Resonance Raman Study of the Superconducting Gap and Low Energy Excitations in $Tl_2Ba_2CuO_{6+\delta}$ Superconductors

Moonsoo Kang,[1] G. Blumberg,[1,2] M. V. Klein,[1] and N. N. Kolesnikov[3]
[1]*Department of Physics, and Science and Technology Center for Superconductivity, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*
[2]*Institute of Chemical Physics and Biophysics, Rävala 10, Tallinn EE0001, Estonia*
[3]*Institute for Solid State Physics, Russian Academy of Science, Chernogolovka, Moscow Region, 142 432, Russia*
(Received 21 August 1996)

Low energy electronic Raman scattering from $Tl_2Ba_2CuO_{6+\delta}$ single crystals with $T_c = 25$ and 85 K has been studied using excitation energies from 1.65 to 3.05 eV. The B_{1g} 2Δ peak position shows that the $2\Delta/k_BT_c$ value decreases as the doping level increases. The resonance profiles of the 2Δ peak and the continuum show similar and strong resonances towards the 3.4 eV optical absorption peak in both crystals, which indicates that (1) the 2Δ peak and the continuum are coupled to light scattering by the same mechanism, and (2) the light scattering mechanism for both features involves the 3.4 eV optical absorption process. [S0031-9007(96)01691-2]

PACS numbers: 74.25.Gz, 74.72.Fq, 78.30.-j

One of the most noticeable features in Raman scattering from cuprates is the existence of a flat and featureless continuum and the appearance of a so-called "2Δ peak" in the superconducting state [1]. This peak is understood as a peak due to excitations of quasiparticle pairs across the superconducting gap, i.e., a pair-breaking peak, based on earlier work on conventional superconductors [2,3]. This peak is most prominent in B_{1g} symmetry, and the B_{1g} peak is observed at higher frequencies than peaks in any other symmetries in cuprate superconductors [4–6]. This is consistent with what we expect from superconductors with the $d_{x^2-y^2}$ gap or a strongly anisotropic s-wave gap with a similar shape [6,7]. Recent study of scanning SQUID microscopy also shows evidence for the $d_{x^2-y^2}$ gap from Tl-2201 [8]. Nevertheless, the existence of such a flat and featureless continuum is not yet clearly understood. Electronic Raman scattering from quasiparticles in Fermi liquid theory can have finite intensity only at very low frequencies ($\omega \leq qv_f$). In a strongly correlated system, incoherent scattering of quasiparticles can give finite Raman scattering intensity over a broad region of frequency [9], but no concrete result has been reported based on this idea. There have been several attempts to explain the 2Δ peak and the continuum theoretically. None so far has been successful in explaining both features correctly, even though some results produce a similar 2Δ peak without considering the continuum. Resonance Raman scattering is particularly useful to study the nature or mechanism of a Raman active excitation. In resonance Raman scattering studies, the Raman intensity of a particular excitation is measured as a function of excitation energy. By finding the resonance energy of the continuum and the 2Δ peak, the intermediate states and, as a result, the process or the mechanism for the excitation can be revealed.

In this Letter, we report detailed Raman scattering studies from $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201) single crystals. Raman scattering from low energy electronic excitations was studied in relation to the doping level, the polarizations, and the excitation energy. The similar resonance behaviors of the 2Δ peak and the continuum were observed, and the implications of the resonance behavior are discussed.

Tl-2201 is an overdoped superconductor with T_c varying from 0 to 110 K. In this material, the whole overdoped regime from superconductor near optimal doping to nonsuperconducting metal is accessible by changing the oxygen doping level [10], and the critical temperature (T_c) is very sensitive to the oxygen content: at or near $\delta = 0$, T_c is approximately 90 K, but T_c vanishes for $\delta \sim 0.1$ [11]. Tl-2201 has a tetragonal unit cell with point group $D_{4h}(I4/mmm)$. Optical studies of Tl-2201 have revealed that there exists a strong peak in the optical absorption curve around 3.4 eV [12], and this material gives relatively strong luminescence under excitation at an energy near the absorption peak energy [13].

The experiments were done on Tl-2201 single crystals with $T_c = 25$ and 85 K grown as described in Ref. [10]. The crystals have natural mirrorlike ab-plane surfaces and typical dimensions of $1 \times 1 \times 0.05$ mm^3. The transition temperatures were determined by a magnetization measurement, and the crystal orientations were determined by x-ray Laue diffraction. The Raman spectra reported here were obtained in pseudobackscattering geometry using several lines from Ar^+ and Kr^+ lasers ranging from near infrared (IR) to near ultraviolet (UV). The laser excitation was focused onto spots less than 100 μm in diameter, and the power was reduced to a level which gives power density less than or about 10 W/cm^2 in order to reduce heating by the laser illumination. The laser heating was determined by analyzing Stokes (energy loss) and anti-Stokes (energy gain) spectra, and was found to be from less than 10 to 20 K, depending on the excitation energy we used. The temperatures referred to in this Letter are the nominal temperatures in-

 0031-9007/96/77(21)/4434(4)$10.00

side the cryostat. The spectra were taken by a triple grating spectrometer with a liquid nitrogen cooled CCD detector, and corrected for the spectral response of the spectrometer and the detector. To investigate the resonance property, we further corrected the spectra to get the Raman scattering cross section considering the absorption of the incident and the scattered photons inside the sample, and transmission at the sample surface using the formula given in Ref. [14]. Throughout this study, we used $x'y'$ geometry, where the incident photons were polarized along the direction 45° from the Cu-O bond, and the scattered photons polarized perpendicular to the incident photons were collected. This experimental geometry gives contributions from excitations of B_{1g} and A_{2g} symmetries. In case of cuprate superconductors, B_{1g} is predominant in $x'y'$ geometry. The B_{1g} Raman spectrum, which has a Raman scattering form factor of $d_{x^2-y^2}$ symmetry, gets contributions mainly from the region in **k** space where the magnitude of the $d_{x^2-y^2}$ superconducting gap has maxima. Thus the B_{1g} 2Δ peak position is a good measure of the $2\Delta_{\max}$ in the case of superconductors with $d_{x^2-y^2}$-type pairing.

Figure 1 shows B_{1g} Raman spectra taken from T_c = 85 and 25 K single crystals using high energy (blue) excitation (2.73 eV) and low energy (red) (1.92 eV). The redistributions of the B_{1g} Raman continuum below the critical temperatures (into a 2Δ peak) are clearly observed from both samples. The 2Δ peak is at about 450 cm^{-1} in the T_c = 85 K sample, and at around 75 cm^{-1} in the T_c = 25 K sample. The observed peak position in the T_c = 85 K sample gives $2\Delta/k_BT_c$ a value of 8, which is consistent with the prior work with a similar sample [13,15]. This $2\Delta/k_BT_c$ value is also similar to the values taken from optimally doped $YBa_2Cu_3O_{6+x}$ (Y-123) [4], $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) [5], and $La_{2-x}Sr_xCuO_4$ (La-214) [6]. However, the 2Δ peak in the heavily overdoped sample (T_c = 25 K) was found to occur at $4.2k_BT_c$, which is closer to the conventional BCS value of 3.5. The change of the $2\Delta/k_BT_c$ value upon the doping level was also observed in Bi-2212, and recently from Tl-2201 [16]. The observed change in the $2\Delta/k_BT_c$ value by doping suggests that doping affects the novel superconductivity at a fundamental level rather than just by changing the number of carriers.

One of the major difficulties in the study of the 2Δ peak is that this peak is usually near or under much stronger phonon peaks of which the shapes are also temperature dependent. But, a clean B_{1g} continuum without phonon peaks could be taken staying out of resonance by using low energy (red) excitations for both samples, as seen in Fig. 1. The pure electronic Raman spectrum without phonons and with the lowest residual intensity at low frequency, from the T_c = 85 K sample was obtained with the 1.92 eV Kr^+ laser line.

The low frequency Raman scattering spectra in B_{1g} symmetry from the T_c = 85 K sample using various excitations from near IR (1.65 eV) to near UV (3.05 eV) are shown in Fig. 2. The measured Raman spectra were corrected for optical properties of the sample at a given frequency. From the T_c = 85 K sample, the 2Δ peaks can be clearly seen in all spectra, but with 454.5 and 406.7 nm excitations 500 cm^{-1} phonons are observed on top of the peaks. This makes it difficult to measure the

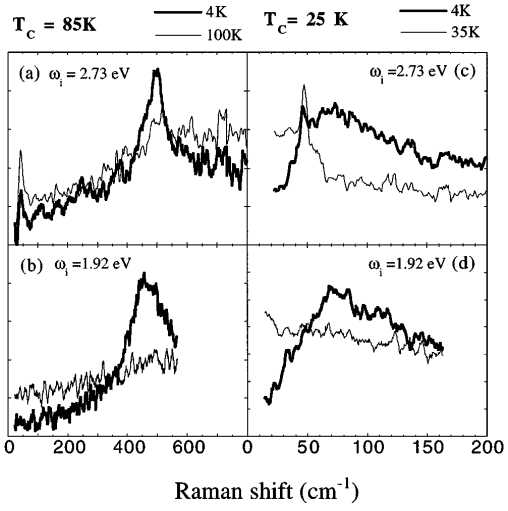

FIG. 1. Low energy Raman spectra in $x'y'$ symmetry from (a) the T_c = 85 K sample, using blue (454.5 nm) excitation, (b) the T_c = 85 K sample, using red (647.1 nm), (c) the T_c = 25 K sample, using blue (454.5 nm, and (d) the T_c = 25 K sample, using red (647.1 nm) excitations. The thick lines denote spectra taken at superconducting states (4 K), and the thin lines at temperatures just above T_c [at 90 K in (a),(b), and 35 K in (c),(d)].

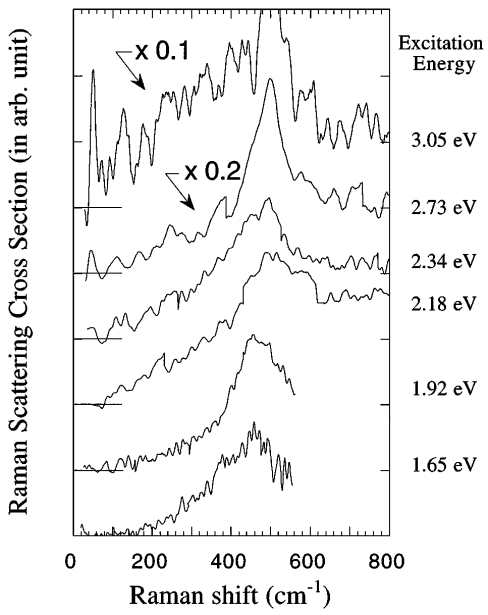

FIG. 2. B_{1g} Raman scattering cross section of the T_c = 85 K sample at 4 K using various excitation lines. The horizontal bars indicate zero intensity level for the curves immediately above the bars.

peak intensity since there is no exact way to separate phonons from the electronic spectra, and this produces relatively large uncertainties in the 2Δ peak intensity with blue and violet excitations. The shape of the low frequency part ($\omega \rightarrow 0$) of the 2Δ peak was found to be dependent on the excitation energy. The low frequency continuum becomes more linear in Raman shift (ω) as we increase the excitation energy. The low frequency line shape change observed in the $T_c = 85$ K sample could result from relatively stronger resonance enhancement for those regions in $\mathbf{k}$ space where the gap has values smaller than the maximum value.

The resonance profiles of the 2Δ peak and the continuum in both samples are presented in Fig. 3. The continuum intensity was measured at high frequencies well above the peak positions where the spectra are flat and featureless, and was further scaled to match the intensity of the 2Δ peak for a comparison. In Fig. 3, it is clearly observed that the 2Δ peak and the continuum gain intensity in a similar way towards an excitation energy of 3.4 eV from both samples, where strong peaks are observed in the optical absorption data. In other words, the 2Δ peak in Tl-2201 resonates towards the optical absorption peak. From the similarity in resonance profiles of the 2Δ peak and the continuum, we can conclude that the 2Δ peak truly results from the redistribution of the continuum rather than comes from a different excitation channel which is opened in the superconducting state.

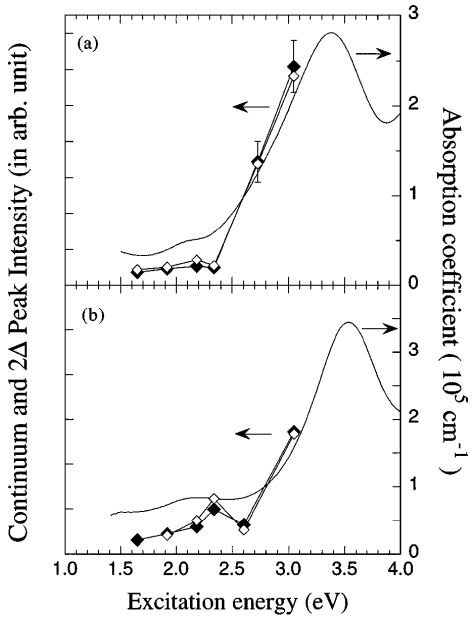

FIG. 3. The resonance Raman excitation profile of the B_{1g} 2Δ peak (solid diamonds) and the continuum (open diamonds, scaled) compared with the optical absorption (from Ref. 12) from (a) the $T_c = 85$ K sample, and (b) the $T_c = 25$ K sample on an absolute energy scale. The connecting lines are guides to the eye. The peak intensities were taken at 4 K in (a) and 2.4 K in (b), and the optical absorption at 300 K.

The Hamiltonian for electromagnetic interactions contains $\mathbf{p} \cdot \mathbf{A}$ and $\mathbf{A}^2$ terms, and the main contributions in Raman scattering come from the first order perturbation from the $\mathbf{A}^2$ term which is nonresonant, and the second order perturbation of the $\mathbf{p} \cdot \mathbf{A}$ term, which is resonant. In the latter case, the resonance occurs when the energy of the intermediate state is higher than the energy of the initial state by the incident photon energy, and is achieved by single photon absorption. Our results imply that the intermediate state for the Raman process of the 2Δ peak may be the same state which produces the peak near 3.4 eV in optical absorption. For a complete understanding, it has great importance to determine the mechanism of the 3.4 eV absorption feature to understand how light couples to the 2Δ peak in Raman scattering.

The band structure calculations based on the local density approximation (LDA) method do not suggest such a peak near 3.4 eV in optical absorption involving a Cu-O band crossing the Fermi energy [17,18]. To explain the resonance profile of the 2Δ peak in such a band picture, a complicated process of higher order than second order Raman scattering mediated by interband transitions may be necessary. In particular, we suggest that the 3.4 eV absorption peak results from strong correlations among carriers which are not included in the framework of LDA.

One simplistic scenario for a strongly correlated system is the following: (1) The optical absorption peak comes from, in the hole picture, transition from the Fermi level to the upper Hubbard band (UHB), and (2) the strong resonance of the 2Δ peak is due to the enhancement of the quasiparticle excitations by the Raman process via interband transitions to the UHB as shown in Fig. 4. The nature of the UHB is suggested to be either doubly occupied Cu $3d$ or doubly occupied O $2p$ band. The Coulomb repulsion on Cu $3d$ is believed to be very strong ($U_d \sim 8$ eV) [19], and the transition energy to the Cu UHB from the Fermi level will be rather high even after a renormalization due to the strong correlation. In doped cuprates, it is widely accepted that additional O holes added to the half-filled antiferromagnetic state form hybridized O $2p$ states, and form singlet states with Cu $3d$ holes [20]. The transition energy to a doubly occupied hybridized O $2p$ state, i.e., O UHB with hybridization, from the Fermi level is estimated to be around 3.2 eV to the leading order using mostly accepted parameters [19]. At least in terms of energy, this model involving the O UHB is a likely candidate for the observed resonance Raman effect and the optical absorption.

On the other hand, the Raman scattering process mediated by an interband transition from Cu $3d$ band to the Fermi level (O $2p$ band) is also possible. The resonance energy in this case, however, is expected to be around 2 eV. As we dope holes from a half-filled insulator, the distinct gap between those two bands no longer exists as a result of a strong correlation between carriers. It is expected that such a transition in an

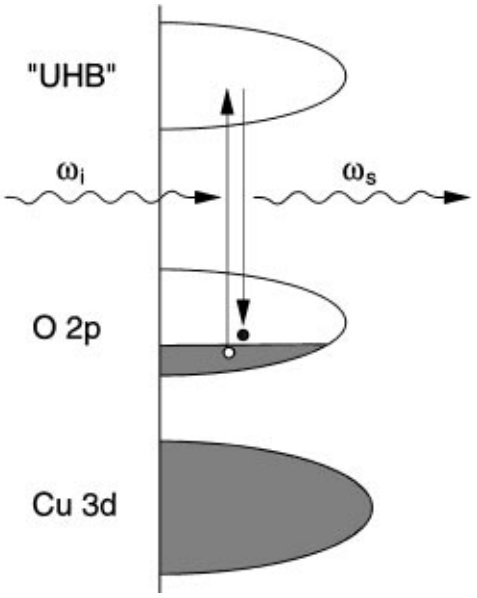

FIG. 4. A schematic diagram for the proposed resonant electronic Raman scattering process. Shaded regions represent filled hole states.

overdoped system loses intensity and sharpness. Small bumps are observed around 2 eV in optical absorption data. The resonace profiles of 2Δ peak also show signs of weak resonace around the bumps. The two-magnon scattering, which is known to result from such transitions, is observed in the metallic phase of some cuprates [21]. We did not observe two-magnon scattering from either sample.

In summary, the $2\Delta/k_BT_c$ values measured from the B_{1g} Raman spectra show a significant difference in the sample with near-optimal doping and the sample with heavy overdoping. By staying out of resonance of phononic scattering, pure electronic Raman spectra were taken using low energy excitations. The peaks from the quasiparticle excitations across the superconducting gap (2Δ peak) and the continua resonate in the same fashion towards optical absorption peaks around 3.4 eV in both samples, which suggests that the 2Δ peak comes from the redistribution of the continuum with the opening of the superconducting gap. A model, based on strongly correlated electronic features, is proposed for the resonance electronic Raman scattering.

We thank M. Karlow and S. L. Cooper for providing the optical absorption data, and A. J. Freeman, D. Novikov, and S. N. Rashkeev for discussions of band structure results. This work has been supported by NSF DMR 91-20000 through the Science and Technology Center for Superconductivity, and NSF DMR 93-20892. M. K. gratefully acknowledges partial support by the University of Illinois Graduate Fellowship.

[1] For a review, see C. Thomson, in *Light Scattering in Solids VI,* edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1991), p. 285.
[2] S. B. Dierker, M. V. Klein, G. W. Webb, and Z. Fisk, Phys. Rev. Lett. **50**, 853 (1983); R. Hackl, R. Kaiser, and S. Schicktanz, J. Phys. C **16**, 1729 (1983).
[3] M. V. Klein and S. B. Dierker, Phys. Rev. B **29**, 4976 (1984).
[4] S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **37**, 5920 (1988); S. L. Cooper, F. Slakey, M. V. Klein, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **38**, 11 934 (1988).
[5] T. Staufer, R. Nemetschek, R. Hackl, P. Müller, and H. Veith, Phys. Rev. Lett. **68**, 1069 (1992).
[6] X. K. Chen, J. C. Irwin, H. J. Trodahl, T. Kimura, and K. Kishio, Phys. Rev. Lett. **73**, 3290 (1994).
[7] T. P. Devereaux, D. Einzel, B. Stadlober, R. Hackl, D. H. Leach, and J. J. Neumeier, Phys. Rev. Lett. **72**, 396 (1994).
[8] C. C. Tsuei, J. R. Kirtley, M. Rupp, J. Z. Sun, A. Gupta, M. B. Ketchen, C. A. Wang, Z. F. Ren, J. H. Wang, and M. B. Bhushan, Science **271**, 329 (1996).
[9] B. S. Shastry and B. I. Shraiman, Phys. Rev. Lett. **65**, 1068 (1990); B. S. Shastry and B. I. Shraiman, Int. J. Mod. Phys. B **5**, 365 (1991).
[10] N. N. Kolesnikov *et al.*, Physica (Amsterdam) **195C**, 219 (1992); N. N. Kolesnikov *et al.*, Physica (Amsterdam) **242C**, 385 (1995).
[11] Y. Kubo, Y. Shimakawa, T. Manako, and H. Igarashi, Phys. Rev. B **43**, 7875 (1991).
[12] M. Karlow, and S. L. Cooper (unpublished).
[13] G. Blumberg, M. Kang, P. Abbamonte, M. V. Klein, M. Karlow, S. L. Cooper, and N. N. Kolesnikov, Physica (Amsterdam) **235C–240C**, 1137 (1994).
[14] D. Reznik, S. L. Cooper, M. V. Klein, W. C. Lee, D. M. Ginsberg, A. A. Maksimov, A. V. Puchkov, I. I. Tartakovskii, and S.-W. Cheong, Phys. Rev. B **48**, 7624 (1993).
[15] R. Nemetschek, O. V. Misochko, B. Stadlober, and R. Hackl, Phys. Rev. B **47**, 3450 (1993).
[16] C. Kendziora and A. Rosenberg, Phys. Rev. B **52**, R9867 (1995); C. Kendziora, R. J. Kelley, and M. Onellion, Phys. Rev. Lett. **77**, 727 (1996).
[17] D. J. Singh and W. E. Pickett, Physica (Amsterdam) **203C**, 193 (1992).
[18] A. J. Freeman and D. Novikov (private communication); S. N. Rashkeev (unpublished).
[19] W. Brenig, Phys. Rep. **251**, 153 (1995), and references therein.
[20] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[21] G. Blumberg, R. Liu, M. V. Klein, W. C. Lee, D. M. Ginsberg, C. Gu, B. W. Veal, and B. Dabrowski, Phys. Rev. B **49**, 13 295 (1994).