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Effect of out-of-plane disorder on superconducting gap anisotropy in $Bi_{2+x}Sr_{2-x}CaCu_2O_{8+\delta}$ as seen via Raman spectroscopy

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We report a systematic study of the variation of electronic Raman spectra as a function of disorder for $Bi_{2+x}Sr_{2-x}CaCu_2O_{8+\delta}$ with different Bi:Sr nonstoichiometry. We have observed that, with increasing disorder, the suppression of the superconducting gap is observed only in the nodal region, while there is no change in the antinodal gap. This dichotomy of the response to disorder in the nodal and the antinodal gap can be interpreted as evidence for different origins of these two gaps.

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The curious superconducting gap structure in high-T_c cuprates has been a subject of intense studies for a long time. Recent experiments have suggested that the nodal and the antinodal gaps have a strong dichotomy, namely, a superconducting gap energy in the nodal region scales with the critical temperature T_c, while that in the antinodal region seems to be correlated with the pseudogap temperature, suggesting two distinct energy scales in the gap structure.[1–3] These results raise the question of the origin of the superconducting gap in the antinodal region. By contrast, recent angle-resolved photoemission spectroscopy (ARPES) reported a simple d-wave gap extending to the antinodal region.[4,5] Thus, in spite of intensive efforts to settle the problem of "gap dichotomy,"[1–7] this issue has been still a long-standing debate.

So far the gap dichotomy has been discussed in the doping dependence of the gap energy. In the present Rapid Communication, we tackle this problem from the viewpoint of disorder effects. Whereas there have been many reports about the effects of disorder at the Cu-site such as Zn in B_{1g} Raman scattering, to the best of our knowledge, none of them has answered the question of how the nodal gap measured for B_{2g} polarization responds to disorders.[8,9] This is partly because the in-plane disorder so strongly scatters the carriers that the response of the superconductivity is obscured, especially in B_{2g} electronic Raman scattering (ERS). Therefore, we focus on disorder outside the CuO_2 plane as another route to control T_c.[10–12]

Out-of-plane disorder in cuprates has attracted much attention in recent years because this type of disorder is inherent and considerably affects T_c without a strong increase in residual resistivity. This effect of out-of-plane disorder can be explained in terms of forward scattering.[13] The most advantageous point is that the effect of out-of-plane disorder on the carrier scattering is much weaker than the case of Zn/Ni substitution,[10,11] which enables us to observe clearly a superconducting response in ERS.

To extract disorder effect, we systematically study the variation of the electronic Raman spectra as a function of disorder at a fixed doping level in bilayer cuprate $Bi_{2+x}Sr_{2-x}CaCu_2O_{8+\delta}$ with different Bi:Sr nonstoichiometry. We measured B_{1g} and B_{2g} superconducting Raman responses, and found that (i) the pair-breaking peak energy in B_{1g} symmetry is robust to out-of-plane disorder and (ii) the low-energy B_{2g} Raman response expands to the lower energy with increasing out-of-plane disorder, suggesting that a gap energy decreases only in the nodal region. Our observation of the different response to disorder in B_{1g} and B_{2g} spectra provides experimental evidence that the origins of the nodal and the antinodal gap are different. We discuss the present Raman results in relation to the model in which a superconducting gap is modulated in the nodal region.

High-quality single crystals of optimally doped $Bi_{2+x}Sr_{2-x}CaCu_2O_{8+\delta}$ with compositions $x = 0.1$, 0.2, and 0.3 were grown by a traveling solvent floating-zone (TSFZ) method.[11] With increasing x, Bi^{3+} ions tend to substitute Sr^{2+} in the SrO block, which generates out-of-plane disorder. At the same time, Bi-Sr substitution changes the doping level in the CuO_2 planes. We therefore controlled the doping level by changing excess oxygen content for each x. The T_c of the samples were 91.5 K for $x = 0.1$, 82 K for $x = 0.2$, and 77 K for $x = 0.3$. These are the maximum T_c values for each x, which means that all of them are optimally doped. Raman scattering experiments were carried out in pseudobackscattering configuration using an Ar laser line (514.5 nm) and T64000 Jobin-Ybon triple grating spectrometer equipped with a nitrogen-cooled charge coupled device (CCD) detector. The laser power was tuned to be less than 20 mW/mm^2 for the measurement. The laser overheating was carefully checked by changing incident laser powers. All spectra have been corrected for Bose-Einstein factor. Although the crystal structure of Bi2212 is orthorhombic, hereafter, all symmetries refer to the tetragonal D_{4h} point group, as the tetragonal treatment of CuO_2 planes has been justified by the previous studies.[14] B_{1g} and B_{2g} Raman spectra have been obtained in $z(x'y')\bar{z}$ and $z(xy)\bar{z}$ scattering geometry, where the first and the second letters in the parentheses denote the polarizations of the incident and the scattered light, respectively. Here, the x and y axes are along the Cu-O bonds, and x' and y' are rotated by 45° relative to the Cu-O bonds. With B_{1g} and B_{2g} polarization, the Fermi-surface state around the antinodal (along the ΓX direction) and the nodal (along the ΓM direction) regions can be selectively probed, where

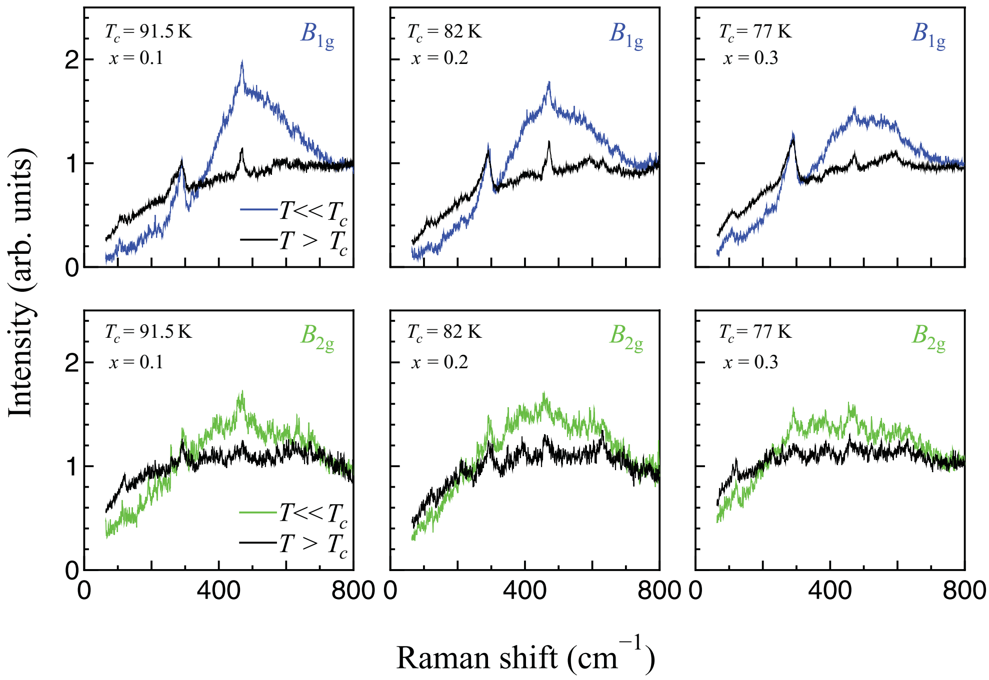

FIG. 1. (Color online) Raman spectra in the normal and superconducting states in B_{1g} (top row) and B_{2g} (bottom row) polarization for $Bi_{2+x}Sr_{2-x}CaCu_2O_{8+\delta}$ with different x.

the amplitude of the d-wave superconducting gap reaches a maximum and vanishes, respectively.[14]

In Fig. 1, we show the normal and superconducting Raman spectra of Bi2212 with different x in B_{1g} and B_{2g} polarizations. The Raman spectra presented here were measured at 10 K (superconducting state) and +10 K above T_c (normal state). In the spectra, several sharp phonon peaks appear, but their intensities and shapes do not change so much upon the superconducting transition. The responses due to superconductivity are seen in the electronic continua. Both B_{1g} and B_{2g} electronic Raman continua exhibit redistribution of spectral weight. The B_{1g} superconducting Raman spectra create broad pair-breaking peaks at 2Δ upon entering the superconducting state, while the B_{2g} pair-breaking peaks are located at energies lower than 2Δ, due to the anisotropy of the d-wave gap. So far, there are only few reports on the observation of the superconducting response of the B_{2g} ERS in disordered high-T_c cuprates, presumably because the B_{2g} Raman response is strongly affected by any scattering source.[15,16] It is remarkable that the out-of-plane disordered Bi2212 displays a clear coherent B_{2g} Raman response. This suggests, as seen in resistivity,[10,11] that the out-of-plane disorder works as a weak scatterer in contrast to the in-plane disorder.

Figures 2(a) and 2(b) summarize the superconducting Raman spectra in B_{1g} and B_{2g} polarization, respectively, all of which are normalized at 800 cm^{-1}. In Fig. 2(a), the B_{1g} peak energy does not change with x, namely, with T_c, but remains constant. This result is different from what one would expect for a conventional superconductor where a superconducting gap energy scales with T_c. The robustness of the antinodal gap energy under the impurity substitution has been reported also for Zn- or Ni-substituted cuprates by ERS.[17] At lower energies, the electronic continuum increases its intensity with increasing x, while the height of the B_{1g} pair-breaking peak is suppressed.

In Fig. 2(b), we compare the B_{2g} superconducting Raman responses. With increasing the amount of out-of-plane disorder from $x = 0.1$ to 0.3, the low-energy B_{2g} Raman response expands to lower energy. This suggests that the nodal gap is suppressed by out-of-plane disorder. The change of the nodal gap energy would be related to the decrease in T_c. The disorder-induced suppression of the superconducting gap in the nodal region is theoretically predicted by Haas *et al.*[18] They indicated that in the case of forward scattering, the superconducting gap should be flattened around the node. The observed changes in the B_{2g} Raman response are in good agreement with the flattening of the superconducting gap in the nodal region due to forward scattering.

The characteristic changes with x in the superconducting B_{1g} and B_{2g} Raman response, namely, the robustness of the B_{1g} peak energy and the expansion of the low-energy B_{2g} Raman response, give evidence for an interesting change in the gap profile. In order to roughly reproduce the observed superconducting Raman response, we should assume modulation of the $d_{x^2-y^2}$ symmetry. Since the possibilities of a higher-harmonic gap function have been suggested by ARPES[19] and heat transport measurements,[20] we introduce the following higher-harmonic gap function for convenience:

$$\Delta_{\mathbf{k}} = \Delta_0[(1 - B)\cos(2\phi) + B\cos(6\phi)], \tag{1}$$

where $0 \leqslant B \leqslant 1$. The parameter B reflects the degree of suppression of $\Delta_{\mathbf{k}}$ around the node. We note that the parameter Δ_0 is constant because the B_{1g} pair-breaking peak is shown to be robust in the presence of out-of-plane disorder. Of course, other nonanalytic modulation of $d_{x^2-y^2}$ symmetry may be possible. For example, an extended gapless arc in the nodal

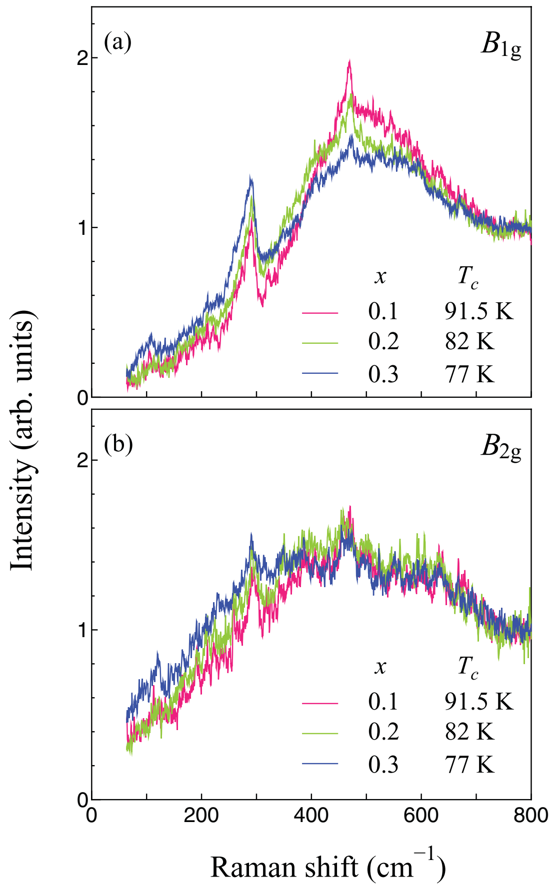

FIG. 2. (Color online) Raman spectra in the superconducting states in (a) B_{1g} and (b) B_{2g} polarization measured at 10 K. Spectra are normalized with intensity at 800 cm^{-1}.

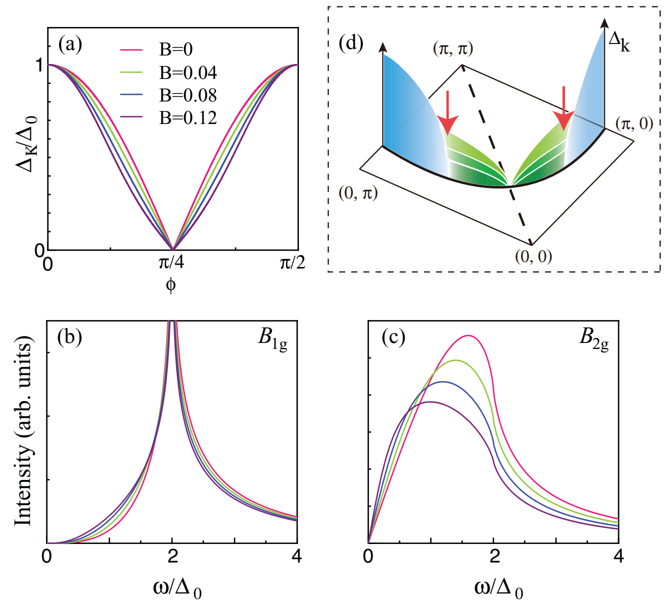

FIG. 3. (Color online) (a) Angular dependence of the phenomenological superconducting gap in Eq. (1). (b), (c) Calculated B_{1g} and B_{2g} Raman responses by integrating Eq. (2) for the parameters described in (a). (d) Two-gap scenario where the nodal gap is suppressed with keeping the antinodal gap unchanged.

region was suggested by ARPES measurements on the in-plane-disordered Bi-2212.[21] But we have adopted a harmonic with the form $\cos(6\phi)$ for simplicity. As demonstrated in Fig. 3(a), gap functions around the node are significantly modified, while the maximum gap size is unchanged.

To reproduce the change in the B_{1g} and B_{2g} Raman responses with increasing the out-of-plane disorder, we calculate a superconducting Raman response function by using a conventional model of light scattering. The Raman response function at zero temperature is given by the following equation:[22]

$$\chi_{\alpha\beta}(\mathbf{q}\rightarrow 0,\omega) = \frac{2\pi N_F}{\omega}\mathrm{Re}\left\langle \frac{\left|\gamma_{\mathbf{k}}^{\alpha\beta}\right|^2\Delta_{\mathbf{k}}^2}{\sqrt{\omega^2-4\Delta_{\mathbf{k}}^2}}\right\rangle_{\mathrm{FS}}. \quad (2)$$

Here, $\alpha\beta = x'y'$ for B_{1g}, $\alpha\beta = xy$ for B_{2g}, $\langle\cdots\rangle_{\mathrm{FS}}$ denotes an average over the Fermi surface, N_F is the density of states at the Fermi level, and $\gamma_{\mathbf{k}}^{\alpha\beta}$ are Raman vertices. Assuming a cylindrical Fermi surface, we take the simple Raman vertices $\gamma_{\mathbf{k}}^{x'y'} \sim \cos(2\phi)$ and $\gamma_{\mathbf{k}}^{xy} \sim \sin(2\phi)$.[23]

Integrating Eq. (2) over the Fermi surface, we obtain the superconducting B_{1g} and B_{2g} Raman response as shown in Figs. 3(b) and 3(c). In Fig. 3(b), the robustness of the peak energy and the enhancement of the low-energy tail in the B_{1g} spectrum are well reproduced. In Fig. 3(c), the spectral weight shift to lower energy is reproduced. According to the ARPES result that shows a simple d-wave gap,[6] $B = 0$ for the sample of $x = 0.1$ with the highest T_c. In order to explain the observed change in the Raman response with increasing x from 0.1 to 0.3, the change of parameter B must be $\Delta B \sim 0.06 \pm 0.02$, which is estimated by comparing the change of the low-energy slope of the spectra. The discrepancy between the calculated spectrum and the measured one is seen in the suppression of the peak intensity in the B_{2g} spectra with increasing B. In the measured spectra, the height of the pair-breaking peak hardly changes. This may be related to the scattering effect.

The present results suggest that the change of T_c is explained by the suppression of $d_{x^2-y^2}$ gap around the node. The fact again raises the question of the role of the pseudogap in superconductivity, that is, whether the gap structure of the cuprate superconductors should be decomposed into two parts (two-gap scenario), or one gap simply modified its k dependence by the disorder effect as in the form of Eq. (1). If the gap profile is modeled as a single gap (one-gap scenario), it should be explained why the gap is modified only in the nodal region. However, to the best of our knowledge, there is no theoretical model that keeps Δ_0 constant for impurity pair breaking. On the other hand, in the two-gap model, the present result could be understood as a suppression of the superconducting gap around the node by keeping the antinodal gap unchanged [Fig. 3(d)]. However, the origin of antinodal gap remains an open question.

A breakdown of the relationship between T_c and the antinodal gap energy has been also observed in the doping dependence of the gap in the underdoped regime, where the antinodal gap energy monotonically increases with decreasing doping level.[1–3] One of the proposals is that T_c is determined by the length of the Fermi arc but not by the maximum gap amplitude in the antinodal region.[3,24] On the basis of this idea, the dichotomy in the B_{1g} and B_{2g} Raman spectra has been interpreted within a single-gap scenario.[25,26] However, the present result of the B_{2g} spectra cannot be understood as a shrinkage of the Fermi arc, as we explain below. Our results rather support the two-gap scenario, where the origins of the nodal and the antinodal gaps are different.

The effects of out-of-plane disorder were reported in the recent ARPES[27,28] and scanning tunneling microscopy (STM) and/or scanning tunneling spectroscopy (STS)[29] studies for $Bi_2Sr_2CuO_{6+\delta}$ (Bi2201), which suggest that out-of-plane disorder stabilizes the pseudogap. The effects were observed as a shrinkage of the Fermi arc and an enhancement of the pseudogap energy. In the present study, the shrinkage of the Fermi arc can be discussed in a similar manner as a kind of modulation of the d-wave gap. However, the present spectra are different from what is expected from the shrinkage of the Fermi arc in Bi2201 in two points. First, the enhancement of the B_{1g} gap energy, which corresponds to the enhancement of the pseudogap, is not seen in our spectra. Second, if the Fermi arc simply shrinks without changing the gap energy, the spectrum near $\omega = 0$ is expected to be unchanged, while in the present study the changes of spectra due to the out-of-plane disorder is obvious at low energies, especially in the B_{2g} spectra. This discrepancy between the Raman result and the ARPES data might be due to a difference between Bi2201 and Bi2212. To investigate in detail such a difference may lead to the understanding of the lower T_c in Bi2201 as well as the role of the pseudogap in superconductivity.

In summary, we have measured ERS for the out-of-plane disorder-controlled Bi2212 to investigate a gap structure from the viewpoint of disorder. We have found that the B_{2g} Raman response expands to lower energy with increasing the out-of-plane disorder. This indicates the suppression of the superconducting gap in the nodal region. By contrast, the B_{1g} peak energy remains constant even if the out-of-plane disorder increases. While the dichotomy has been observed so far in the doping dependence of the B_{1g} and B_{2g} gaps in Raman spectra, we found in the present work the gap dichotomy in the disorder effect. This strongly suggests that the origins of the nodal and the antinodal gap are different.

Note Added. We note that recently N. Munnikes *et al.* published a paper[30] claiming that the B_{1g} peak corresponds neither to a superconducting gap nor to a pseudogap.

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