RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 4 1 AUGUST 1989

Raman scattering from superconducting gap excitations in $Tl_2Ca_2Ba_2Cu_3O_{10}$ single crystals

M. C. Krantz and H. J. Rosen
IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120

J. Y. T. Wei and D. E. Morris
Physics Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

(Received 21 March 1989)

Raman spectra taken from several well-characterized superconducting $Tl_2Ca_2Ba_2Cu_3O_{10}$ (2:2:2:3) single crystals ($T_c = 105$ K) display the characteristic phonon spectrum of the 2:2:2:3 phase on top of a broad background continuum interpreted as electronic scattering. The electronic scattering continuum decreases substantially below T_c for frequency shifts of smaller than 400 cm^{-1}, indicating the formation of a superconducting gap. The gap does not show the expected abrupt onset but a linearly rising electronic scattering background similar to observations in $YBa_2Cu_3O_7$, possibly indicating a distribution of gaps or the presence of electronic excitations within the gap.

Many questions about the nature of the pairing mechanism and the nature of the superconducting gap in the new high-temperature superconductors remain open. Significant experimental effort has been spent on these questions. Gap parameters derived from tunneling[1] and infrared reflectivity (IR) data[2] differ and so it is not possible to determine if the coupling is strong or weak. Determination of the superconducting gap in high-temperature superconductors with electronic Raman scattering has yielded detailed information about the gap structure.[3-8] Results on $YBa_2Cu_3O_7$ (1:2:3) single crystals indicate no abrupt onset of scattering intensity as expected for a Bardeen-Cooper-Schrieffer (BCS) superconductor[9] such as Nb_3Sn (Ref. 10), but a scattering contribution rising linearly with frequency shift. This has been interpreted as a distribution of gaps with "normal electrons" coexisting with the superconducting state. A similar behavior was found in $Bi_2CaSr_2Cu_2O_8$ (2:1:2:2). Interaction between Raman-active zone-center phonons of A_g and B_{1g} symmetry and the electronic continuum during the opening of the gap is indicated by anomalous phonon frequency shifts,[11] line broadening,[12] and Fano line shapes[4] in the 1:2:3 and 2:1:2:2 compounds.[13] Raman spectra of Tl-based high-T_c superconductors have been investigated and intrinsic phonon modes identified,[14-16] but no gap scattering data have yet been presented. Given the many unanswered questions about the superconducting gap and, in particular, the origin of the low-energy linear scattering contribution in the 1:2:3 and 2:1:2:2 compounds, further investigation appears necessary. In this paper, we present the results of a Raman study of the electronic gap scattering in the new Tl 2:2:2:3 superconductors.

The Tl-based high-T_c superconductors are layered perovskites with a body-centered tetragonal structure, space group *I*4/*mmm*. They are nearly identical to the Bi compounds but different from the orthorhombic 1:2:3 structure (space group *Pmmm*) which shows an *a*-*b* inequality and the presence of linear chains. The electronic structure in all three compounds differs significantly as reflected in the varying density of states for corresponding bands and different shapes of the Fermi surfaces.[17-20] Gap scattering in the Tl 2:2:2:3 compound which has the highest T_c (125 K) thus offers the possibility to gain further insights into gap formation. Furthermore, these studies should help to determine if the gap can be quantitatively related to the critical temperature.

In this paper, we present Raman spectra of Tl 2:2:2:3 single crystals between 70 and 1200 cm^{-1} taken between 10 K and room temperature. Single crystals of $Tl_2Ca_2Ba_2Cu_3O_{10}$ were grown by a melt method similar to the one described by Ginley *et al.*[21] Powders of Tl_2O_3, CaO, BaO, and CuO (all 99.9% purity or better) in cation ratio of 2:1:1:2 were mixed and ground by mortar and pestle. The mixture was sealed in gold tubing (0.2 mm thick, 11-mm diameter) with the ends cold welded in air. The firing profile was 950 °C for 30 min, quick cooling to 900 °C, annealing at 900 °C for 1 h, slow cooling (15 °C/h) to 700 °C, followed by furnace cooling. Crystals used for the measurement were a mosaic adhered to the gold by residual melt. The crystals were shiny black squarish platelets, typically $0.5 \times 0.5 \times 0.05$ mm^3 in size and weighing ~ 250 μg. The Raman spectra of the crystals were used to show that the crystalline phase was primarily 2:2:2:3 with small intergrowths of $TlCa_2Ba_2Cu_3O_9$ (1:2:2:3). The 500-cm^{-1} line of the 2:2:2:3 phase was approximately five times more intense than the 520-cm^{-1} mode associated with the 1:2:2:3 material,[15] suggesting that about 80% of the crystal was in the 2:2:2:3 phase. Investigation of the crystals under a microscope showed a smooth surface with only a few terraces in the *a*-*b* plane. The steps produced by these layers, however, were host to small amounts of impurity compounds as evidenced by 1-5-μm crystallites covering less than 0.1% of the surface of the Tl crystal. By taking Raman spectra of samples with different impurity concentrations, the impurity phase was identified as $BaCuO_2$ by its strong Raman modes at 580 and 640 cm^{-1}. Since the surface coverage by these impurity crystals is small ($< 0.1\%$), their contribution to the electronic Raman scattering is believed to be negligible.

The Raman data were taken with a 0.64-m *F*/6 single monochromator and detected with an intensified diode array. The samples were excited with a single-mode 514.5-nm argon laser tuned to a prominent absorption line of an I_2-vapor cell that was inserted in the path of the scattered beam to suppress elastically scattered light. The crystals were excited at a 60° angle of incidence with the s polarization parallel to the edges of the crystal. The scattered light was collected at 90° to the incident radiation with parallel polarization. The entrance slit was set for 10-cm^{-1} resolution. The crystals attached to gold foils as-grown were about 0.05 mm thick with the c axis normal to the surface. They were mounted in a helium-flow cryostat under He exchange gas and one crystal at a time was illuminated with a laser power density of less than 10 W/cm^2. The temperature increase in the focal region was estimated to be less than 10 K.

Figure 1 shows the results of Meissner susceptibility measurements (constant field cooling) obtained from the $Tl_2Ca_2Ba_2Cu_3O_{10}$ (2:2:2:3) single crystal. This indicates a superconducting transition temperature of ~105 K. Figure 2 shows Raman spectra of the 2:2:2:3 crystal between 70 and 1200 cm^{-1} for 10, 50, 80, 110, and 300 K taken in (x,x) polarization to select A_{1g} and B_{1g} symmetry. The peaks of the phonon spectra are suppressed in order to emphasize the electronic scattering and its temperature dependence. The room-temperature spectrum shows an inelastic scattering continuum of nearly constant strength that extends beyond 2000 cm^{-1} (not shown). Superimposed on this background (but embedded in the absorption features produced by the I_2-vapor cell) is the characteristic phonon spectrum of 2:2:2:3; the strong 500-cm^{-1} A_{1g} mode and the 230-cm^{-1} B_{1g} mode are clearly visible. The sharp peaks at 212, 424, 636, 848, and 1060 cm^{-1} are due to I_2-vapor luminescence lines, and the strong peaks at 580 and 640 cm^{-1} are caused by minute amounts (<0.1% surface coverage) of $BaCuO_2$ surface impurities that produce large Raman signals due to their large Raman cross sections and the greater penetration depth of the laser light. The inelastic scattering continuum between 700 and 2000 cm^{-1} (shown only to 1200 cm^{-1}) remains constant at all temperatures measured. Below T_c, the electronic continuum is redistributed as low-energy scattering intensity is shifted to the region between 300 and 700 cm^{-1}. This is shown more clearly in Fig. 3 in the form of difference spectra to the 110-K scattering signal. By subtracting the 110-K spectrum from the 80-, 50-, and 10-K spectra, the superimposed

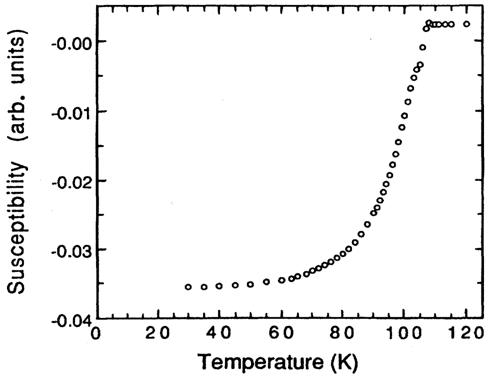

FIG. 1. Temperature dependence of the Meissner susceptibility (constant field cooling) of the $Tl_2Ca_2Ba_2Cu_3O_{10}$ single crystal showing a superconducting transition temperature of 105 K.

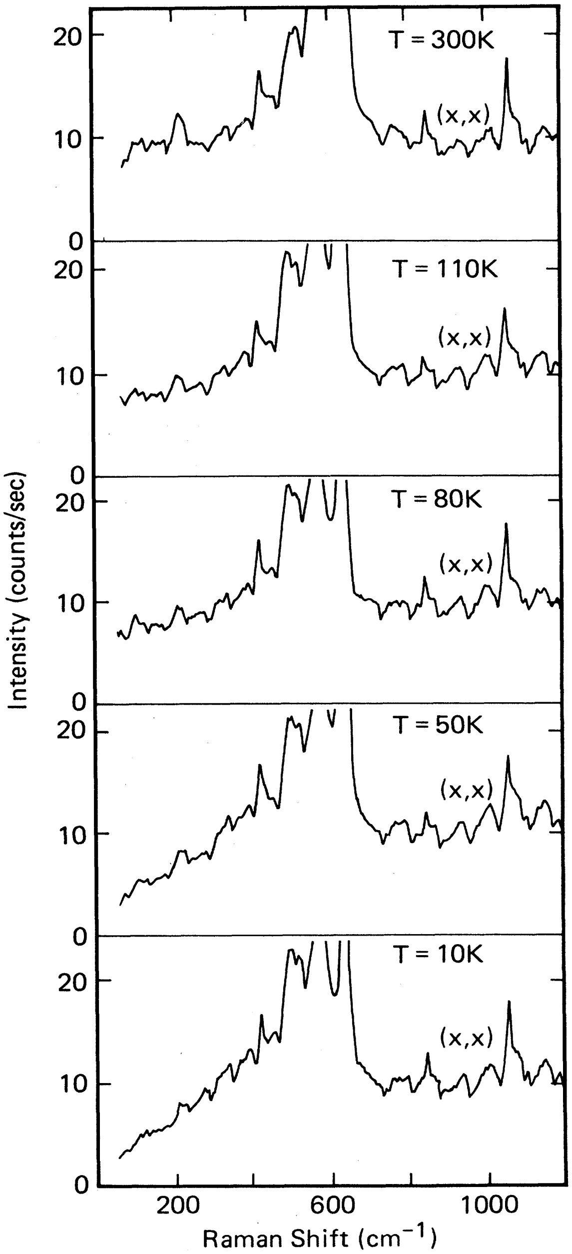

FIG. 2. Raman spectra of the superconducting $Tl_2Ca_2Ba_2Cu_3O_{10}$ single crystal in (x,x) polarization $(A_{1g}+B_{1g})$ showing the redistribution of electronic scattering below T_c. Phonon peaks produced by small amounts of $BaCuO_2$ are truncated to emphasize the temperature dependence of the electronic scattering continuum. At low temperatures (10 and 50 K) the scattering background decreases nearly linearly with frequency, approaching zero at low frequency. At higher temperature (80 K) the slope decreases, giving substantial scattering at low frequency.

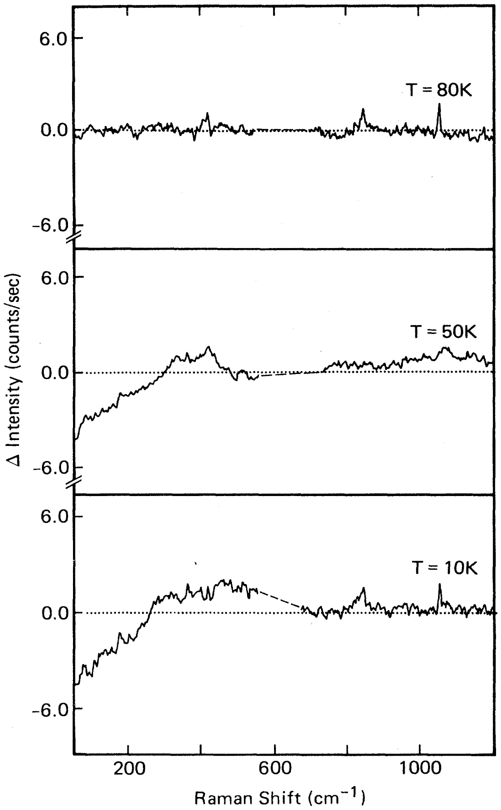

FIG. 3. Polarized (x,x) Raman spectra of the $Tl_2Ca_2Ba_2Cu_3O_{10}$ single crystal at 80, 50, and 10 K after subtraction of the 120-K spectrum. The phonons are suppressed making the redistribution of the electronic scattering continuum more apparent. The frequency of the zero crossing increases with temperature and can be interpreted as gap energy.

phonon spectra and absorption features introduced by the I_2-vapor cell are removed, and the redistribution of the electronic scattering continuum is seen more clearly. The 80-K spectrum shows no redistribution above the noise limit. At 50 K, gap formation and redistribution of electronic states become apparent below 540 cm^{-1}. As the continuum scattering is suppressed at low frequencies, a broad peak forms at higher energy with a center of mass at 390 cm^{-1} and a linewidth of approximately 180 cm^{-1}. At 10 K, the electronic scattering at low frequency is further depressed, with substantial redistribution into a broad peak centered at 460 cm^{-1}, with an increased linewidth of 250 cm^{-1}. Similar peaks observed in Y 1:2:3 and Bi 2:1:2:2 have been interpreted as arising possibly from the breaking of superconducting pairs. Unlike a BCS-type superconductor, where an abrupt onset of electronic scattering at 2Δ is expected below T_c,[9] we observe a scattering background which increases linearly with a frequency shift from 70 to 300 cm^{-1} at the lowest temperatures. This linear background is consistent with similar observations in Y 1:2:3 and Bi 2:1:2:2, and possibly indicates the presence of relatively low-lying electronic excitations in the superconducting state. It is important to note, however, that our results are consistent with a gap in the excitation spectrum. At low temperatures (~10 K), the scattering background extrapolates to nearly zero as the Raman shift decreases (Fig. 2), indicating partial or complete absence of low-lying states. This is consistent with the absence of a measurable linear $\gamma(0)$ contribution to the low-temperature specific heat of Tl 2:2:2:3 single crystals which were synthesized by an identical method, and measured below 11 K (Ref. 22). As the temperature is increased, the slope of the scattering background decreases, and its (extrapolated) value at zero-frequency shift increases, which suggests that low-lying excited states are becoming occupied. However, the increase of the scattering at low shift begins at relatively low temperatures. By 80 K (about $\frac{3}{4} T_c$), the scattering is nearly as great as at 110 K (above T_c), although according to BCS, the gap size would have reached about half its low-temperature value.

It is interesting to compare these results on Tl 2:2:2:3 with the ones obtained for Y 1:2:3 and Bi 2:1:2:2 single crystals.[4-8] The overall features in these spectra are quite similar at 10 K, with an almost linear depleted low-frequency region and a peak at high frequencies that has been associated with pair breaking. Although a theoretical understanding of this redistribution is far from complete, we can make a comparison of the frequency of the pair-breaking peak in these materials. The positions of the A_{1g} pair-breaking peak at 15 K have been reported to be 340 and 320 cm^{-1} in Y 1:2:3 (T_c = 90 K) and Bi 2:1:2:2 (T_c = 84 K), respectively. Our results, with a 10-K pair-breaking peak at 460 cm^{-1}, indicate a monotonic behavior with reasonable scaling with the superconducting transition temperature of 105 K, given the uncertainties in determining the peak energy. If one interprets the gap as the crossover point where the electronic scattering remains unchanged during gap formation below T_c, our result of about 280 cm^{-1} is consistent with the BCS gap parameter $2\Delta = 3.5k_BT_c$ for weak coupling. The temperature dependence of the gap shows a gradual increase in the redistributed spectral weight, unlike the relatively rapid opening of the gap below T_c predicted by BCS theory. The apparent pair-breaking peak shifts to higher frequency as more scattering intensity is redistributed with the opening of the gap.

Electronic structure calculations on the Bi 2:1:2:2 and Tl 2:2:2:3 compounds show a significant number of states at the Fermi energy for the Cu d and O p bands in the Cu-O planes, but very few states in the bridging O p bands, and even less in the O p and Tl s bands of the Tl-O layers. Despite very similar crystal structures, the electronic structure[20] in Tl-based 2:1:2:2 and 2:2:2:3 compounds differs substantially from that of the Bi-based 2:1:2:2 compound.[19] The latter shows significant numbers of states present in all bands, including the ones associated with the Bi-O layers. The similar Raman gap scattering in the two compounds after scaling with T_c and, in particular, the strength of the scattering continuum in the Tl crystal, suggest that the electronic scattering may not significantly involve states in the Bi-O or Tl-O layers. This conclusion, however, is based on model calculations of idealized structures, which is contrary to some recent photoemission studies.[23]

In conclusion, we have observed the gap structure of Tl 2:2:2:3 single crystals by investigation of their electronic scattering. Below T_c, the broad constant scattering continuum redistributes into a linearly rising low-frequency component and a broad high-frequency peak, which has been attributed to the breaking of superconducting pairs. This redistribution is similar to that previously observed in Y 1:2:3 and Bi 2:1:2:2 compounds and may be indicative of a distribution of superconducting gaps in these materials. Approximate scaling of the frequency of the pair-breaking peak with T_c is observed in Y 1:2:3, Bi 2:1:2:2, and Tl 2:2:2:3.

The authors would like to acknowledge helpful discussions with R. M. Macfarlane and S. P. S. Parkin. D.E.M. wishes to express his appreciation for the encouragement and support of L. W. Alvarez, R. A. Muller, and P. J. Oddone. Work at the Lawrence Berkeley Laboratory was supported in part by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

---

[1] J. S. Tsai, I. Tacheuchi, J. Fujita, T. Yoshitake, S. Miura, S. Tanaka, T. Terashima, Y. Bando, K. Iijima, and K. Yamamoto, Physica C **153-155**, 1385 (1988); M. Lee, D. B. Mitzi, A. Kapitulnik, and M. R. Beasley, Phys. Rev. B **39**, 801 (1988).

[2] G. A. Thomas, H. K. Ng, A. J. Millis, R. N. Bhatt, R. J. Cava, E. A. Rietman, D. W. Johnson, G. P. Espinosa, and J. M. Vandenberg, Phys. Rev. B **36**, 846 (1987); D. A. Bonn, J. A. Greedan, C. V. Stager, T. Timusk, M. G. Doss, S. L. Herr, K. Kamaras, and D. B. Tanner, Phys. Rev. Lett. **58**, 2249 (1987).

[3] A. V. Bazhenov, A. V. Gorbunov, N. V. Klassen, S. F. Kodakov, I. V. Kukushkin, V. D. Kalakovskii, O. V. Misochko, V. B. Timofeev, L. I. Chernichova, and B. N. Shepel, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 32 (1987) [JETP Lett. **46**, 32 (1987)].

[4] S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **37**, 5920 (1987).

[5] R. Hackl, W. Gläser, P. Müller, D. Einzel, and K. Andres, Phys. Rev. B **38**, 7133 (1988).

[6] 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).

[7] A. Yamanaka, T. Kimura, F. Minami, K. Inuoe, and S. Takekawa, Jpn. J. Appl. Phys. **27**, L1902 (1988).

[8] F. Slakey, M. V. Klein, S. L. Cooper, E. D. Bukowski, J. P. Rice, and D. M. Ginsberg (unpublished).

[9] M. V. Klein and S. B. Dierker, Phys. Rev. B **29**, 4976 (1987).

[10] S. B. Dierker, M. V. Klein, G. W. Webb, and Z. Fisk, Phys. Rev. Lett. **50**, 853 (1983).

[11] R. M. Macfarlane, H. J. Rosen, and H. Seki, Solid State Commun. **63**, 831 (1987).

[12] M. C. Krantz, H. J. Rosen, R. M. Macfarlane, and V. Y. Lee, Phys. Rev. B **38**, 4992 (1988).

[13] G. Burns, G. V. Chandrashekhar, F. H. Dacol, and P. Strobel, Phys. Rev. B **39**, 775 (1989).

[14] M. C. Krantz, H. J. Rosen, R. M. Macfarlane, and V. Y. Lee, Phys. Rev. B **38**, 11 962 (1988).

[15] K. F. McCarty, D. S. Ginley, D. R. Boehme, R. J. Baughman, and B. Morosin, Solid State Commun. **66**, 217 (1988).

[16] M. C. Krantz, H. J. Rosen, R. M. Macfarlane, V. Y. Lee, and R. Savoy, Solid State Commun. **69**, 209 (1989).

[17] S. Massida, J. Yu, and A. J. Freeman, Phys. Lett. A **122**, 198 (1987).

[18] A. J. Freeman, J. Yu, S. Massida, and D. D. Koellig, Physica B **148**, 2120 (1987).

[19] S. Massida, J. Yu, and A. J. Freeman, Physica C **152**, 251 (1988).

[20] J. Yu, S. Massida, and A. J. Freeman, Physica C **152**, 2732 (1988).

[21] D. S. Ginley *et al.*, Physica C **152**, 233 (1988).

[22] J. S. Urbach, D. B. Mitzi, A. Kapitulnik, J. Y. T. Wei, and D. E. Morris, Phys. Rev. B **39**, 12 391 (1989).

[23] H. M. Meyer III, T. J. Wagener, and J. H. Weaver, Phys. Rev. B **39**, 7343 (1989).