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Gap anisotropy and phonon self-energy effects in single-crystal $YBa_2Cu_3O_{7-\delta}$

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We report a Raman scattering investigation of superconducting gap anisotropy in single-crystal $YBa_2Cu_3O_{7-\delta}$. Gap anisotropy is investigated by studying the peak in the low-temperature Raman continuum in various symmetries. Roughly a 35% difference in the energy of this peak is observed between different symmetries, suggesting the presence of substantial gap anisotropy. Anisotropy is further evidenced by the damping behavior of the 340-cm^{-1} Raman-active phonon below T_c, which displays increased attenuation due to phonon-induced pair breaking. The temperature dependence of this attenuation is consistent with a $T=0$ pair-breaking peak which is much larger than the 340-cm^{-1} phonon in certain regions of the Fermi surface.

Many of the recent experimental studies of $YBa_2Cu_3O_{7-\delta}$ have been devoted to understanding the nature of the superconducting gap in this compound. Unfortunately, even an identification of the pairing strength in $YBa_2Cu_3O_{7-\delta}$ has been obscured by the diversity of gap parameters ($r=2\Delta/k_BT_c$) reported for this material. For example, while infrared reflectivity measurements[1-3] have generally afforded gap parameters which are consistent with weak-coupling Bardeen-Cooper-Schrieffer (BCS) theory ($r\sim3.5$), tunneling measurements[1,4-6] exhibit gap parameters which are well within the strong-coupling regime ($r\sim4.8$). More recently, a theoretical analysis of the softening of certain Raman-active[7-9] and infrared-active[10] phonons below T_c has concluded that $YBa_2Cu_3O_{7-\delta}$ is in the strong-coupling limit.[11] This conclusion is based on the assumption that the renormalized phonons have energies larger than the superconducting gap, $\hbar\omega>2\Delta$ ($T=0$).

In this paper, we present a Raman scattering study of the superconducting gap in single-crystal $YBa_2Cu_3O_{7-\delta}$, in an attempt to understand the conflicting results listed above. The efficacy of using this technique to probe the superconducting gap has been demonstrated in polycrystalline[12,13] and single-crystal[9] samples of $YBa_2Cu_3O_{7-\delta}$. The present Raman scattering investigation extends these results to the study of the symmetry properties of 2Δ. Our data provide evidence for substantial gap anisotropy in $YBa_2Cu_3O_{7-\delta}$, and thus may afford insight into the structure of the superconducting gap. Furthermore, in addition to the phonon frequency renormalization which has been observed earlier below T_c,[7-10] we present new evidence that superconductivity dramatically affects the lifetime of one of the observed Raman-active phonons. The damping behavior of this phonon below T_c is consistent with possible gap anisotropy in $YBa_2Cu_3O_{7-\delta}$.

The $YBa_2Cu_3O_{7-\delta}$ samples used in this study were pure-phase single crystals having narrow transition temperatures near $T_c=90$ K. The preparation of these samples has been described elsewhere.[9] Raman scattering measurements on $YBa_2Cu_3O_{7-\delta}$ single crystals were performed in a near backscattering geometry, with light polarized in the *a-b* plane. A number of scattering geometries were studied in this investigation, including polarized (**y**,**y**) and (**y**′,**y**′) [$\mathbf{y}=(0,1,0)$; $\mathbf{y}'=(1/\sqrt{2})(1,1,0)$] geometries and depolarized (**y**,**x**) and (**y**′,**x**′) [$\mathbf{x}=(1,0,0)$; $\mathbf{x}'=(1/\sqrt{2})(-1,1,0)$] geometries. Considered within the *tetragonal* point group, these geometries allow coupling to $A_{1g}+B_{1g}$, A_{1g}, B_{2g}, and B_{1g} symmetries, respectively.

Figure 1 illustrates the 300-K Raman scattering spectra of single-crystal $YBa_2Cu_3O_{7-\delta}$ in a number of scattering geometries. Each dashed line shown in Fig. 1 defines the zero intensity level for the spectrum directly above it. The

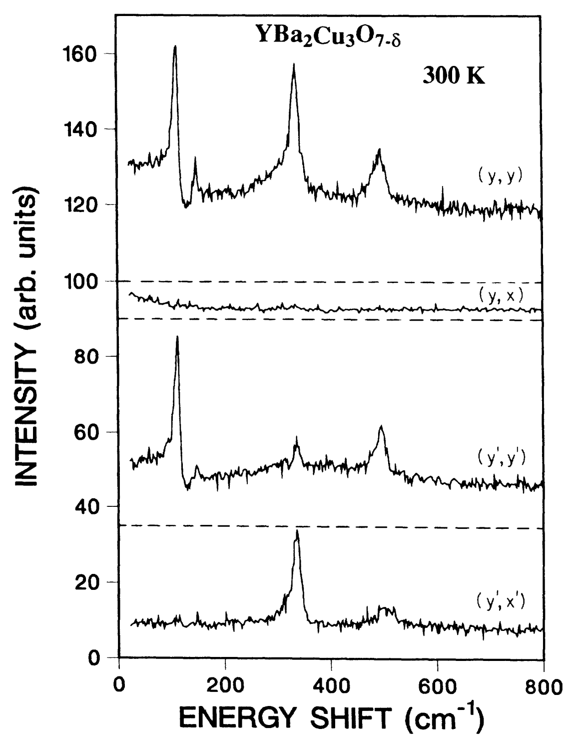

FIG. 1. 300-K spectra of single-crystal $YBa_2Cu_3O_{7-\delta}$ for various scattering geometries, including (**y**,**y**) [$A_{1g}+B_{1g}$ (tetragonal)], (**y**,**x**) (B_{2g}), (**y**′,**y**′) (A_{1g}), and (**y**′,**x**′) (B_{1g}). Each dashed line indicates the zero-intensity level for the spectrum immediately above it. Resolution: 4 cm^{-1}.

top, (y,y) ($A_{1g}+B_{1g}$), spectrum demonstrates a number of optical phonon peaks, as well as an intense electronic background which strongly interferes with the optical phonons at 116 and 340 cm^{-1}.[9] These interference effects are reflected in the asymmetric line shapes associated with the 116 and 340 cm^{-1} phonons, as well as in the "antiresonance" evident on the high-energy side of the 116-cm^{-1} mode. The 340-cm^{-1} phonon is particularly notable in that it switches to the *depolarized* (y′,x′) spectrum upon rotating the incidence polarization by 45° [see (y′,y′) and (y′,x′) in Fig. 1]. This suggests that, within the tetragonal point group, the 340-cm^{-1} phonon transforms according to the B_{1g} representation, while all of the other Raman-active phonons have A_{1g} symmetry.[14]

Figure 1 also illustrates that the electronic continuum background has both A_{1g} [(y′,y′)] and B_{1g} [(y′,x′)] contributions, as may be observed by comparing the background levels of the four spectra shown in Fig. 1. Indeed, the interference effects associated with the 116 cm^{-1} A_{1g} and 340 cm^{-1} B_{1g} phonons confirm that the electronic continuum has both A_{1g} and B_{1g} symmetries, since phonons only interfere with a continuum of like symmetry. Note also that the B_{2g} [(y,x)] spectrum manifests a negligible electronic continuum contribution, while the $A_{1g}+B_{1g}$ [(y,y)] background is simply the sum of the (y′,y′) and (y′,x′) contributions.

Figure 2 shows the (y′,y′) (A_{1g}) and (y′,x′) (B_{1g}) spectra well below T_c, allowing us to separately examine the effects of the superconducting gap on the A_{1g} and B_{1g} contributions to the electronic continuum. The electronic continuum in both these symmetries displays a loss of scattering strength at low energies, as electronic scattering below 2Δ is suppressed by the opening gap. As reported earlier,[9] this suppression is incomplete, as evidenced by the residual low-energy electronic scattering present in both spectra of Fig. 2. Furthermore, a peak in the continuum, which is believed to arise from the direct excitation of superconducting quasiparticles above the gap (2Δ), is apparent in both symmetries. It is evident in Fig. 2 that the pair-breaking peak in the B_{1g} spectrum occurs at roughly a 35% larger energy than is observed in the A_{1g} spectrum. Specifically, the A_{1g} continuum is observed to peak near the 340-cm^{-1} B_{1g} phonon, while the B_{1g} continuum peaks well above the B_{1g} phonon, at roughly 530 cm^{-1}. Additionally, in the 15-K B_{1g} spectrum, the suppression of the continuum intensity below its normal-state value is evident at much higher frequencies than is observed in the 15-K A_{1g} spectrum. Note that the (y,y) ($A_{1g}+B_{1g}$) spectrum is simply the sum of the (y′,y′) and (y′,x′) contributions, and, therefore, does not provide independent symmetry information. Furthermore, due to the absence of an electronic continuum in the (y,x) spectrum, no gap structure is observed in this symmetry.

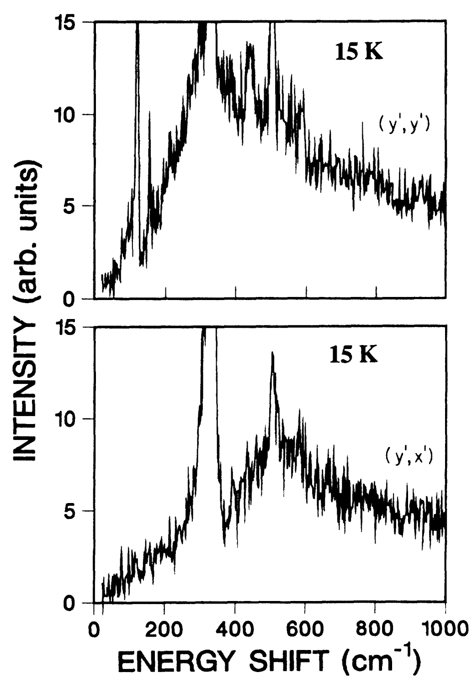

FIG. 2. Polarized [(y′,y′) $-A_{1g}$] spectrum (top) and depolarized [(y′,x′) $-B_{1g}$] spectrum (bottom) well below T_c (15 K) in single-crystal $YBa_2Cu_3O_{7-\delta}$, illustrating the large difference in gap structures in these two symmetries. Resolution: 4 cm^{-1}.

The disparity between the A_{1g} and B_{1g} low-temperature spectra appears to reveal substantial gap anisotropy in $YBa_2Cu_3O_{7-\delta}$. A precise estimate of this anisotropy is difficult, due to the absence of a well-defined gap in these spectra.[9] However, it appears that the pair-breaking energy associated with B_{1g} symmetry is roughly 35% larger than that having A_{1g} symmetry. In order to isolate the origin of this anisotropy, we note that light scatters from superconducting gap excitations through fluctuations in the matrix element, $\gamma_{\mathbf{k}}$, where $\gamma_{\mathbf{k}}$ is related to the inverse effective-mass tensor, $\mu_{\mathbf{k}}^{-1}$. Because deviations of the $YBa_2Cu_3O_{7-\delta}$ structure from D_{4h} symmetry are small, we may decompose this matrix element into irreducible tensor components of the tetragonal space group. Those tensor components relevant to our data are given by

$$|\gamma^{A_{1g}}|^2 = \tfrac{1}{3}\,|\mathrm{Tr}\gamma|^2 , \qquad (1)$$

$$|\gamma^{B_{1g}}|^2 = |\gamma^{xx} - \gamma^{yy}|^2 . \qquad (2)$$

Equations (1) and (2) illustrate that whereas the A_{1g} Raman contribution to the gap represents an average gap value, the B_{1g} spectra should arise from those regions of the Fermi surface in which the inverse effective masses in the x and y directions have the largest differences. Our results consequently suggest that the gap associated with Fermi-surface regions in which $|(\mu^{-1})^{xx} - (\mu^{-1})^{yy}|^2$ is large should be roughly 35% larger than the average (A_{1g}) gap. Detailed Fermi-surface calculations are needed to elucidate the shape of the Fermi surface in $YBa_2Cu_3O_{7-\delta}$. However, because the Fermi surface associated with the Cu-O chains should manifest extremely large effective-mass differences between the x and y directions, it is tempting to speculate that the large gap apparent in the B_{1g} Raman spectrum is related to the Cu-O chains.

The high energy of the B_{1g} pair-breaking peak also appears to be reflected by phonon renormalization effects in the superconducting phase. This is demonstrated in Fig. 3, where we show the phonon spectra of the Fano-coupled

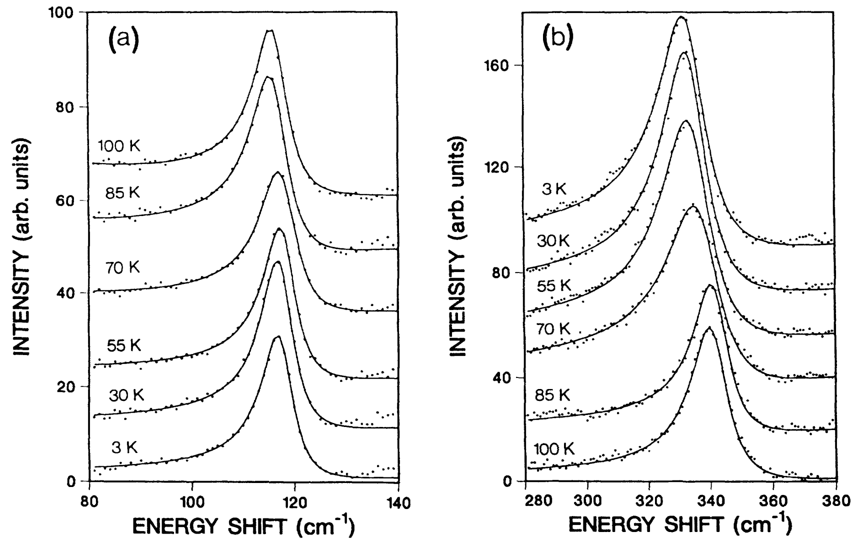

FIG. 3. Temperature dependence of the (a) A_{1g} phonon at 116 cm^{-1} and the (b) B_{1g} phonon at 340 cm^{-1} below T_c. These phonons have been fit to a Fano line shape (solid lines) as described in the text. Note that the temperature increases from bottom to top in (a) and from top to bottom in (b).

116-cm^{-1} A_{1g} (tetragonal) and 340-cm^{-1} B_{1g} (tetragonal) phonons below T_c. The coupling of these two phonons to the electronic continuum is illustrated by fits to a Fano line shape in Fig. 3 (solid line)

$$S(\omega) \propto \frac{[1-\exp(\hbar\omega/k_B T)]^{-1} 2\Gamma\omega(\Omega_a^2-\omega^2)^2}{(\omega_0^2-\omega^2)^2+4\Gamma^2\omega^2}, \quad (3)$$

where Ω_a is the antiresonance frequency, Γ is the coupled-phonon linewidth, and ω_0 is the renormalized phonon frequency. In addition to displaying a Fano line shape, the 340-cm^{-1} phonon manifests an abrupt softening below T_c (between 85-K and 70-K spectra in Fig. 3). This softening has been attributed to phonon self-energy effects, wherein the phonon frequency is screened by the superconducting quasiparticles.[11,14] Additionally, our phonon results indicate an abrupt enhancement in the damping of the 340-cm^{-1} phonon just below T_c (see Fig. 3), which is followed by a decreased damping at still lower temperatures. The behavior of the 340-cm^{-1} phonon linewidth Γ below T_c is illustrated in Fig. 4. These phonon renormalization effects (see Figs. 3 and 4) are much more striking than those observed previously,[9] due to the sharper transition temperatures of the present samples. We attribute the increased phonon damping in the superconducting phase to the presence of a phonon-induced pair-breaking relaxational channel which is allowed for phonons satisfying $\hbar\omega > 2\Delta(T)$. Note particularly that the sharp enhancement, then gradual decrease of the 340-cm^{-1} linewidth below T_c suggests that the "center of mass" of the B_{1g} pair-breaking energy distribution moves *through* the B_{1g} phonon frequency as a function of temperature.[15] The fact that the B_{1g} phonon attenuation does not drop discontinuously, or even significantly, as in the case of a superconductor with a well-defined gap,[15] is presumably due to the absence of a distinct gap in $YBa_2Cu_3O_{7-\delta}$ (see Fig. 2 and Ref. 9). Thus, the temperature dependence of the B_{1g} phonon linewidth below T_c is further confirmation that the B_{1g} pair-breaking energy at $T=0$ peaks at a significantly higher energy than that of the 340-cm^{-1} phonon.

In conclusion, we have presented strong Raman evidence for substantial superconducting gap anisotropy in single crystal $YBa_2Cu_3O_{7-\delta}$. Specifically, the quasiparticle pair-breaking peak in the B_{1g} Raman spectrum appears to occur at a significantly higher energy ($\sim$530 cm^{-1}) than that found in the A_{1g} spectrum ($\sim$340 cm^{-1}). Additionally, in the B_{1g} spectrum suppression of the low-frequency continuum occurs to much higher energies than in the A_{1g} spectrum. These results suggest that the largest gaps are associated with those regions of the Fermi surface which exhibit large reciprocal effective-mass differences between the x and y directions. These re-

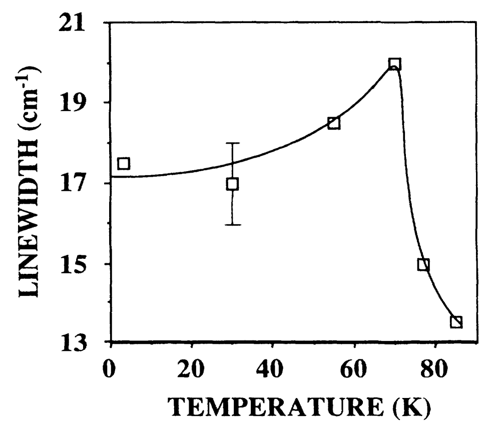

FIG. 4. Observed temperature dependence of the 340 cm^{-1} phonon linewidth Γ below T_c (open squares), illustrating the dramatic damping enhancement below the superconducting transition. The solid line is a guide to the eye.

sults also suggest that the diversity of gap energies observed by different techniques may simply reflect the large gap anisotropy apparent in $YBa_2Cu_3O_{7-\delta}$. Finally, we have also observed phonon self-energy effects below T_c related to the damping behavior of the 340-cm^{-1} Raman-active phonon. This phonon exhibits an abrupt linewidth increase below T_c which is thought to arise from phonon-induced quasiparticle pair breaking. The behavior of this phonon linewidth with temperature below T_c is also consistent with an average B_{1g} pair-breaking energy (at $T=0$) which is significantly larger than the 340-cm^{-1} phonon frequency.

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[1]J. R. Kirtley, R. T. Collins, Z. Schlesinger, W. J. Gallagher, R. L. Sandstrom, T. R. Dinger, and D. A. Chance, Phys. Rev. B **35**, 8846 (1987).

[2]D. A. Bonn, J. E. 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]G. A. Thomas, H. K. Ng, A. J. Millis, R. N. Bhatt, R. J. Cava, E. A. Rietman, D. W. Johnson, Jr., G. P. Espinosa, and J. M. Vandenberg, Phys. Rev. B **36**, 846 (1987).

[4]J. Moreland, J. W. Ekin, L. F. Goodrich, T. E. Capobianco, A. F. Clark, J. Kwo, M. Hong, and S. H. Liou, Phys. Rev. B **35**, 8856 (1987).

[5]I. Iguchi, H. Watanabe, Y. Kasai, T. Mochiku, A. Sugishita, and E. Yamaka, Jpn. J. Appl. Phys. **26**, L645 (1987).

[6]J. R. Kirtley, C. C. Tsuei, S. I. Park, C. C. Chi, J. Rozen, and M. W. Shafer, Phys. Rev. B **35**, 7216 (1987).

[7]R. M. Macfarlane, H. Rosen, and H. Seki, Solid State Commun. **63**, 831 (1988).

[8]A. Wittlin, R. Liu, M. Cardona, L. Genzel, W. König, M. V. Cabanas, and E. Garcia-Alvarado, Solid State Commun. **64**, 477 (1987).

[9]S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **37**, 5920 (1988).

[10]C. Thomsen, R. Liu, A. Wittlin, L. Genzel, M. Cardona, W. König, M. V. Cabanas, and E. Garcia, Solid State Commun. **65**, 219 (1988).

[11]R. Zeyher and G. Zwicknagl, Solid State Commun. **66**, 617 (1988).

[12]A. V. Bazhenov, A. V. Gorbunov, M. V. Klassen, S. F. Kodakov, I. V. Kukushkin, V. D. Kalakovskii, O. V. Misochko, V. B. Timofeev, L. I. Chernyshova, and B. N. Shepel, in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 699; and Pis'ma Zh. Eksp. Teor. Fiz. **46**, 35 (1987) [JETP Lett. **46**, 32 (1987)].

[13]K. B. Lyons, S. H. Liou, M. Hong, H. S. Chen, J. Kwo, and T. J. Negran, Phys. Rev. B **36**, 5592 (1987).

[14]C. Thomsen, M. Cardona, B. Gegenheimer, R. Liu, and R. Simon, Phys. Rev. B **37**, 9860 (1988).

[15]V. M. Bobetic, Phys. Rev. **136**, A1535 (1964).