation energy E_{exc} ranging from 1.9 eV to 2.7 eV were used for Bi-2212. The power was about 10 mW, focused to a spot of about 0.4×0.5 mm^2 on the sample surface. The overheating

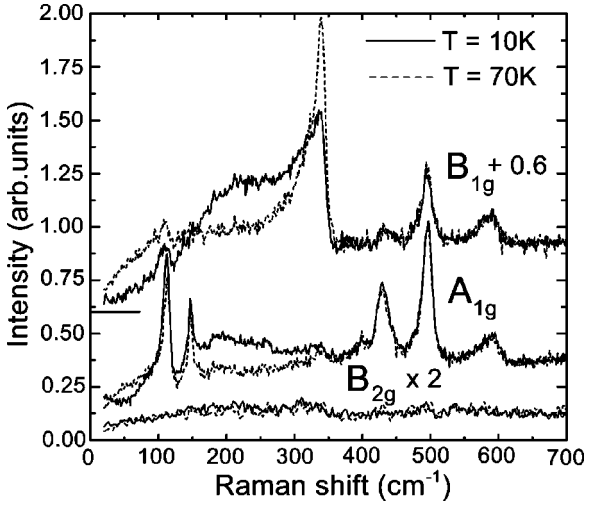

FIG. 1. Raman spectra of overdoped Y/Ca-123 crystal in B_{1g}, A_{1g}, and B_{2g} polarizations above and below $T_c = 65$ K. B_{1g} spectra are shifted in the vertical scale by 0.6.

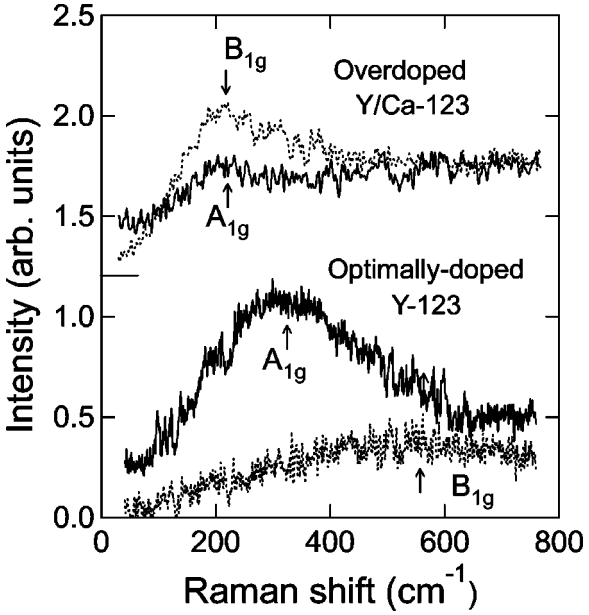

FIG. 2. The electronic component of overdoped Y/Ca-123 and optimally doped Y-123 crystals in B_{1g}, A_{1g} polarizations at $T = 10$ K. The spectra of Y/Ca-123 are shifted in the vertical scale by 1.2.

was estimated to be less than 10 K. All the measured spectra were corrected for the spectrometer sensitivity by comparison with that of BaF_2, and the contribution of the Bose factor has been removed. For low-temperature measurements, a closed-cycle cryostat was used with temperature stabilization better than 1 K.

Although the crystal structures of Y/Ca-123 and Bi-2212 are orthorhombic, hereafter all symmetries refer to a tetragonal D_{4h} point group, as the tetragonal treatment for the CuO_2 plane has been commonly adopted and proved to work well in the previous studies.[11] For Y/Ca-123 crystals, we extracted B_{1g} $(X'Y')$, B_{2g} (XY), and A_{1g} $(X'X'\text{-}XY)$ Raman responses. For Bi-based superconductors, X and Y are indexed along the Bi-O bonds, rotated by 45° relative to the Cu-O bonds. Therefore, for Bi-2212 crystals the above three Raman channels were taken as B_{1g} (XY), B_{2g} $(X'Y')$, and A_{1g} $(XX-X'Y')$.

Figure 1 shows the B_{1g}-, A_{1g}-, and B_{2g}- Raman spectra of Y/Ca-123 single crystals above and below T_c. The phonon peaks' profile is not much different from that of Y-123, except for a decrease of peak intensity in B_{1g} phonon at ~ 340 cm^{-1}. In the electronic continuum, a broad bump appears at around 220 cm^{-1} below T_c, which can be ascribed to a pair-breaking peak. Note that the pair-breaking peak intensity is weaker in the A_{1g} spectrum than in the B_{1g}. The electronic Raman responses were extracted by fitting in the same way as in Ref. 17, where electron-phonon coupling is taken into account. The obtained spectra are plotted in Fig. 2 together with the spectra of optimally doped pure Y-123 ($T_c = 93$ K) in comparison. The spectra of Y-123 are in good agreement with the previously reported results.[18]

While considering the overdoping effect, there are three remarkable features in Figs. 1 and 2. First, both for the A_{1g} and B_{1g} polarizations the pair-breaking peak energies ($E_p \approx 220$ cm^{-1}) are substantially lower in overdoped Y/Ca-123 than those in optimally doped Y-123. A weaker but similar tendency was reported for the B_{1g} spectra of slightly overdoped $(Y_{0.95}Ca_{0.05})Ba_2Cu_3O_{7-\delta}$ with $T_c = 82.7$ K (Ref. 19), where E_p $(B_{1g}) \approx 300$ cm^{-1}. Second, the symmetry dependence of the pair-breaking peak energy E_p is significantly weakened in the overdoped Y/Ca-123, the B_{1g} and A_{1g} pair-breaking peaks being located close to each other at around 220 cm^{-1}. As for the B_{2g} spectrum, the intensity is too weak to conclude the pair-breaking peak position. Third, the height of A_{1g} pair-breaking peak is suppressed in overdoped Y/Ca-123, while a large bump is observed in optimally doped Y-123.[20]

Similar overdoping effects are observed in Bi-2212. Figure 3 illustrates the Raman spectra in A_{1g}, B_{1g}, and B_{2g} channels for the overdoped Bi-2212 crystals. To suppress the phonon features in B_{1g} and B_{2g}, the laser light with $E_{exc} = 1.92$ eV was used.[21] The pair-breaking peaks are observed

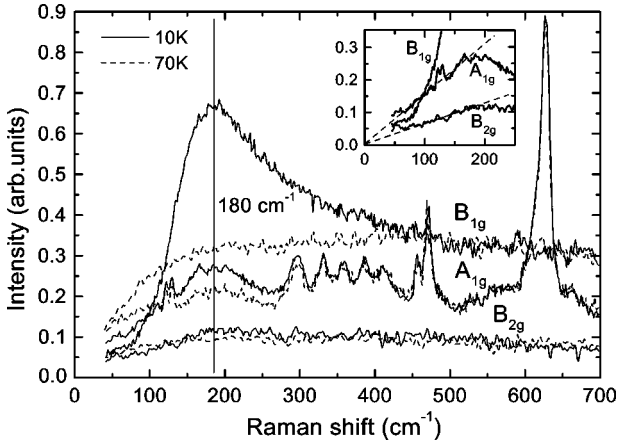

FIG. 3. Raman spectra of heavily overdoped Bi-2212 crystals in B_{1g}, A_{1g}, and B_{2g} polarizations above and below $T_c = 55$ K, measured at an excitation energy of 1.92 eV. Inset shows the low-ω parts at $T = 10$ K.

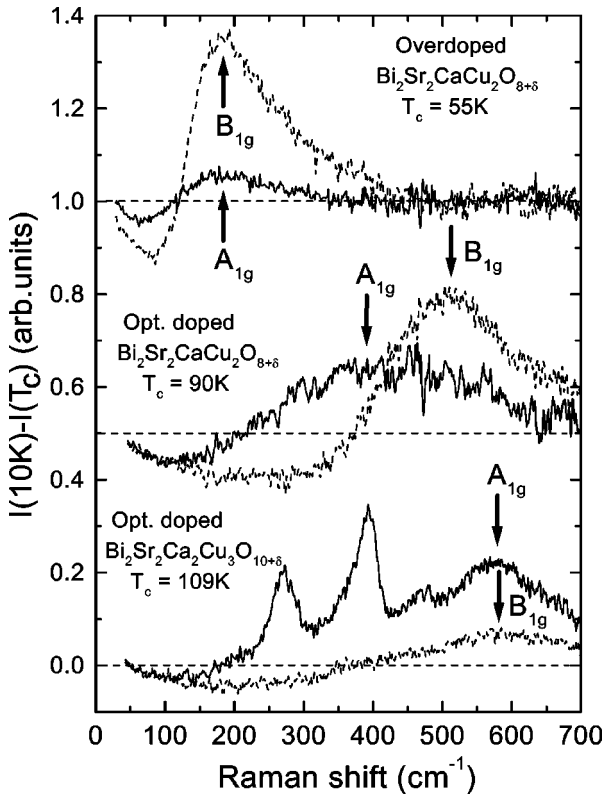

FIG. 4. The A_{1g} and B_{1g} differential spectra I (10 K)-I (T_c) of overdoped Bi-2212, nearly optimally doped Bi-2212 and Bi-2223, measured at the excitation wavelength of 1.92 eV. In the A_{1g} spectrum of Bi-2223, two phonons are apparent due to a strong resonance effect accompanied by the large phonon renormalization (Ref. 23).

at the polarization independent energy of about 180 cm^{-1}, which is in sharp contrast to the polarization dependent peak energies in optimally doped Bi-2212 crystals.[22] It is clearly demonstrated in Fig. 4, where a pure superconducting response I (10 K)-I (T_c) is presented. In the case of optimally doped Bi-2212 with $T_c=90$ K, the peaks were observed at about 520 cm^{-1} in the B_{1g} and 390 cm^{-1} in the A_{1g} spectra. Note that E_p (B_{1g}) in overdoped Bi-2212 becomes one-third of the value for optimally doped samples, although T_c is suppressed by only 30%. The weakened polarization dependence of E_p and the radical decrease in E_p were reported also for the famous overdoped material Tl-2201,[7,10] and thus we believe that this is a common property in all overdoped HTSC.

For the loss of polarization dependence of E_p, three possible origins can be considered. First, the gap symmetry changes to s wave and E_p indicates $2\Delta_s$, where Δ_s is an s-wave gap energy. Second, the screening effect disappears in the A_{1g} spectrum, as is observed in the three-layer compounds such as $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223).[23] Here E_p corresponds to $2\Delta_0$, Δ_0 being the maximum amplitude of a d-wave gap. Third, the s-wave component is mixed into the d wave, introducing the screening effect in the B_{1g} spectrum. In this case, E_p becomes smaller than $2\Delta_0$, as demonstrated by Nemetschek *et al.*[15]

The first possibility of s-wave gap was proposed by Kendziora *et al.*[7] However, it is unlikely because the low-ω Raman scattering shows the polarization dependence typical for a d-wave superconductor. As seen in Fig. 3 and in previous reports,[24] linear ω law for the A_{1g} and B_{2g} polarizations and ω^3-like-law for the B_{1g} polarization were observed. These are in general agreement with the theoretical predictions for d-wave pairing symmetry[11,25] but in contrast to the results[7] reporting polarization independent low-frequency profiles.

In order to distinguish the remaining two cases, it is crucial to know the maximum gap energies Δ_0. For the overdoped Bi-2212, the gap values are available from angle-resolved photoemission spectroscopy (ARPES) (Ref. 26) and STM studies.[6] According to the STM result on the Bi-2212 crystal with $T_c=56$ K which is similar to ours, the gap energy Δ_0 is 21 meV (≈ 170 cm^{-1}).[6] The ARPES on the Bi-2212 crystal with $T_c=65$ K also suggests that $\Delta_0=20$ meV(≈ 160 cm^{-1}).[26] It turns out that the B_{1g} peak energy (~ 180 cm^{-1}) observed in the present Raman study is closer to Δ_0 rather than $2\Delta_0$. This fact can exclude not only the first possibility of an s-wave gap but also the second possibility that the screening effect disappears in the A_{1g} channel. In the latter case, the A_{1g} and B_{1g} peaks should be located at $2\Delta_0$. Another support to exclude the second possibility is the weak intensity of the A_{1g} pair-breaking peak which should be strong in the screening-free case.

The third possibility was proposed by Nemetschek *et al.*[15] For fully oxygenated Y-123, s-wave mixing was indicated by the XY anisotropy of gap amplitude in Raman[17] and ARPES (Ref. 27) studies and by the gap peak splitting in tunneling spectra.[28] For a cylindrical Fermi surface, when the s component is mixed, the order parameter is given by[12,15] $\Delta(\mathbf{k})=\Delta_d[\cos(2\phi)+r]$. Here ϕ is the angle that $\mathbf{k}$ makes with the a axis in the a-b plane and r represents the s-component mixing rate.[29] The gap amplitude $|\Delta(\mathbf{k})|$ shows double maxima $\Delta(1\pm|r|)$. Correspondingly, unscreened Raman response has two peaks at $2\Delta_0=2\Delta_d(1+|r|)$ and $2\Delta_d(1-|r|)$. In the case of pure d wave with $|r|=0$, the screening effect manifests itself only in A_{1g} channel while, for the $d+s$ case, admixture of an s component to the predominant d component introduces the screening effect also in the B_{1g} channel. When $|r|$ becomes large, the higher-energy peak in B_{1g} spectrum is smeared out by the screening, leaving the lower-energy peak as a predominant peak in B_{1g}. In this case, E_p corresponds to $2\Delta_d(1-|r|)$. This feature appears to be unique to the $d+s$ wave superconductor, among the possible candidates for order parameter in HTSC such as $d+is$ and $d+g$.[15] The present result for the overdoped Bi-2212 corresponds to the case for $|r|\sim 0.3$, in which the peak energies of B_{1g}, A_{1g}, and B_{2g} channels are close to Δ_0.[15] In fact, E_p (B_{1g})$\approx E_p$ (A_{1g})≈ 180 cm^{-1} is close to $\Delta_0=170$ cm^{-1} determined by the STM measurement on the Bi-2212 crystal with nearly the same T_c as ours.[6] As for our overdoped Y/Ca-123 crystal, we have measured angle-resolved photoemission spectra,[30] and observed a gap of about 18 ± 2 meV ($\approx 145\pm 15$ cm^{-1}) near the X point, while a newly developed one-dimensional state conceals the gap structure near the Y point. In analogy to the overdoped

Y-123,[27] the gap near the X point is expected to reflect the smaller gap $\Delta_d(1-|r|)$ as E_p (B_{1g}) does in Raman spectrum. Thus, $|r|$ cannot be estimated in this case. However, judging from the very close positions of the A_{1g} and B_{1g} pair-breaking peaks, we speculate that $|r|$ is larger than 0.15 (Ref. 15) but close to 0.3.

As an example of the screening-free case, we show the A_{1g} and B_{1g} superconducting response of optimally doped Bi-2223 with $T_c=109$ K at the bottom of Fig. 4.[23] Here, the Coulomb screening in the A_{1g} channel disappears owing to the band splitting specific to a multiple layer superconductor,[31] giving E_p $(B_{1g})=E_p$ $(A_{1g})=580$ cm^{-1} $\approx 2\Delta_0$. This interpretation of E_p $(A_{1g})=2\Delta_0$ was supported by the ARPES data for the same compound,[32] where the maximum gap energy Δ_0 of about 37 meV ($2\Delta_0$ $=590$ cm^{-1}) was obtained. It should be noted that a strong intensity of the A_{1g} peak in Bi-2223 is also the evidence for the disappearance of screening effect, which is in sharp contrast to the very weak A_{1g} peak in the overdoped Bi-2212 and Y/Ca-123. Disappearance of screening effect due to band splitting was first observed in Bi-2223 under the resonance condition at the orange-red excitation ($E_{exc}<2.3$ eV).[23] A similar strong enhancement of A_{1g} pair-breaking peak was also observed in Hg-1223 and some other multilayer cuprates.[23] On the other hand, although we examined several excitation energies for the measurement of Bi-2212 spectra, neither the resonance phenomenon nor the band splitting effect was observed within the present energy range.

The most intriguing problem is the origin of the s component in overdoped HTSC. Although the orthorhombic distortion in Y-123 crystals favors the $d+s$ mixing,[12,33] this cannot explain the present Raman results. First, the orthorhombicity is smaller in our overdoped Y/Ca-123 crystals than in the fully oxygenated Y-123. Nevertheless, the s-wave mixing rate $|r|$ is larger in the former than in the latter ($|r|\sim 0.15$).[15] Therefore, orthorhombicity does not correlate with the s-wave mixing rate.

Second, the Raman spectra of the less orthorhombic Bi-2212 and the tetragonal Tl-2201 also require the $d+s$ model, although the $d+s$ symmetry is less favorable for the tetragonal structures.[13] Therefore, it is necessary to consider that the s-wave mixing is of purely electronic origin linked to overdoping. If the inhomogeneous electronic state induces local lattice distortion, it might introduce an s-wave component. It is interesting to examine a more radical scenario that the pairing mechanism itself changes with overdoping.

In summary, we investigated Raman-scattering spectra of two heavily overdoped compounds, Y/Ca-123 ($T_c=65$ K) and Bi-2212 ($T_c=55$ K). Comparing the results of ARPES and STM with our Raman results, we found that the pair-breaking peaks for B_{1g} and A_{1g} polarizations are located at the energies substantially lower than $2\Delta_0$, just as predicted theoretically for a $d+s$-wave superconductor. The change of the gap symmetry seems to be intrinsic to the overdoped regime in HTSC. The present findings, a drastic change of the gap nature in the overdoped regime of HTSC, must be a crucial test for the theoretical models for the electronic phase diagram of HTSC as well as for the high-T_c mechanism. Further theoretical works to explain the mechanism of s-wave mixing are desired.

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