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Behavior of the Raman continuum and Raman "gap" in $T_c = 60$ K $YBa_2Cu_3O_{7-\delta}$

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Numerous Raman investigations of the 90-K phase of $YBa_2Cu_3O_{7-\delta}$ have revealed broad features at approximately 350 and 500 cm^{-1} in the A_{1g} and B_{1g} symmetries, respectively, which exhibit behavior qualitatively similar to the "gap" redistribution expected of a BCS-like superconductor. We find, however, that in decreasing the oxygen concentration to achieve an untwinned $T_c = 60$ K single crystal the gaplike features do not exhibit straightforward BCS behavior. Rather, the 500-cm^{-1} B_{1g} peak is found to be insensitive to the change in carrier concentration and is found to persist well into the normal state while the A_{1g} peak exhibits significant broadening and no apparent softening. In addition, we present results on the room-temperature phonons and on an anomalous response of the background continuum to incident laser power.

A substantial amount of experimental evidence supports the claim that a characteristic energy (E_c) descriptive of a pairing state exists in the high-T_c superconductors $YBa_2Cu_3O_7$ (93 K) and $Bi_2Sr_2CaCu_2O_8$ (85 K) at approximately 500 cm^{-1} ($\sim$62.5 meV). Initially, Raman investigations revealed a low-temperature evolution of the prominent background continuum below T_c in these materials that was decidedly unlike the thermal dependence expected of a normal metal.[1,2] More detailed examinations of the symmetries of the continuum revealed that the low-energy spectral density of the B_{1g} component of the continuum in both Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O begins to shift to higher energies at $T \sim T_c$ and at 4 K develops into a broad peak at approximately 500 cm^{-1}.[3,4] This shifting of the density of states and the low-temperature peak formation strongly suggest that the 500-cm^{-1} peak denotes the energy for the formation of a pair of quasiparticles. Tunneling experiments on Y-Ba-Cu-O reveal appreciable structure about an energy of 30 meV ($\sim$240 cm^{-1}) in the superconducting state which has been assigned as a possible value of the gap Δ.[5] Further support comes from photoemission results on Bi-Sr-Ca-Cu-O that suggest an energy gap Δ of approximately 30 meV ($\sim$240 cm^{-1}) and reveal a density of states strikingly similar to that evidenced by Raman techniques.[6] Finally, infrared experiments show a low-temperature threshold in the conductivity at 500 cm^{-1} which has been associated with an in-plane energy gap 2Δ (Ref. 7) and a conspicuous and multiply interpreted "knee" in the reflectivity at 435 cm^{-1} (Ref. 8) which has recently been found to persist into the normal state.[9]

Tending to obscure the assignment of the A_{1g} and B_{1g} Raman peaks as straightforward pair-breaking energies is the persistence of continuum scattering in the superconducting state for $T \ll T_c$ at energies well below expected values of the gap. This anomalous character also finds confirmation in various experimental techniques: the zero-bias conductance in $T < T_c$ tunneling experiments on both Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O,[5,10] a density of states within the "gap" seen in low-temperature photoemission experiments,[6] and the recently observed low-energy residual absorptivity in the superconducting state revealed through ir techniques.[11] Cumulatively, the various results suggest that there exists a characteristic energy $E_c \sim 500$ cm^{-1} together with possible excitations within the gap in the high-temperature superconductors having $T_c \sim 90$ K.

In this paper, we examine the behavior of the Raman gaplike peaks in the $T_c = 60$ K phase of Y-Ba-Cu-O in order to determine the sensitivity of these features to the change in T_c. We present evidence that the characteristic energy of 500 cm^{-1} seen as a low-temperature peak in the B_{1g} Raman spectra is insensitive to the carrier concentration and persists well into the normal state. Further, we examine the behavior of the A_{1g} peak and briefly discuss the characteristics of the room-temperature phonon spectra and background continuum.

The $YBa_2Cu_3O_{7-\delta}$ crystals were grown by a flux-growth method and then oxygenated to form the 90-K phase, followed by a further oxygen anneal at a temperature just below the orthorhombic-to-tetragonal transition to convert a 90-K crystal into the untwinned 60-K single crystal in this study.[12] The superconducting transition was less than 15 K wide as determined through dc magnetic susceptibility measurements at fields of 10–20 Oe. The Raman scattering measurements were taken in a pseudobackscattering configuration with the 5145-Å line of an argon-ion laser polarized in the *a-b* plane, and power densities were maintained at approximately 10 W/cm^2 unless otherwise stated. The designation x, y, x', and y' used in the figures refer to the crystalline axis a and b, and the diagonals [110] and [1$\bar{1}$0], respectively. The various scattering geometries allowed for coupling to the *tetragonal* symmetries A_{1g}, B_{1g}, and B_{2g} and are described in detail elsewhere.[13]

The room-temperature spectra of the 60-K phase of the untwinned Y-Ba-Cu-O single crystal are shown in Fig. 1. The dissimilar bond polarizabilities along different crystalline axis for the various phonons require that there be anisotropy of the phonon spectral intensities characteristic of the orthorhombic structure. The 116- and 500-cm^{-1} phonons are found to have stronger intensity when the in-

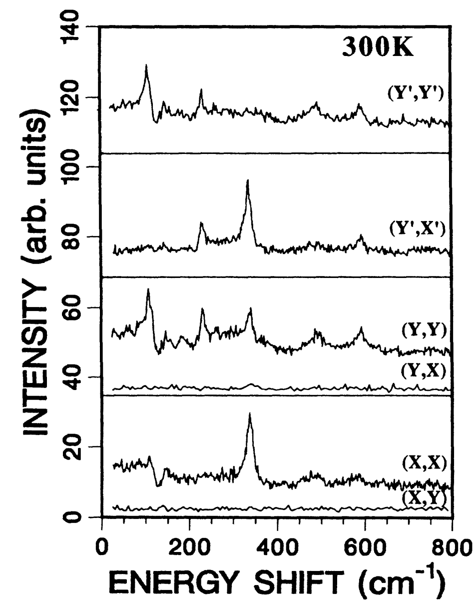

FIG. 1. The 300-K Raman spectra of an untwinned 60-K $YBa_2Cu_3O_{7-\delta}$ single crystal for various scattering geometries. Each solid line marks the zero-intensity level for the spectrum or pair of spectra immediately above it.

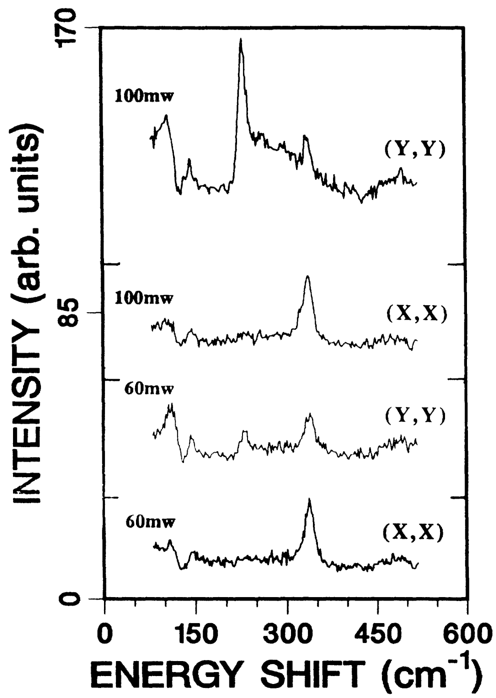

FIG. 2. Room-temperature spectra displaying the sensitivity of the continuum to incident laser power in geometries parallel and perpendicular to the Cu-O chains. The short lines running along the vertical axis indicate the zero-intensity level for the spectrum directly above it.

cident light is polarized along the chains, and the 340-cm^{-1} mode is found to have greater intensity when the light is polarized perpendicular to the chains. This anisotropy of the intensities is identical to results on the 90-K untwinned compound,[14] and indicates that the partial vacancy of the chain oxygen O(1) site does not dramatically affect the bond polarizabilities of the first-order Raman phonons. The vacancies, however, do relax the selection rules sufficiently to allow for the appearance of the nominally Raman-forbidden 220- and 580-cm^{-1} infrared phonons to appear in the spectra.[15] Also evident in Fig. 1 is the prominent background continuum characteristic of the Raman spectra of several high-T_c superconductors.[16] For reasons discussed in previous work,[2] we believe that this continuum constitutes real inelastic scattering over the entire spectral range presented in our data of 20–1000 cm^{-1}.

In Fig. 2 the behavior of the continuum on variation of incident laser intensity is detailed. The spot size was held constant for the 60- and 100-mW spectra yielding power densities of roughly 35 and 60 W/cm^2, respectively. The behavior was found to be reversible, reproducible on all samples examined, and independent of excitation wavelength. Further, the spectra were taken in ambient conditions and the Stokes to anti-Stokes ratios revealed substantial laser heating. The spectra illustrate two distinct characteristics: anisotropic continuum scattering and an anomalous response to incident laser power. The anisotropic background scattering between the a and b crystalline directions is evidenced as a stronger scattering intensity in the geometry parallel to the chains for the 100-mW spectra, and indicates that the chains contribute to the continuum scattering despite the diminished presence of oxygen at the O(1) chain site. Contrasting the anisotropy

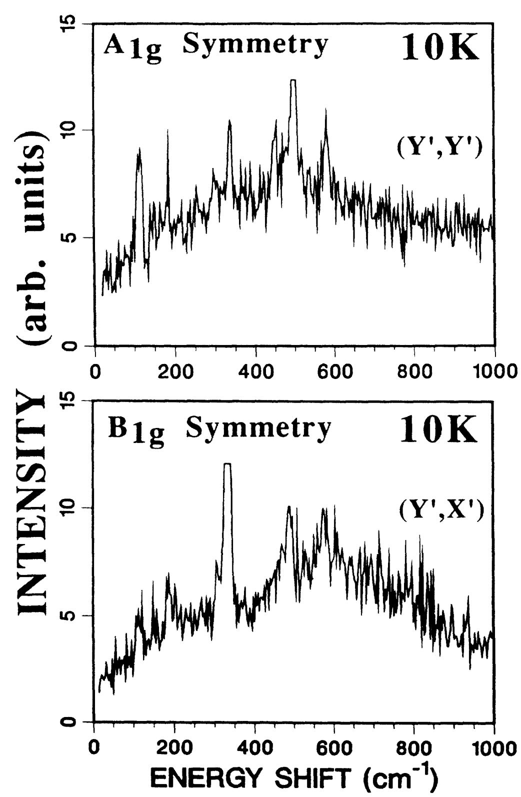

FIG. 3. The 10-K spectra of the 60-K phase of $YBa_2Cu_3O_{7-\delta}$ in the A_{1g} and B_{1g} geometries. The phonons have been truncated to clarify the background features.

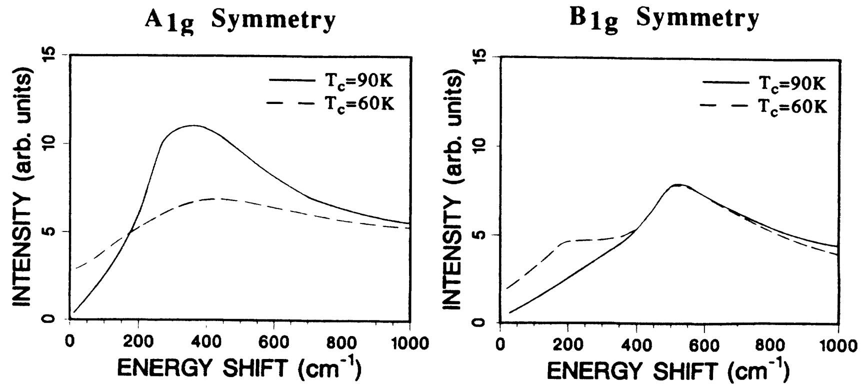

FIG. 4. A comparison of the smoothed approximately 10-K Raman spectra of the 90-K phase (solid line) and the 60-K phase (dashed line) of $YBa_2Cu_3O_{7-\delta}$ in the two distinct symmetries.

evident in the 90-K material,[17] the anisotropy of the 60-K material is clearly evident only for relatively large power densities. This anomalous response of the chains to incident laser power may be a manifestation of a structural alteration upon increased temperature due to the laser heating. However, since the rate for diffusion of oxygen into the O(1) chain site is known to be small,[18] the effect may instead be evidence of a nonlinear optical process in the oxygen-deficient compounds. Current investigations are examining these possibilities in detail.

Illustrated in Fig. 3 are the low-temperature spectra of the A_{1g} and B_{1g} scattering geometries. The A_{1g} spectrum reveals a shallow rise to a broad peak possibly indicating an incomplete suppression of scattering below any moderate coupling value ($2\Delta > 2kT_c$) of the gap for this material. This residual scattering is also observed in the B_{1g} spectrum as a linear rise in the low-energy scattering. The B_{1g} rise is apparently enhanced by the presence of a 200-cm^{-1} shoulder to the broad peak at approximately 500 cm^{-1}. Strikingly, a feature in the ir which has been forwarded as a possible gap value for the 60-K material is conspicuously similar to this 200-cm^{-1} feature.[19] The presence of this low-energy contribution may also be inferred from a previous Raman examination of the 60-K material.[20]

A comparison of the low-temperature features of the smoothed Raman spectra in the $T_c = 90$ K and $T_c = 60$ K phases of Y-Ba-Cu-O is shown in Fig. 4. All the phonon features and temperature dependences have been extracted and the data have been normalized to the high-energy background. The broad B_{1g} 500-cm^{-1} peak exhibits no variation upon change of T_c. Rather, the overall line shape for energies greater than 400 cm^{-1} appears nearly identical. This behavior argues against an assignment of the peak to an electronic-band-structure feature as the increase in the Fermi level effected by the decrease in oxygen stoichiometry would likely shift a band transition. The A_{1g} gaplike feature has broadened substantially but likewise shows no evident decrease in the peak value as might be expected of a straightforward BCS gap. This increased damping is not fully explained by possible increased disorder of the 60-K phase, since the B_{1g} line shape has experienced little broadening. Instead, the substantial decrease in the scattering lifetime of the quasiparticles of A_{1g} symmetry may indicate the augmentation of a scattering mechanism in the 60-K phase that is not disorder induced.

The temperature dependence of the B_{1g} feature in the 60-K phase is elucidated in Fig. 5. Because of the weak signal, it cannot be determined whether any shifting of the spectral weight occurs on formation of the 500-cm^{-1} B_{1g} peak. However, a comparison of the 150–10-K data indicates a suppression of the spectral density in a manner inconsistent with the thermal Bose-factor dependence. The weakness of the signal also precludes a quantitative tracking of the 500-cm^{-1} peak with temperature, though the feature is still resolvable at 100 K, well above T_c for this material. This finding is in agreement with recent results from various experimental techniques. In ir reflectivity

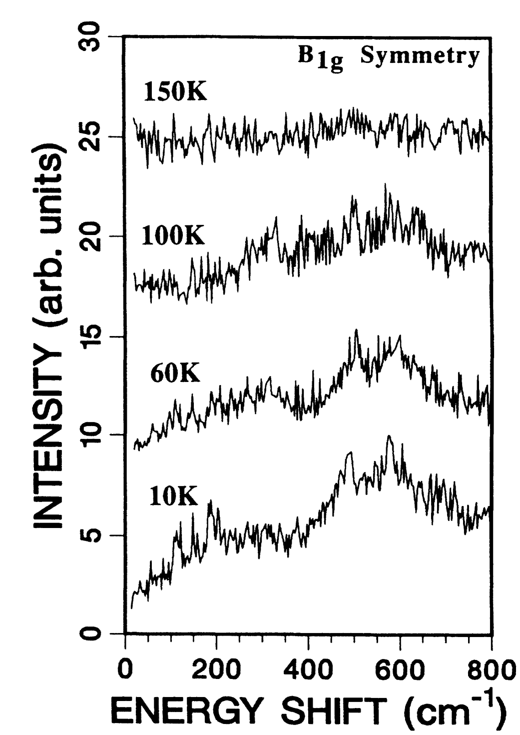

FIG. 5. The temperature development of the B_{1g} continuum with the phonon features subtracted out.

the 435-cm^{-1} "edge" was found both to persist into the normal state and be insensitive to carrier concentration.[9] The NMR experiments of Warren *et al.*[21] show a drop in the Cu(2) relaxation rates at a temperature well above T_c in the 60-K superconductor which they have forwarded as evidence for precursor pairing. Recent Raman results on the $T_c=90$ K phase of Y-Ba-Cu-O have also been interpreted as revealing the persistence of the B_{1g} peak into the normal state.[22] Thus, if $E_c=500$ cm^{-1} is to be considered as a pairing energy, then it is descriptive of pairing in the normal state and it exhibits no significant temperature dependence below 100 K. This would suggest that the characteristic energy of 500 cm^{-1} cannot solely describe the transition toward bulk superconductivity, indicating that an appeal to a gap energy in the superconducting state must still be made. Theoretical descriptions of the high-temperature superconductors that entail two characteristic energies in a manner consistent with these results have recently been forwarded.[23] Randeria, Duan, and Shieh suggest that in a coupling regime descriptive of the high-T_c superconductors where the coherence length ξ_0 is comparable to the interparticle spacing k_F^{-1}, bound pairs could exist at temperatures $T > T_c$; and, for $T \leq T_c$, these particles undergo condensation to bulk superconductivity.

In summary, room-temperature Raman spectra of the 60-K superconductor display anisotropic phonon spectral intensities similar to that of the 90-K superconductor and a Cu(1)-O(1) chain contribution to the background continuum which displays an anomalous sensitivity to incident laser power. The low-temperature data reveal behavior consistent with the formation of a pairing state. Specifically, in both A_{1g} and B_{1g} geometries, the background is found to redistribute in a manner suggesting a shifting of the density of states; and, at low temperatures, broad peaks develop in the two distinct symmetries. The assignment of the B_{1g} peak to a band-structure effect or a BCS-like gap is precluded by the constancy of the peak on variation of the Fermi level from the 90- to 60-K phases and the persistence of the peak into the normal state. The low-temperature peak of A_{1g} symmetry in the 60-K phase exhibits increased attenuation relative to the 90-K phase but shows no apparent softening.

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