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Temperature dependence of the linewidths of the Raman-active phonons of $YBa_2Cu_3O_7$: Evidence for a superconducting gap between 440 and 500 cm^{-1}

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The linewidths and frequencies of three Raman-active phonons have been measured in twin-free single crystals of $YBa_2Cu_3O_7$. Below T_c, the phonon at 340 cm^{-1} sharpens dramatically, the phonon at 440 cm^{-1} sharpens slightly, and the phonon at 500 cm^{-1} broadens. The temperature dependence of the phonon linewidths places the superconducting energy gap (2Δ) between 440 and 500 cm^{-1}, or $2\Delta=(6.8-7.7)k_BT_c$. Based upon the observed change in linewidth, the electron-phonon coupling strength of the 340-cm^{-1} phonon is estimated to be between 0.6 and 0.8.

Despite intensive investigation, the magnitude of the superconducting energy gap (2Δ) of $YBa_2Cu_3O_7$ is not well established. Values of $2\Delta(T\approx 0)$ range from about $4.7k_BT_c$ to about $8k_BT_c$.[1-4] In part, this range of values may be due to gap anisotropy or come from the presence of two gaps. Indeed, evidence exists for a smaller energy gap ($2\Delta\approx 3.5k_BT_c$) associated with the c axis.[3,5]

In conventional (i.e., low-temperature) superconductors, electron-phonon interactions mediate the pairing of electrons. Electron-phonon coupling causes phonons to acquire complex self-energies. The real part of the self-energy describes the shift of the phonon frequency that is caused by electron-phonon coupling.[6] The imaginary part of the self-energy describes the additional phonon linewidth that results from electron-phonon coupling. Due to electron-phonon coupling, superconductivity can produce experimentally observable changes in phonon frequency and linewidth in conventional superconductors. For example, the linewidths of the acoustic phonons have been shown to be sensitive measures of 2Δ in Nb_3Sn and Nb.[7,8] Physically, linewidths of phonons with $\omega<2\Delta$ decrease below T_c because gap formation reduces the rate of phonon decay by electron-hole production, leading to increased phonon lifetimes. In contrast, phonons with $\omega>2\Delta$ can decay in the superconducting state by breaking Cooper pairs. This scattering, along with the increased density of electronic states near the Fermi level resulting from gap formation, leads to an increase in phonon linewidth below T_c.

The role of electron-phonon coupling in the superconductivity of the copper oxide materials is still largely unresolved. However, at least some of the phonons have significant electron-phonon couplings, as indicated by calculation[9] and experiment. For example, the Raman-active phonons of $YBa_2Cu_3O_7$ at 120 and 340 cm^{-1} were found to have Fano line shapes,[10] indicative of strong electron-phonon coupling. In addition, Huang *et al.* have found the electron-phonon coupling constant λ to be 1.2 for $Ba_{1-x}K_xBiO_3$ and 1.0 for $Nd_{2-x}Ce_xCuO_{4-y}$.[11] Dynes performed tunneling measurements on $YBa_2Cu_3O_{7-x}$ and finds $\lambda=2.2$ indicating strong coupling.[12] Recently, Friedl, Thomsen, and Cardona[2] have used the temperature dependence of the Raman-active photons to deduce $2\Delta(T\approx O)=316$ cm^{-1} for $RBa_2Cu_3O_y$ (R is a rare earth). Central to this determination was the behavior of the linewidths of the B_{1g}-like phonon at about 340 cm^{-1} and the A_g phonon at about 440 cm^{-1}.

In this paper, we show that in high-quality, twin-free single crystals of $YBa_2Cu_3O_7$, the 340-cm^{-1} phonon dramatically *sharpens* below T_c and its frequency softens (decreases). While while to 500-cm^{-1} phonon broadens below T_c, the 440-cm^{-1} phonon *does not broaden.* These observations establish that the superconducting energy gap that affects these zone-center phonons is between 440 and 500 cm^{-1}.

The Raman measurements of twin-free single crystals of $YBa_2Cu_3O_7$ were made using 514.5-nm excitation as previously described.[5,13] The crystals were grown in gold crucibles and representative crystals were found by inductively coupled plasma emission spectroscopy to contain 0.74-at.% gold. As seen in Fig. 1, the B_{1g}-like phonon at 340 cm^{-1} is significantly sharper at 4 K than at 115 K, and is well described by a Lorentzian line shape plus a linear background. Sharpening, not broadening, of the 340-cm^{-1} phonon below T_c was observed in three different crystals and in three different polarization geometries—with the incident light propagating perpendicular to the c axis [i.e., polarization geometries $x(yy)\bar{x}$ and $y(xx)\bar{y}$] and parallel to the c axis [i.e., polarization geometry $z(y'x')\bar{z}$].[5] The temperature dependence of the linewidths of the phonons at 340, 440, and 500 cm^{-1} is shown in Fig. 2. The solid lines in Fig. 2 are fits to a model[2] that describes the linewidth γ (half-width at half maximum) by the anharmonic decay of a phonon of frequency

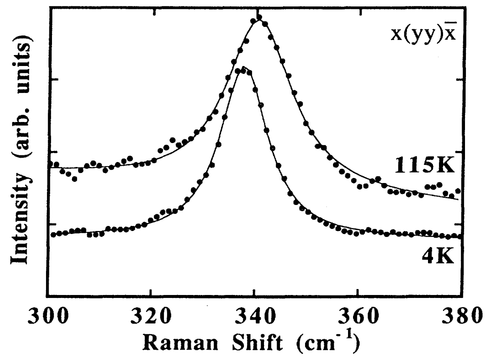

FIG. 1. Comparison showing that the B_{1g}-like phonon of $YBa_2Cu_3O_7$ is narrower at 4 K than at 115 K. Circles are the experimental data, while the solid curves are fits to a Lorentzian line shape plus a linear background.

ω and wave vector $q \approx 0$ into two phonons of opposite wave vector and frequency $\sim \omega/2$:

$$\gamma(\omega,T) = \gamma(\omega,0)[1+2n(\omega/2)] + \text{const},$$

where n is a thermal occupancy factor. With $\gamma(\omega,0)$ as an adjustable parameter, the experimental linewidths of all three phonons are well described for temperatures above $T_c = 93$ K. While the linewidth of the 440-cm^{-1} phonon is well described at all temperatures, the phonons at 340 and 500 cm^{-1} deviate significantly below T_c from the simple model of phonon decay. Specifically, the 340-cm^{-1} phonon becomes unexpectedly narrower and the 500-cm^{-1} phonon becomes unexpectedly broader. These unexpected changes in linewidths result from superconductivity and the different behavior of the three phonons allows the energy gap to be estimated.

Gap determination from phonon linewidths is possible since phonons with $\omega > 2\Delta$ will broaden below T_c, while phonons with $\omega < 2\Delta$ will not broaden below T_c. This premise is supported both by the detailed theory of Zeyher and Zwicknagl[6] and measurements of conventional superconductors. For example, when Nb is cooled below T_c, phonons with $\omega > 2\Delta$ broaden, phonons with $\omega < 2\Delta$ sharpen, and phonons with $\omega \approx 2\Delta$ exhibit little change in linewidth.[8] Physically, phonons with $\omega > 2\Delta$ can scatter by breaking Cooper pairs in the superconducting state. This decay channel, and the increased density of electronic states near the Fermi energy that results from gap formation, lead to reduced phonon lifetimes and thus broader linewidths. This behavior (see Fig. 2) is observed for the 500-cm^{-1} phonon in $YBa_2Cu_3O_7$, and thus 500 cm^{-1} > 2Δ. Similar behavior of the 500-cm^{-1} phonon has recently been observed by other groups.[14,15] In contrast, the 440-cm^{-1} phonon sharpens slightly below T_c. The amount of change is about that expected from purely thermal effects (see the curve fit in Fig. 2), suggesting that the phonon is close to 2Δ. However, since the 440-cm^{-1} phonon does not broaden below T_c, it lies below the gap.[2,6]

For $YBa_2Cu_3O_7$, the linewidth results of Fig. 2 dictate that the gap is between 440 and 500 cm^{-1}, or $2\Delta = (6.8\text{–}7.7)k_BT_c$. This range is quite consistent with values determined by electron-energy loss[4] and ir

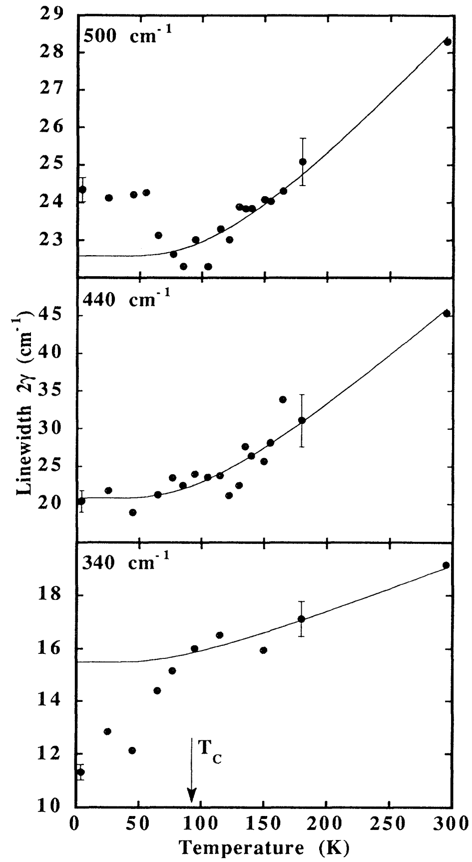

FIG. 2. Linewidths of the 340-, 440-, and 550-cm^{-1} phonons as a function of temperature. Data collected with a $x(zz)\bar{x}$ polarization geometry for the 440- and 500-cm^{-1} phonons and a $x(yy)\bar{x}$ geometry for the 340-cm^{-1} phonon (Ref. 5). Linewidths (full width at half maximum) were determined by numerically fitting the 340- and 440-cm^{-1} phonons to Lorentzian line shapes plus a linear background, while the 500-cm^{-1} phonon was more accuratley described by a Fano line shape plus a linear background. Due to the small degree of asymmetry in the 500-cm^{-1} phonon (Fano asymmetry parameter $q = -6.2$ at 115 K and $q = -5.2$ at 4 K), essentially the same linewidths and frequencies are found using a Lorentzian line shape. Error bars represent standard deviations of multiple measurements. Solid lines are fits to a model of phonon-phonon decay: all temperatures were included in fitting the linewidths of the 440-cm^{-1} phonon, but only temperatures above T_c were used in fitting the 340- and 500-cm^{-1} phonons.

reflection:[3] $2\Delta \approx 8k_BT_c$. However, $2\Delta = (6.8\text{–}7.7)k_BT_c$ is significantly larger than the value ($2\Delta = 316$ cm^{-1} $= 4.95k_BT_c$) deduced by Friedl, Thomsen, and Cardona[2] based upon the linewidths of the Raman-active phonons.

As shown in Fig. 2, the 340-cm^{-1} phonon of $YBa_2Cu_3O_7$ sharpens considerably below T_c. This phonon lies well below the energy gap discussed above. Consistently, acoustic phonons in Nb and Nb_3Sn with $\omega < 2\Delta$ sharpen below T_c.[7,8] For these phonons, gap formation below T_c removes a scattering channel. That is, the phonons can no longer decay by electron-hole production and their linewidths decrease. Apparently as a consequence of assuming zone-center photons ($q=0$), the Zeyher-Zwicknagl theory[6] does not allow phonons of any energy to sharpen below T_c. While in the strict $q=0$ limit, phonons cannot scatter electrons within a band in the normal state, the phonons measured in this Raman experiment have small but nonzero wave vector. It is also possible that there are interband contributions to the electron-phonon coupling. While most of the present results agree at least qualitatively with the theory of Zeyher and Zwicknagl, the linewidth behavior of the 440-cm^{-1} phonon does not. The 440-cm^{-1} phonon does not broaden below T_c, and is therefore below the energy gap. However, the phonon hardens below T_c, and should therefore be above the energy gap according to the strong-coupling theory, at least as numerically presented.[6] The phonon shifts predicted in either the BCS limit or a strong-coupling form for $q=0$ phonons[6] are also not seen in the acoustic phonons of Nb. That is, phonons above the gap would be expected to harden when Nb becomes superconducting, but instead they are found to soften.[8] Given these discrepancies and the fact that phonon linewidth is a more sensitive measure of the energy gap,[2] the above determination of 2Δ considers only the linewidth behavior.

At least for conventional superconductors, the temperature-dependent gap goes to zero at T_c. Then, for a phonon with $\omega < 2\Delta(T=0)$, there is a temperature T^* for which $\omega = 2\Delta(T^*)$. Since this phonon can break Cooper pairs between T_c and T^*, the phonon should broaden between T_c and T^*. Below T^*, $\omega < 2\Delta(T)$ and the linewidth will decrease. This behavior has been observed in Nd_3Sn and Nb,[7,8] but is apparently not observed here in the 340-cm^{-1} phonon of $YBa_2Cu_3O_7$ (Fig. 2). Even if the 340-cm^{-1} phonon does initially broaden below T_c, the failure to observe such behavior here is not surprising considering the error bars of the data and the limited number of temperatures examined.

The linewidth behavior of the 340- and 440-cm^{-1} phonons reported here is markedly different from the results of previous investigators. For example, Cooper *et al.*[16] and Friedl, Thomsen, and Cardona[2] found the 340-cm^{-1} phonon to dramatically broaden below T_c. Behavior intermediate between these studies and the present study has recently been observed.[14] Friedl, Thomsen, and Cardona also observe the 440-cm^{-1} phonon to broaden by about 5 cm^{-1} (full width at half maximum) below T_c. Whereas we see a dramatic sharpening of the 340-cm^{-1} phonon and a slight sharpening of the 440-cm^{-1} phonon, in conflict with former results, the frequencies as a function of temperature of the two phonons agree well with literature results.[2,16,17] Below T_c, as shown in Fig. 3, the 340-cm^{-1} phonon softens by about 4 cm^{-1} and the 440-cm^{-1} phonon hardens by about 4 cm^{-1}. Figure 3 also shows that the 500-cm^{-1} phonon hardens below about 150 K. It is not clear, however, whether this hardening begins at T_c or above T_c.

The differing results of the linewidths are believed to be related to sample quality. The linewidth behavior of the 340-cm^{-1} phonon is known to be sensitive to sample quality. Compare, for example, the early results of Cooper *et al.*[10] with later results using a better crystal.[16] While the linewidth behavior is quite sensitive to sample quality, the frequency behavior is much less so. That is, the large softening of the 340-cm^{-1} phonon was observed very early on in ceramic materials[17] and the behavior has remained essentially unchanged with time. This difference between linewidth and frequency is plausible in that in lower quality materials, phonon lifetimes could be dominated by defect scattering, hindering the observation of intrinsic behavior. Furthermore, not all of the sample may develop the maximum energy gap.

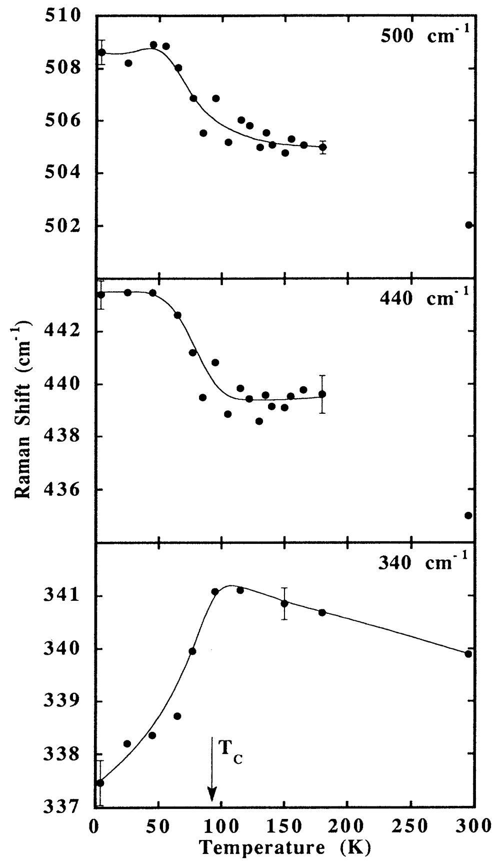

FIG. 3. Frequencies of the 340-, 440-, and 500-cm^{-1} phonons as a function of temperature. Solid lines are guides to the eye. Error bars represent standard deviations of multiple measurements.

It is emphasized that the single crystals of the present study are of the highest quality. First, the crystals are twin-free. Second, the T_c's are high and the superconducting transitions are very sharp. For example, two of the crystals of the present study were examined by magnetization analysis. The onset of diamagnetism in an applied field of 20 Oe occurred at 93 K with (10–90)% transition widths of 1.6 and 2.5 K, respectively.[5,13] Resistive transition widths of less than 200 mK in zero magnetic field have been observed in crystals from the same growth batches.[18] The high quality of the crystals has allowed the observation of phenomena that are absent in lower quality crystals.[18] While the phonon-linewidth behavior is different, the present samples do reproduce other Raman-scattering features described in the literature.[16] For example, the present crystals exhibit intense scattering from an electronic continuum and this continuum interferes strongly with scattering from the 120-cm^{-1} phonon.[5] Below T_c, the continuum scattering redistributes itself.[5,16]

The observed sharpening of the 340-cm^{-1} phonon below T_c allows the electron-phonon coupling strength (λ_q) of this phonon to be crudely estimated since λ_q is simply related to the additional phonon linewidth γ_q that results from electron-phonon coupling:

$$\lambda_q = (\gamma_q/\omega_q)[\pi N(E_F)\hbar\omega_q]^{-1},$$

where $N(E_F)$ is the density of states at the Fermi level and ω_q is phonon frequency.[8,19,20] The total electron-phonon coupling strength λ is found by averaging λ_q over the Brillouin zone and summing the contributions from each of the 39 phonon branches. Here γ_q is taken as ~ 2.5 cm^{-1}, the difference between the experimental linewidth above T_c and at 4 K, where there should be no electron-phonon contribution to the linewidth. With $N(E_F)$ taken from band-structure calculations, 2.77–3.4 states/[eV ($YBa_2Cu_3O_7$ cell spin],[21–23] $\lambda_{340} \approx 0.016$–0.020. It is more usual to consider the value $39\lambda_{340} \approx 0.64$–0.78, since this represents the average contribution of the phonon to the total coupling strength λ. Clearly, the 340-cm^{-1} phonon is at least moderately coupled. This estimate of λ_{340} may represent a lower bound, since the linewidth at 4 K may still contain contributions from electron-phonon coupling associated with any gapless parts of the Fermi surface.[10] Furthermore, there may be nonintrinsic contributions (e.g., defect related) to the experimental linewidth. The λ_{340} value can be compared to results of first-principles calculations. Cohen, Pickett, and Krakauer[9] determined electron-phonon coupling strengths of the A_g phonons at given k (electronic) points after averaging the phonons over the Brillouin zone. An average of k points gave $39\lambda_{340} = 1.0$.

In summary, the linewidths and frequencies of three Raman-active phonons have been measured in twin-free single crystals of $YBa_2Cu_3O_7$. Below T_c, the phonon at 340 cm^{-1} sharpens dramatically, the phonon at 440 cm^{-1} sharpens slightly, and the phonon at 500 cm^{-1} broadens. This behavior places the energy gap 2Δ of $YBa_2Cu_3O_7$ between 440 and 500 cm^{-1} ($6.8k_BT_c$–$7.7k_BT_c$). Based upon the linewidth behavior, the electron-phonon coupling strength of the 340 cm^{-1} phonon is estimated to be $39\lambda_{340} \approx 0.6$–0.8.

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