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Raman scattering from superconducting gap excitations in single-crystal $YBa_2Cu_3O_{7-\delta}$

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The results of a polarized light scattering study of single-crystal $YBa_2Cu_3O_{7-\delta}$ are presented. Strong interband electronic scattering in $YBa_2Cu_3O_{7-\delta}$ is observed through interference effects with certain phonons. Below T_c, this electronic scattering undergoes a redistribution due to gap formation, which is monitored by a rapid change in the damping rates of the strongly coupled phonons. Our lowest temperature data further indicate the presence of residual electronic scattering well below the expected 2Δ gap onset, suggesting that a continuum of electronic states exists inside the gap.

The newly discovered[1] class of high-temperature superconductors, $MBa_2Cu_3O_{7-\delta}$, has recently undergone intense experimental and theoretical scrutiny, much of which has been devoted to understanding the nature of the superconducting mechanism in these compounds. Two techniques which have been particularly important have included tunneling[2] and far-infrared absorption measurements,[3] which have both been used to study the superconducting gap in these materials. Such experimental characterization of the gap structure in $YBa_2Cu_3O_{7-\delta}$ is essential in order to elucidate the degree to which these important superconductors may be described by simple Bardeen-Cooper-Schrieffer (BCS) theory. Raman scattering offers still another means of directly studying the superconducting gap.[4] Indeed, the utility of this technique for probing gap excitations in these materials has been demonstrated recently on polycrystalline samples.[5]

In this paper, we report the results of a polarized Raman scattering investigation of single-crystal $YBa_2Cu_3O_{7-\delta}$. Our study provides clear evidence of superconducting gap excitations, which are observed with sufficient strength to observe the gap's temperature development. Among the new results provided by our data is evidence that a residual electronic continuum of states remains well inside the gap (down to energies $\sim k_BT_c/4$), down to the lowest temperatures observed ($\sim T_c/30$). In addition, newly observed evidence for strong electron-phonon coupling is presented in our study, manifested as asymmetric Fano line shapes observed for certain phonon modes. These strongly coupled phonons are particularly notable in that they sensitively gauge the redistribution of electronic spectral weight below T_c.

Each sample of $YBa_2Cu_3O_{7-\delta}$ used in this study was a pure-phase single crystal having a superconducting transition which was both high ($T_c = 90$ K) and narrow (14.9 K transition in the zero-field-cooled magnetic susceptibility). The preparation technique is essentially that recommended by Schneemeyer *et al.*[6] Crystals were made from high-purity chemicals which were mixed, then heated in a box furnace in air at a constant rate. The high, sharp transition temperature crystals were obtained by next annealing these samples in flowing oxygen. The resulting crystals are thin platelets presenting (001) faces, as confirmed by x-ray diffraction. For our scattering experiments, we used the surfaces which had been exposed to the oxygen during the annealing process.

Raman scattering measurements on these single crystals were made using the polarized 5145 and 4765 Å lines of an argon laser. Measurements were made in a near backscattering geometry, with the incident light polarized perpendicular to the c axis. This allowed a coupling to A_g symmetry excitations in the polarized (xx) spectrum, and to B_{1g} symmetry excitations in the depolarized (xy) spectrum. Scattered light was dispersed using a triple stage monochromator, and a liquid-helium cryostat was used for temperature control. Small power densities of roughly 10 W/cm^2 were used in order to minimize laser heating, and to prevent boiling of the superfluid liquid helium during low-temperature (3 K) runs.

Figure 1(a) illustrates the Raman spectra just above T_c. The upper spectrum shows that three phonons previously associated with the superconducting $YBa_2Cu_3O_{7-\delta}$ structure[7,8] are clearly evident at 340, 440, and 504 cm^{-1}. These phonons are identified as having A_g symmetry from their absence in the depolarized spectrum [bottom spectrum, Fig. 1(a)]. Additionally, we observe phonons at 116 and 150 cm^{-1}, which we ascribe to the A_g phonons of Cu(2) and Ba expected in orthorhombic $YBa_2Cu_3O_{7-\delta}$. These latter mode assignments are motivated in part by the sharpness of the 150 cm^{-1} phonon, which we expect to result from the weak electron-phonon coupling associated with this Ba mode. The assignment of the 116 cm^{-1} mode to Cu(2) breathing vibrations is also quite consistent with the *strong* electron-phonon coupling expected of this mode, as we will now discuss.

The most striking features associated with the 90 K spectra shown in Fig. 1(a) are the conspicuous asymmetric Fano line shapes associated with the A_g phonons at 116 and 340 cm^{-1}. Such line shapes evolve from Auger-like processes, wherein a broad continuum interacts with a discrete phonon state, providing a "radiationless" decay channel for the phonon.[9] The most dramatic manifestation of this interaction is an energy for which the transition probability of the coupled system is zero, resulting in an exact cancellation between phonon and continuum Raman amplitudes. This interference gives rise to the dip on the high-energy sides of the 116 and 340 cm^{-1} phonons in

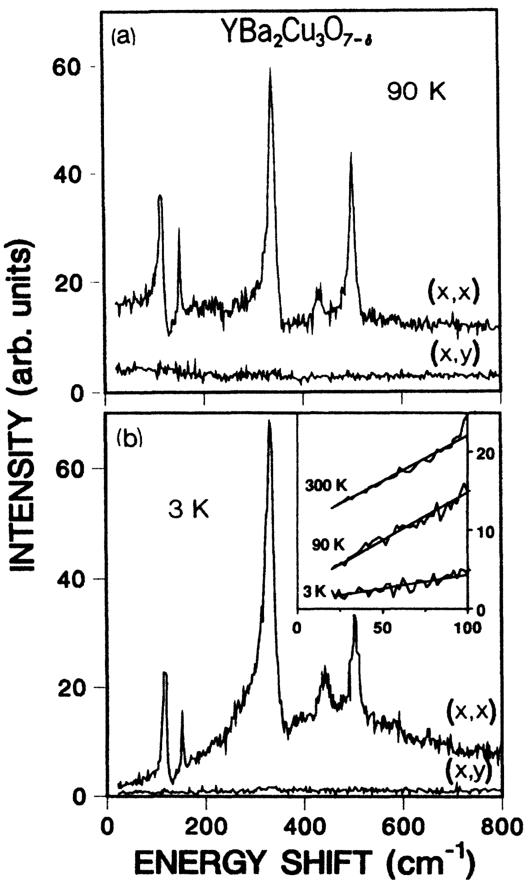

FIG. 1. Polarized [$(x,x)=A_g$] and depolarized [$(x,y)=B_{1g}$] spectra for single-crystal $YBa_2Cu_3O_{7-\delta}$ at (a) 90 K, and (b) 3 K. The inset shows the small frequency linear regime, after dividing by the thermal Bose factor, at 3 K, 90 K (offset by 2 units), and 300 K (offset by 10 units).

Figs. 1(a) and 1(b).

These large interference effects result from strong electronic scattering in $YBa_2Cu_3O_{7-\delta}$ which is also directly observable in the spectra, and which we attribute to interband scattering similar to that observed in the $A15$ compounds.[10] The possibility that the observed continuum is due to two-phonon processes may be excluded, as the temperature dependence of the continuum between 300 and 90 K is fully consistent with a single excitation process. Furthermore, earlier ir and Raman results[11] have shown this continuum to extend beyond 3000 cm^{-1}, well beyond the energy range of one- or two-phonon contributions. The large scattering strength of the electronic continuum is somewhat surprising, but inasmuch as $YBa_2Cu_3O_{7-\delta}$ often behaves like a heavily doped *p*-type semiconductor, we might better understand its origin by considering previous studies of heavily doped *n*-type SiC.[12] In the latter system, strong intervalley scattering of electrons by the short-range part of the potential from the donors produces a continuum, which strongly interferes with Raman-active phonons. An approximate sum rule holds, which states that the mean energy for the continuum is some average of the matrix element of the intervalley potential.[13] The resulting electronic scattering cross section per electron is the Thomson cross section r_0^2, multiplied by the square of the appropriate projection of the reciprocal effective-mass tensor difference $\delta\mu$ onto photon polarization vectors. Here $\delta\mu$ equals the difference between the μ of one valley and that of another. Therefore, in the case of $YBa_2Cu_3O_{7-\delta}$, we attribute the continuum scattering to hole scattering from the Fermi surface of the Cu(2)-O(2,3) planes to that of the Cu(1)-O(1) chains. The latter would be roughly described as parallel sheets, and the former roughly described as cylinders. The differences between projections of μ would therefore be considerable, resulting in large electronic scattering intensities.

Perhaps the most important result of the observed Fano resonances, however, is that they provide a definitive illustration that electron-phonon interaction effects are important in this material. Specifically, we believe that the strong coupling apparent in these modes arises from a strong modulation of the Cu($d_{x^2-y^2}$)-O(p) orbital overlap by the bond-bending A_g Cu(2) and A_g O(2)/O(3) modes at 116 and 340 cm^{-1}.

The Raman spectra well below T_c are illustrated in Fig. 1(b). The electronic background has developed a very broad, asymmetric peak, while the electronic continuum scattering at the lowest energies has dropped to a near-zero count rate. The absence of this broad scattering in the lower, depolarized spectrum confirms that the electronic continuum has A_g symmetry, as we would expect from its strong coupling to the A_g phonons. This redistribution of electronic states to higher energies is clear evidence of gap formation, as electronic states below the gap become unavailable and spectral weight is piled above 2Δ. However, it is clear from Fig. 1(b) that the spectral distribution of gap excitations in $YBa_2Cu_3O_{7-\delta}$ noticeably differs from the abrupt onset of 2Δ that one expects and observes in a fully gapped superconductor such as Nb_3Sn and V_3Si.[4] Instead, in $YBa_2Cu_3O_{7-\delta}$ one observes a gradual linear rise in scattering from near zero at 16 cm^{-1} (2 meV) to a maximum near 470 cm^{-1} (58 meV), suggesting the presence of residual electronic states well below the expected gap onset (at $2\Delta = 225$ cm^{-1} according to BCS theory, and at $2\Delta > 260$ cm^{-1} for strong coupling). By comparing the slopes of the low-frequency Raman spectra at several temperatures [inset, Fig. 1(b)], after dividing by the thermal Bose factor $1+n(\omega)$, we conclude that a normal-state spectral weight representing roughly 20% of the gapped strength is still present at $T \sim 3$ K. Indeed, the presence of a residual electronic continuum at low energies is most strikingly illustrated by noting that the 116 cm^{-1} phonon is still resonating with the residual continuum at 3 K. It is not likely that these low-energy excitations arise simply from a surface layer of nonsuperconducting $YBa_2Cu_3O_{7-\delta}$, as such a layer would be too small to account for the large spectral weight of scattering we observe. This contention is supported by the absence of any phonon structure in the 470–490 cm^{-1} range, which is the energy determined for the A_g O(4) mode in severely oxygen-poor $YBa_2Cu_3O_{7-\delta}$.[8] However, it is the diminished, but nonvanishing, Fano interference associated with the 116 cm^{-1} phonon at 3 K which is the strongest evidence tying the superconducting excitations and the low-energy residual scattering to the same high-T_c phase.

This residual scattering suggests the presence of a substantial spectral weight of states inside the "gap." An interpretation of this scattering in terms of specific models requires further theoretical analysis, however, we again point out that the linear rise in the residual continuum is indicative of a normal (i.e., fully gapless) metal. On the contrary, in a superconductor with gapless regions along lines or nodes, residual scattering inside the gap would be expected to exhibit a faster decline below 2Δ.

A more detailed look at the gap formation and the residual low-energy continuum is presented in Fig. 2, where the featureless background just above T_c is gradually observed to develop into a broad peak as electronic spectral weight is shifted to higher energies below T_c. The bottom spectrum (3 K) of Fig. 2 more clearly illustrates the broad peak due to gap excitations, as well as the linear continuum scattering inside the gap. The gap opening is also reflected in the two strongly coupled phonons at 116 and 340 cm^{-1}, which are sensitive to the local electronic continuum density. In Fig. 2 one can see the gradual suppression, with decreasing temperature, of the antiresonance associated with the 111 cm^{-1} phonon as low-energy electronic scattering is reduced by the maturing gap, while the 335 cm^{-1} phonon resonates more strongly at low temperatures.

The effects of gap formation on the 340 and 116 cm^{-1} phonons are summarized in Fig. 3, which illustrates the

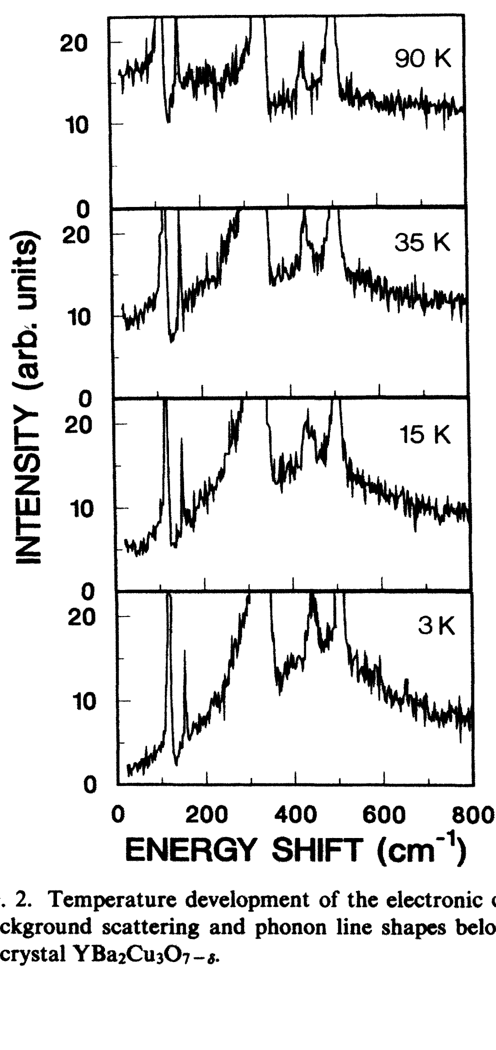

FIG. 2. Temperature development of the electronic continuum background scattering and phonon line shapes below T_c in single-crystal $YBa_2Cu_3O_{7-\delta}$.

temperature dependence of the phonons' linewidths [Fig. 3(a) and 3(b)] and peak positions [Fig. 3(c) and 3(d)]. In the latter graphs, the bare phonon frequencies, as determined from our Fano line-shape fits, are included with the renormalized (observed) frequencies. Below T_c, one can clearly see the shifting of electronic strength to higher energies, as the 335 cm^{-1} phonon's linewidth dramatically increases. This indicates greater damping due to the rapid increase in the local electronic density of states. Simultaneously, the 116 cm^{-1} phonon exhibits a decreasing linewidth as continuum states are pushed to higher energies. Also indicated in Fig. 3 is that near T_c the phonon at 340 cm^{-1} begins to soften significantly, in agreement with the Raman scattering results of Macfarlane, Rosen, and Seki[7] on polycrystalline samples. However, the softening of both the bare and renormalized frequencies indicates that this phonon behavior is not the result of the shifting continuum.

To conclude, we have presented evidence of superconducting gap excitations in single-crystal $YBa_2Cu_3O_{7-\delta}$ by Raman scattering, corroborating earlier results on polycrystalline samples. A new feature demonstrated by our data is the presence of strong interference effects observed between a strong electronic continuum and two discrete phonon levels associated with orthorhombic $YBa_2Cu_3O_{7-\delta}$, providing definitive evidence for strong electron-phonon coupling in this material. Below T_c, this electronic continuum undergoes a dramatic redistribution, manifested by a loss of continuum strength at low energies, and a piling of spectral weight around 470 cm^{-1}. The opening of the gap is most clearly reflected, however, in the

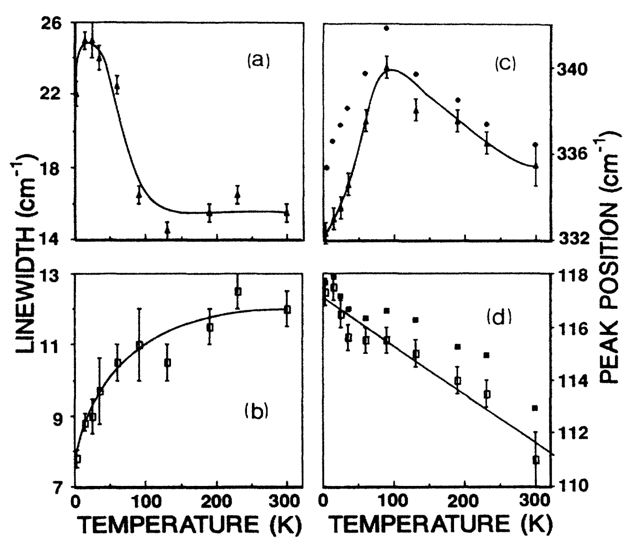

FIG. 3. (a) and (b) Full width at half maximum linewidths of O(2)/O(3) A_g mode (filled triangles) and Cu(2) A_g mode (open squares), determined from fits to Fano line shapes (Refs. 9 and 10). (c) O(2)/O(3) A_g phonon frequencies, including observed (renormalized) frequencies (filled triangles) and bare phonon frequencies from fits to Fano line shapes (diamonds). (d) Observed (open squares) and bare (filled squares) phonon frequencies for the Cu(2) A_g phonon. The data represent averages over many spectra, and the error bars are standard deviations. The solid lines are guides to the eye.

strongly coupled phonons, which show dramatic changes in their damping rates as the electronic spectral weight is shifted to higher energies below T_c. Yet the key feature of this data is the observation at 3 K of a rather large amount of continuum scattering well below the expected gap energy, suggesting the presence of a continuum of electronic states inside the gap.

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