Anisotropic charge transfer mechanism in La$_{2-x}$Sr$_x$CuO$_4$ and Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$

S. Sugai, N. Hayamizu, and T. Hosokawa

Department of Physics, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-8602, Japan

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Abstract

Raman spectra of La$_{2-x}$Sr$_x$CuO$_4$ are similar to those of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ except for the split two-magnon peaks at the stripe phase and the stronger step-like decrease in the low energy $B_{2g}$ spectra. The suppressed $B_{1g}$ spectral region below the two-magnon peak decreases as the carrier density increases, whereas the energy of the step-like suppression is little dependent on the carrier density. It suggests the anisotropic charge transfer mechanism coupled with magnetic excitations along the nearest neighbor Cu sites and the phononic excitations along the diagonal direction.

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Angle resolved photoemission spectroscopy (ARPES) disclosed the similarity and the difference in La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) and Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+\delta}$ (BSCCO). In BSCCO the low energy spectra at ($\pi$,0) are suppressed at low carrier densities via the interaction with collective magnetic excitations at ($\pi$, $\pi$) [1–4]. The energy region of the suppressed intensity decreases as the carrier density increases. The spectra at ($\pi$/2, $\pi$/2) are not suppressed at all carrier densities. On the other hand, in the spectra at ($\pi$,0) of LSCO a new hump appears at the insulator-metal transition and the hump develops to a peak with decreasing the energy as the carrier density increases [5–7]. The low energy region at ($\pi$/2, $\pi$/2) is strongly depleted at $x \leq 0.12$ and suddenly increases at $x = 0.15$. These anomalous features in LSCO were attributed to the stripe structure [8–10].

Wide-energy Raman scattering can observe electronic excitations at the selective k-space region along (0,0) – ($\pi$,0), and (0,0) – ($\pi$, $\pi$) correspondingly to ARPES [11,12]. In Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$ (BSCYCO) the Raman spectra are consistent with the results of ARPES [13], but in LSCO they are rather different from ARPES [14–16]. The 300 K spectra, in which the stripe structure almost disappears at all carrier densities in LSCO, are qualitatively same in both superconductors except for the enhanced step-like decrease below about 1100 cm$^{-1}$ in the $B_{2g}$ spectra of LSCO. As temperature decreases, the spectra do not change so much except in the stripe phase of LSCO ($0.035 \leq x \leq 0.06$ and $x = 0.115$).

The Raman spectroscopy is valuable as an alternative method to measure the electronic excitation spectra to ARPES, because Raman spectra can detect anisotropic superconducting gap at ($\pi$,0) and ($\pi$/2, $\pi$/2) in consistent with other experiments [13,17,20] and the wide-energy Raman spectra in BSCYCO are consistent with the ARPES [13]. The merit of Raman scattering is less sensitivity to the surface condition. The measurement of ARPES of LSCO is limited to low temperatures from the instability of the surface at high temperatures, while Raman scattering can measure up to about 500-600 K without disturbing the electronic states.

Raman scattering detects $B_{1g}$ and $B_{2g}$ excitations separately by choosing the polarizations of incident and scattered light as ($\hat{E}_i$, $\hat{E}_s$) = ($xy$) and ($ab$), respectively [11,12]. Here
\(a = [1, 0, 0]\) and \(b = [0, 1, 0]\) are directions along the Cu-O-Cu bonds, and \(x = [1, 1, 0]\) and \(y = [1, -1, 0]\) are diagonal directions. The base function of \(B_{1g}\) is \(k_x x - k_y y\) and then it has a maximum at the \((0, 0) - (\pi, 0)\) direction. Thus the \(B_{1g}\) electronic Raman spectrum represents the excitation along the \((0, 0) - (\pi, 0)\). On the other hand the base function of \(B_{2g}\) is \(k_x k_y\) and has a maximum at \((0, 0) - (\pi, \pi)\). The \(B_{2g}\) spectrum represents the excitation along \((0, 0) - (\pi, \pi)\).

The single crystals were synthesized by the TSFZ method utilizing an infrared radiation furnace with four elliptic mirrors (Crystal system, FZ-T-4000). The Néel temperature \((T_N)\) at \(x = 0\) is 293 K. The superconducting transition temperature \(T_c\)'s determined from the middle point of the transition in the electric resistivity are 12 K \((x = 0.06)\), 33 K \((x = 0.1)\), 33 K \((x = 0.115)\), 42 K \((x = 0.15)\), 32 K \((x = 0.2)\), and 13 K \((x = 0.25)\). The details will be presented elsewhere \([21]\).

Raman spectra were measured on fresh cleaved surfaces in a quasi-back scattering configuration utilizing a triple monochromator (JASCO, NR-1810), a liquid nitrogen cooled CCD detector (Princeton, 1100PB), and a 5145 Å Ar-ion laser (Spectra Physics, stabilite 2017). The cleaved surfaces give intrinsic spectra which are different from those on the surfaces prepared by mechanical polishing or chemical etching \([21]\). The laser beam of 10 mW was focused on the area of 50 \(\mu m\times500 \mu m\). The obtained Raman intensity was corrected by the spectroscopic efficiency of the optical system.

Figure 1 shows the \(B_{1g}\) and \(B_{2g}\) Raman spectra at 100 K in the normal phases of optimally doped LSCO and BSCYCO. The solid curves indicate the expected ideal electronic Raman spectra in the strongly correlated metal. The \(B_{1g}\) Raman spectra in overdoped LSCO and BSCYCO show these ideal metallic spectra. As the carrier density decreases the suppressed region increases at low energies. On the other hand the \(B_{2g}\) spectra are very different from \(B_{1g}\). The carrier density dependence is very small. The suppression in the low energy spectra is much larger in LSCO than in BSCYCO.

Figure 2 shows the carrier density dependence of the \(B_{1g}\) and the \(B_{2g}\) spectra of LSCO at 5 K and 300 K. The intensity is normalized so that the total integrated intensity below
6000 cm$^{-1}$ is the same. The sharp peaks below 700 cm$^{-1}$ are due to one-phonon scattering and the peaks from 700 to 1400 cm$^{-1}$ are due to two-phonon scattering. The two-phonon intensity is much larger in the $A_{1g}$ spectrum than in the $B_{2g}$ spectrum. The 3117 cm$^{-1}$ peak at 300 K in the $B_{1g}$ spectra of the insulating phase ($x = 0$) is the two-magnon peak. This energy is near $3J$, where $J$ is the exchange interaction energy between the nearest neighbor spins at copper sites. As the carrier density increases, the peak energy at 300 K shifts monotonically to low energy via electron-magnon interactions. It is consistent with the experiments by Naefini et al. [14,15]. The peak energies are shown in Fig. 3. The $B_{1g}$ spectrum of overdoped sample ($x = 0.25$) is close to the ideal metallic spectrum in Fig. 1. The overall spectra at 5 K are similar to that at 300 K, unless stripe structure develops. However, in the stripe phase ($0.035 \leq x \leq 0.06$ and $x = 0.115$) at 5 K, the two-magnon peak splits into double peaks near $3J$ and $2J$ [16]. The clear split of the two-magnon peak is observed only at narrow carrier density region corresponding to the decrease of $T_c$ measured by electric resistivity. It is very different from the results of neutron scattering in which the incommensurate magnetic peaks have been observed at whole carrier densities [22–24]. It is also different from ARPES in which the carrier density dependence for the stripe phase is not observed. In the stripe phase, the low energy spectra below about 1100 cm$^{-1}$ are just like the metallic spectra [16]. The threshold energy is exactly the same as one of the two-phonon energies in the $A_{1g}$ spectra. This phonon is assigned to the zone boundary $(\pi, 0, 0)$ longitudinal optical (LO) phonon mode with anomalous dispersion measured by neutron scattering [25,27]. Oxygen atoms are vibrating in this mode.

The decrease of the two-magnon peak energy at 300 K, as the carrier density increases, can be considered as the decrease of the suppressed spectral region below the two-magnon peak. ARPES at $(\pi, 0)$ and 11 K showed the appearance of a new peak at about 0.1 eV at $x = 0.05$. The binding energy decreases and the intensity increases, as the carrier density increases [7]. The energy is lower than a half of the $B_{1g}$ peak energy. The spectra do not change by the formation of the stripe structure at $0.035 \leq x \leq 0.06$ and $x = 0.115$ contrary to the 5 K Raman spectra in Fig. 2. In the case of BSCYCO the carrier density dependence
is consistent with the ARPES.

As for the $B_{2g}$ spectra at 300 K, the carrier density dependence is very different. The 4170 cm$^{-1}$ peak at $x = 0$ is due to the two-magnon scattering. In the $B_{2g}$ symmetry the two-magnon scattering is inactive, if only the nearest neighbor exchange interaction is considered \[28\]. The diagonal next neighbor interaction and four spin cyclic exchange interaction can make it active \[28\,[30\]. The peak energy 4170 cm$^{-1}$ is just 4$J$, that is, twice the zone boundary magnon energy. It suggests that the magnon-magnon interaction does not work. The two-magnon peak energy decreases from $x = 0$ to 0.1 and becomes constant above it as shown in Fig. 3. In the stripe phase at 0.035 $\leq x \leq$ 0.06 and $x = 0.115$, the spectra change into the similar structure to the $B_{1g}$ spectra, as temperature decreases to 5 K, because the crystal symmetry relaxes by the stripe structure. The spectrum is composed of the split two-magnon peaks at about 3$J$ and 2$J$ above about 1100 cm$^{-1}$ and the metallic spectrum below it. This metallic spectrum can be viewed as a step-like decrease of the scattering intensity below about 1100 cm$^{-1}$. This step-like decrease is commonly observed at 5 K even in the compound in which the stripe structure does not develop. And also this step-like decrease is reserved even at 300 K at which the stripe structure almost disappears even at 0.035 $\leq x \leq$ 0.06 and $x = 0.115$. The energies of the valleys at the steps are shown in Fig. 3. The energies are almost independent of the carrier density. This suggests that the step-like decrease does not result from the magnetic origin, because the collective magnetic excitation energy decreases clearly with the increase of the carrier density as shown in the $B_{1g}$ two-magnon peak energy in Fig. 3. The origin is possibly the electron-phonon interaction with the zone boundary ($\pi, 0, 0$) LO phonon, because the energy is the same as discussed in the $B_{1g}$ spectra of the stripe phase \[25\,[27\).

The ($\pi/2, \pi/2$) ARPES spectra subtracted the (0, 0) spectra is very different from the $B_{2g}$ Raman spectra \[9\]. The low-energy intensity is very weak at $x \leq 0.12$. The carrier density dependence relating to the stripe phase (0.035 $\leq x \leq$ 0.06 and $x = 0.115$) is not observed. The sudden increase of the low energy spectral intensity at $x = 0.15$ in the ARPES spectrum is inconsistent with the Raman spectrum.
The step-like decrease below about 1100 cm$^{-1}$ is also observed in lightly underdoped to overdoped BSCYCO [13]. Figure 4 shows the $B_{2g}$ spectra at $x = 0.3$ (underdoping $T_c$=75 K), $x = 0.2$ (underdoping $T_c$=87 K), $x = 0.1$ (optimal doping $T_c$=95 K), and $x = 0$ (overdoping, $T_c$=84 K). The low energy peaks at 20 K are the superconducting peaks [13]. The step-like decrease is not observed at $x = 0.3$, but it increases as the carrier density increases and the temperature decreases from 300 K to 100 K. The stripe structure is probably limited to much narrower carrier density region than in LSCO, even if it exists [31]. Therefore the suppression of the low energy $B_{2g}$ spectra at wide carrier density region indicates again that the suppression in the $B_{2g}$ spectra is not related to the stripe structure. The stronger suppression in LSCO than in BSCYCO results from the stronger electron-phonon interaction in LSCO. It is consistent with the stronger two-phonon Raman intensity in LSCO than in BSCYCO.

The phononic origin for the depletion in the $B_{2g}$ spectra can be confirmed by comparing the energy of the step between oxide and sulfide, because almost only chalcogen atoms are vibrating in the relevant LO phonon mode. In the metallic phase of BaCo$_{1-x}$Ni$_x$S$_2$ (BCNS), the same small step-like decrease is observed below about 480 cm$^{-1}$ [32]. The energy difference, 1100 cm$^{-1}$ in LSCO and 480 cm$^{-1}$ in BCNS, indicates that the origin of the step-like decrease in $B_{2g}$ is the electron-phonon interaction.

The present Raman scattering experiment clearly shows the different origin of the spectral suppression in the $B_{1g}$ spectra corresponding to the excitations along $(0,0) - (\pi,0)$ and the $B_{2g}$ spectra along $(0,0) - (\pi,\pi)$. That is, the electronic excitations along $(0,0) - (\pi,0)$ is affected by the electron-magnon interaction, whereas those along $(0,0) - (\pi,\pi)$ by the electron-phonon interaction. It can be interpreted in the real space that the charge transfer along the Cu-O-Cu direction is coupled with magnetic excitations, while the charge transfer along the diagonal direction is coupled with phonons. It is plausible, because the direction of spins are opposite at the nearest neighbor Cu sites but the same at the diagonal sites. The anomalous LO phonon with the carrier density dependent energy is observed at $(\pi,0)$ [25–27]. The breathing phonon mode clusters formed from the LO phonon modes at $(\pi,0)$ and $(0,\pi)$
are located along the diagonal direction. It is consistent with the above interpretation.

In conclusion, the wide-energy $B_{1g}$ and the $B_{2g}$ Raman spectra provide electronic excitation spectra corresponding to ARPES along $(0, 0) - (\pi, 0)$ and $(0, 0) - (\pi, \pi)$, respectively. In the $B_{1g}$ spectra the suppression below the two-magnon peak decreases as the carrier density increases, whereas in the $B_{2g}$ spectra the step-like suppression is little dependent on the carrier density. The former can be attributed to the results of the electron-magnon interaction and the latter to the electron-phonon interaction. The above results suggest that the charge transfer mechanism is anisotropic in the real space, that is, electrons couple dominantly with magnetic excitations for the transfer along the Cu-O-Cu direction and with phonons along the diagonal direction. These anisotropic charge transfer mechanisms are probably related to the high $T_c$ superconducting mechanism.

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FIGURES

FIG. 1. The $B_{1g}$ and $B_{2g}$ Raman spectra in the normal phase at the optimal doping of La$_{2-x}$Sr$_x$CuO$_4$ and Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$. The $B_{1g}$ spectra approach the typical metallic spectra (solid curves) as the carrier density increases. However, the $B_{2g}$ spectra approach the typical metallic spectra as the carrier density decreases in Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$.

FIG. 2. The carrier density dependence of the $B_{1g}$ and the $B_{2g}$ spectra at 300 K at which the stripe structure almost disappears and at 5 K at which the influence of the stripe is observed at $0.035 \leq x \leq 0.06$ and $x = 0.115$ by the split of the two-magnon peaks. The intensity is normalized so that the integrated intensity below 6000 cm$^{-1}$ is the same.

FIG. 3. The carrier density dependence of the $B_{1g}$ and the $B_{2g}$ two-magnon peak energies at 300 K and the energies at the valley (or kink) in the $B_{2g}$ spectra at 5 K and 300 K. The small effect of the split two-magnon peak is retained in the $B_{2g}$ spectra at 300 K.

FIG. 4. The temperature and carrier density dependence of the $B_{2g}$ Raman spectra in Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$. The $T_c$’s are shown in the parentheses. UD: underdoping, OP: optimal doping, and OD: overdoping.
Fig. 1  Sugai, Hayamizu, and Hosokawa

\( B_{1g} \) (xy)  
100 K

\( B_{2g} \) (ab)  
100 K

\( T_C = 95 \text{ K} \)

\( T_C = 42 \text{ K} \)
Fig. 2  Sugai, Hayamizu, and Hosokawa
La$_{2-x}$Sr$_x$CuO$_4$

Fig. 3    Sugai, Hayamizu, and Hosokawa
Fig. 4  Sugai, Hayamizu, and Hosokawa