Temperature dependences of the 340-, 440-, and 500-cm⁻¹ Raman modes of $YBa_2Cu_3O_{\nu}$ for $6.7 \leq y \leq 7.0$

E. Altendorf, X. K. Chen, and J. C. Irwin

Physics Department, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

R. Liang and W. N. Hardy

Physics Department, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1 (Received 27 July 1992; revised manuscript received 12 October 1992)

The temperature dependences of the linewidths and frequencies of the 340-, 440-, and 500-cm^{-1} Raman-active phonons have been measured in lightly twinned single crystals of $YBa_2Cu_3O_{\nu}$ with different oxygen concentrations y. The observed superconductivity-induced changes in the linewidths and frequencies that occur for temperatures below the critical temperature have been found to depend on the oxygen concentration within the range $6.7 \le y \le 7.0$, with the most sensitive dependence occurring in the 340-cm⁻¹ phonon-linewidth variations near $y \approx 7.0$. The linewidth and frequency dependences of the 340-cm⁻¹ B_{1g} mode for $T < T_c$ suggest that the redistribution of electronic states below T_c is very sensitive to the oxygen or hole concentration within this range. Estimates for the superconducting energy gap 2Δ have been obtained from comparisons of the temperature dependence of the 340-cm⁻¹ mode with strong-coupling theory and these indicate that 2Δ increases as the oxygen or hole concentration y decreases from y = 7.0 where $2\Delta \approx 5.4$ kT_c. The linewidth and frequency of the 440-cm⁻¹ A_g mode are, however, relatively insensitive to variations in y and it is suggested that the 440- and 500-cm⁻¹ phonons couple to a different set of electrons than does the 340-cm⁻¹ mode.

I. INTRODUCTION

The temperature dependences of the Raman-active A_{ρ} modes in YBa₂Cu₃O₇ have been the subject of numerous investigations in the five years since the discovery of superconductivity in this compound. Macfarlane, Rosen, and Seki¹ observed that in fully oxygenated samples of polycrystalline material the 340-cm⁻¹ phonon decreased in frequency by about 2% as the sample was cooled from the critical temperature (T_c) near 90 K to about 10 K. This result was subsequently confirmed in experiments on polycrystalline samples,²⁻⁴ thin films,⁵ and single crystals⁶⁻⁹ and furthermore it was found⁶ that the linewidth of this same mode increased by up to 50% when the crystal was cooled below T_c . These superconductivityinduced changes in the frequency and linewidth of the 340-cm⁻¹ phonon, in conjunction with its distinctive Fano line shape,^{7,10} appear to provide evidence of strong electron-phonon interactions in YBa2Cu3O7. Subsequently it was found that the Raman-active oxygen vibrations at 440 and 500 cm^{-1} also exhibited superconductivityinduced changes in frequency and linewidth^{8,9,11-14}. Qualitatively one expects that phonons with energies less than the superconducting gap will become narrower^{15,16} as the temperature falls below T_c because of a reduction in the number of available decay channels. On the other hand, phonons with energies greater than 2Δ can decay via a pair-breaking mechanism and hence should broaden¹⁵⁻¹⁷ as the temperature is reduced below T_c . These effects were first observed in neutron-scattering experiments^{15,16} on Nb₃Sn and Nb. Thompsen *et al.*¹¹ and Friedl, Thomsen, and Cardo-

na¹⁸ utilized the temperature dependences of the frequencies (ω_{ν}) and linewidths (FWHM= $2\gamma_{\nu}$) of the Ramanactive phonons to obtain an estimate for the superconducting gap (2Δ) in several polycrystalline RBa₂Cu₃O₇ compounds (R is a rare-earth element, e.g., Y, Eu, Gd), all of which had a critical temperature T_c of about 90 K. They obtained a value¹⁸ of $2\Delta \approx 5.0kT_c$ by comparing their experimental observations to the predictions of a strong-coupling model.¹⁷ The formulation of this model by Zeyher and Zwicknagl¹⁷ (ZZ) was motivated by the significant softening and broadening of the 340-cm⁻¹ mode, which also implied that its energy was close to 2Δ . Not surprisingly the experimentally measured values for the superconductivity-induced changes in frequency $(\Delta \omega_{\nu})$ and linewidth $(\Delta 2\gamma_{\nu})$ for the 340-cm⁻¹ mode played a more important role in the gap determination of Thomsen and co-workers^{11,18} than did those for the 440and 500-cm^{-1} modes. More recently, however, several experiments^{8,9} have been carried out on samples in which the 340-cm⁻¹ linewidth exhibited a very different behavior than that observed previously. Altendorf et al.⁸, from experiments on lightly twinned single crystals, found that the 340-cm⁻¹ mode did not broaden at all as the temperature was reduced below T_c , and obtained a value of $2\Delta/kT_c = 5.9$ for the gap energy from comparisons with the ZZ model.¹⁷ McCarty et al.⁹ found that the 340-cm⁻¹ mode actually narrowed for $T < T_c$ and obtained an estimate of $6.8kT_c < 2\Delta < 7.7kT_c$ for the gap from measurements on untwinned crystals. Thomsen et al.¹⁹ have suggested that these quite different results could be attributed to the presence of impurities in the samples. In particular, the crystals studied by Altendorf

et al.8 were grown in Thoria crucibles and contained 2.5% Th (atoms/unit cell) while the crystals of McCarty et al.⁹ contained some gold. Thomsen et al.¹⁹ suggested that these impurities could lead to a symmetrization of the gap around the Fermi surface and, under appropriate circumstances, to larger measured values for 2Δ . In support of this suggestion it was demonstrated that the addition of significant amounts of gold led to a reduction of the observed broadening although the null result of McCarty et al.9 was not duplicated. However, more recent investigations by Altendorf *et al.*^{20,21} and by McCarty *et al.*^{22,23} on pure crystals grown in zirconia crucibles have demonstrated that a narrowing of the 340 cm^{-1} mode occurs even in high-quality crystals with very small impurity concentrations. Furthermore, McCarty *et al.*²² found that the 440-cm⁻¹ mode narrowed slightly below T_c while Altendorf *et al.*²⁰ observed a small broadening for this same mode. As is noted above, these results imply very different values for the superconducting gap energy in the various samples studied despite the fact that all the samples had approximately the same critical temperature ($T_c \approx 90$ K).

The above results imply that the temperature dependences of the Raman-active oxygen vibrations in $YBa_2Cu_3O_{\nu}$ ($y \approx 7.0$) are very sensitive to relatively minor differences in the properties of the samples studied. To explore this possibility in a more quantitative manner we have carried out a systematic study of the phonons at 340, 440, and 500 cm⁻¹ as a function of oxygen concentration. These experiments were carried out on lightly twinned single crystals with oxygen concentrations 6.7 $\leq y \leq$ 7.0. In a previous paper²¹ which focused on the 340-cm⁻¹ phonon, results of Raman measurements on crystals with $6.85 \le y \le 7.0$ were presented. It was found that for the 340-cm⁻¹ phonon, the linewidth and frequency shifts below T_c depended sensitively on the oxygen concentration near y = 6.95. In particular, for crystals with y > 6.95, the 340-cm⁻¹ mode substantially broadened below T_c while for crystals with $y \leq 6.95$ the 340-cm⁻¹ mode narrowed. These results are consistent with those of Hadjiev, et al.²⁴ where broadening in the 340-cm⁻¹ mode below T_c was obtained only from heavily twinned, and hence assumed to be fully oxygenated, areas of single-crystal films. It should be noted that T_c varies from approximately 88 K to about 94 K in the five crystals previously studied,²¹ with the maximum T_c being found in the crystal with an oxygen concentration of $y \approx 6.95$. This indicates that there is a lack of correlation between the superconducting gap energy 2Δ , as estimated from the linewidth and frequency shifts of the 340-cm⁻ phonon below T_c , and the critical temperature T_c . In addition, if the changes in linewidth and frequency of the 340-cm⁻¹ phonon below T_c result from the formation of a superconducting gap, or more generally, a redistribution of electronic states below T_c , then this redistribution of electronic states is very sensitive to the oxygen or hole concentration in $YBa_2Cu_3O_{\nu}$.

In this paper the results of measurements on crystals with seven different values of y (6.7 $\leq y \leq$ 7.0) for all three oxygen vibrations (340, 440, and 500 cm⁻¹) are presented. The 440- and 500-cm⁻¹ phonons exhibit variations in

 $\Delta \omega_{\nu}$ and $\Delta 2 \gamma_{\nu}$ as a function of oxygen concentration but do not demonstrate the dramatic changes observed for the 340-cm⁻¹ phonon. In particular, the linewidth of the 440-cm⁻¹ mode does not undergo any significant narrowing or broadening below T_c in any of the crystals studied. Measurements of the 340-cm⁻¹ phonon were taken from the faces of the crystals with the incident and scattered light propagating along the c-axis direction while measurements of the 440- and 500-cm⁻¹ phonons were taken from the edges of the crystals with the incident and scattered light propagating in the ab plane. Comparisons of strong-coupling models^{17,25} with the 340-cm⁻¹ mode gives an estimate of $2\Delta \approx 340 \text{ cm}^{-1}$ (5.4kT_c) for the superconducting energy gap of the crystals with $y \approx 7.0$. Reduction in the oxygen concentration from $y \approx 7.0$ results in changes in the linewidth and frequency shifts below T_c ($\Delta 2\gamma_v$ and $\Delta \omega_v$), which are consistent with larger superconducting gap energies, and also, for y < 6.9, with an increasing concentration of defects, or decreasing hole concentration. The behavior of the 440and 500-cm⁻¹ phonons is not consistent with this picture, however, and it is suggested that these two models interact with a different group of electrons.

II. EXPERIMENT

The seven crystals studied in this work were initially obtained from batches of high-purity crystals which were grown in zirconia crucibles by a flux method which has been described elsewhere.²⁶ The crystals contained less than 10 ppm Zr by weight and the sum of all other impurities was less than 500 ppm by weight. Crystals with seven different oxygen concentrations (designated A, B, C, D, E, F, and G, see Table I) were then obtained by annealing the crystals at appropriate temperatures, pressures, and for suitable lengths of time.²¹ Known dependences²⁷ of oxygen content on temperature and oxygen pressure during annealing gave the initial oxygen concentration estimates. Crystals annealed under the same conditions as crystal C ($y \approx 6.95$) show a specific-heat jump as narrow as 0.25 K indicating a high degree of homogeneity.²⁶ The crystals had dimensions of up to 6 mm in the a-b plane and up to 0.5 mm along the c axis. The latter dimension is of particular interest here in that it allows one to study the (zz) element of the Raman tensor. The 440- and 500-cm⁻¹ modes of YBa₂Cu₃O₇ have A_g symmetry²⁸ and hence diagonal Raman tensors with a (zz) component. Five of these crystals (A, B, C, D, and *F*) were previously used²¹ to study the temperature dependence of the 340-cm⁻¹ mode and the results of this investigation were published in a recent paper²¹ along with the annealing conditions used to prepare the crystals. The two new crystals (E and G) included in this paper were prepared as follows. Crystal E was grown and annealed in the same way as crystal C whose preparation is described in a previous paper.²¹ Additional annealing for about 4 days at 540 °C in 1 atm of flowing O₂ resulted in crystal whose oxygen concentration was estimated to be $y \approx 6.85$ and a transition temperature of 91.1 K, which was determined, from dc magnetization measurements

Crystal	y (initial estimate)	<i>c</i> -axis parameter (Å)	y (refined value)	<i>T</i> _c (K)	ΔT_c (10%–90%) (K)	Applied field (Oe)
A	7.0	11.688	7.0	89.7	2.5	10.0
В	> 6.95, < 7.0	11.689	6.99	92.8	0.8	0.1
С	6.95	11.698	6.93	93.7	< 0.2	0.05
D	6.9	11.703	6.90	92.0	2.2	5.0
Ε	6.85	11.710	6.86	91.1	2.7	0.1
F	6.85	11.718	6.81	87.7	1.3	0.05
G	6.7	11.738	6.68	59.2	4.3	10.0

TABLE I. Initial oxygen concentration estimates y, c-axis parameters, refined oxygen concentrations, and results of dc magnetization measurements.

with an applied field of 0.1 Oe. Crystal G was also initially grown and annealed in a manner similar to crystal C and additional annealing for about 110 h at 700 °C and 1 atm of flowing O₂ resulted in a crystal with an estimated oxygen concentration of $y \approx 6.7$, and a T_c of 59.2 K, as determined from dc magnetization measurements with an applied field of 10.0 Oe. The T_c values quoted in this paper were determined from the intersection of the linear portion of the transition with the normal-state baseline.²⁹ Transition curves measured for crystals A, C, D, and G using dc magnetization techniques are shown in Fig. 1.

The variation in the applied fields used in the magnetization measurements was not intentional and merely reflects the fact that some of the measurements were made with a commercial SQUID magnetometer (applied fields of 5.0 and 10.0 Oe) while the remaining measurements (applied fields of 0.05 and 0.1 Oe) were carried out with a highly sensitive SQUID magnetometer designed by Gygax at Simon Fraser University. The choice of which magnetometer to use was dictated by availability and time constraints. Differences in the superconducting transition widths, listed in Table I and shown in Fig. 1, could be due in part to the differences in applied fields used in the magnetization measurements.

The oxygen concentrations of these crystals, initially estimated from the annealing conditions, are refined in this paper through x-ray-diffraction determined c-axis spacings. Cava et al.³⁰ have demonstrated that the c-axis spacing in $YBa_2Cu_3O_{\nu}$ varies approximately linearly with the oxygen concentration y. Comparison of our data with the curve of Cava et al.³⁰ gives the refined oxygen concentrations which are listed in Table I along with the initial oxygen concentration estimates, c-axis parameters, and results of magnetization measurements. In obtaining these concentrations we have fixed the oxygen content of crystal A at our initial estimate of y = 7.0 which was based on annealing conditions.²⁷ The slope of the expected linear dependence given by Cava et al.³⁰ is then used to determine the remaining oxygen concentrations from the measured c-axis spacings. A nonlinear least-squares fit to eight (00n) diffraction peaks (allowing for off-axis crystal displacement) was used to determine the c-axis spacings.

The Raman spectra investigated in this paper were obtained with both the 514.5- and 488.0-nm lines of an argon-ion laser. The incident light was focused on the crystals using either a cylindrical lens to obtain an excited area of about 50 μ m×3 mm or a spherical lens to obtain an excited area of about 100 μ m×100 μ m. The incident power was kept low, typically below 6 mW, in order to avoid local heating of the sample. The crystal was mounted on the cold finger of a displex refrigerator for all measurements and this allowed the sample temperature to be varied from 15 to 300 K. The scattered light was



FIG. 1. dc magnetization as a function of temperature for crystals A, C, D, and G cooled in fields, H_0 , of 10.0, 0.05, 5.0, and 10 Oe, respectively, with H_0 parallel to the c axis of the crystals.

analyzed with a triple grating spectrometer and detected with an ITT-Mepsicron imaging detector.

III. RAMAN SPECTRA

Raman spectra were obtained from crystals A, B, C, D, E, F, and G, with the incident and scattered light polarized in the *a-b* plane. The crystals are lightly twinned, however, and thus the polarization of the light is not specified in terms of a definite direction in the *a-b* plane of the crystal. We will simply refer to the spectra obtained in this geometry as (ab) and typical examples obtained at room temperature from crystals A and E are shown in Fig. 2(a). Spectra have also been obtained from the edges of the crystals with the incident and scattered light polarized parallel to the c axis; these will be referred to as (zz) spectra and typical spectra obtained at room temperature from crystals A and E are shown in Fig. 2(b). In this paper we will focus our attention on the three most energetic modes with nominal frequencies of 340, 440, and 500 cm⁻¹ all of which should have A_g symmetry in an orthorhombic (D_{2h}) system. However, in the tetragonal (D_{4h}) compound the 340-cm⁻¹ mode has B_{1g} symmetry and, because of the small orthorhombic distortions involved, it has been found²⁸ to retain this symmetry in the fully oxygenated orthorhombic structure and is

FIG. 2. Raman spectra obtained at room temperature (295 K) from crystals A and E with the incident and scattered light polarized in (a) the *a-b* plane (*ab*), (b) along the *c* axis of the crystals (*zz*).

often designated as a B_{1g} mode. Lattice dynamics models^{31,32} have been employed to calculate the frequencies and eigenvectors of the phonons in YBa₂Cu₃O₇. These calculations^{31,32} predict that the 340-cm⁻¹ mode corresponds to the out-of-phase *c*-axis vibrations of the oxygen atoms [O(2) and O(3)] in the CuO₂ planes, the 440-cm⁻¹ mode corresponds to the in-phase *c*-axis vibrations of the same atoms and the 500-cm⁻¹ mode corresponds to the *c*-axis motion of the oxygen atoms [O(4)] bridging the CuO chains and CuO₂ planes. Note that group theoretical methods²⁸ also predict the out-of-phase eigenvector of the 340-cm⁻¹ mode, given the observed B_{1g} symmetry²⁸ of this phonon. The additional modes at 235 and 598 cm⁻¹ seen in the *ab* spectra of crystal *E* are defectinduced chain modes which are the result of oxygen vacancies in the deoxygenated crystals.^{32,24} These modes are observed in all crystals with $y \leq 6.95$ in agreement with the findings of Liu *et al.*³² and Hadjiev *et al.*²⁴

A. The 340-cm $^{-1}$ phonon

All measurements of this phonon were carried out with the incident light in the *a-b* plane of the crystals. The absence of this phonon in the (zz) spectra [Fig. 2(b)] is consistent with the fact that it has B_{1g} -like symmetry²⁸ (tetragonal notation). Values for the frequencies and linewidths of the 340-cm⁻¹ phonon were obtained by fitting the corresponding 340-cm⁻¹ Raman feature to a Fano profile¹⁸ given by

$$I = I_0 \left[\frac{(\varepsilon + q)^2}{1 + \varepsilon^2} \right] + \text{background} , \qquad (1)$$

where $\varepsilon = (\omega - \omega_0)/\gamma$, ω_0 is the phonon frequency, γ is the phonon linewidth (HWHM), q is a parameter that defines the asymmetry of the measured line profile, and the background is taken to be a linear term of the form $B\omega + C$, where B and C are adjustable parameters. The asymmetry of the 340-cm⁻¹ Raman peak is due to the interaction of the 340-cm⁻¹ phonon with an electronic continuum,^{6,33-35} which is observed in the Raman spectra as a broad background.⁶ An example of such a fitted profile is shown in Fig. 3 superimposed on the experimental data of crystal A at 40 K. Fits of similar quality were obtained for all the crystals.

In Fig. 4, the temperature dependences of the frequencies of the 340-cm^{-1} mode are plotted. A softening in the frequency near T_c is observed in all seven crystals in accordance with the observations of other groups.^{1-4,36} The largest shift is observed in crystal A in which the frequency softens by approximately 8 cm⁻¹ between 100 and 15 K while the amount of softening is greatly reduced in the deoxygenated crystals and vanishes in crystal G. Such a reduction in the softening has also been observed in deoxygenated polycrystalline samples by Krantz *et al.*³⁶

The temperature dependences of the linewidths of the 340-cm⁻¹ mode are shown in Fig. 5 for all crystals. The solid lines in Fig. 5 indicate a fit of the experimental data points above T_c to a model of anharmonic decay.¹⁸ Crystal $C (T_c = 93.7 \text{ K})$ shows an overall narrowing below T_c



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FIG. 3. The 340-cm⁻¹ Raman peak obtained at 40 K in the (ab) geometry from crystal A (dots). The corresponding fitted Fano profile (Ref. 18) and linear background is indicated by the solid line.

of about 2 cm⁻¹ as indicated by the departure of the experimental data points from the anharmonic decay curve, while for crystals D, E, and F (y = 6.9 to about 6.8) the degree of narrowing increases by approximately 1 cm⁻¹. Finally, linewidth broadening below T_c in a manner similar to that reported by other groups^{7,18,36} is observed in crystals A and B, which are essentially completely oxygenated ($y \approx 7.0$). It therefore appears that the oxygen content, or more generally, the hole concentration,²¹ is the dominant factor in determining the nature of the superconductivity-induced linewidth and frequency shifts of the 340-cm⁻¹ mode in these crystals. The enhanced broadening observed in crystal A is perhaps²¹ partially linked to the presence of potassium (~ 500 ppm by weight) which should substitute for Ba and thus effectively increase the hole concentration in the crystals.

Finally, the dependences of the inverse of the Fano parameter (-10/q) of the 340-cm⁻¹ mode are plotted for all seven crystals in Fig. 6. Displaying the Fano parameter dependences in this way allows all the data points to



1 (20 (b) 16 12 20 (c) 1 6 FWHM (cm⁻¹) 1 2 18 (d) LINEWIDTH 10 (e) 18 1 10 18 (f) 14 10 18 (g) 14 10 300 50 100 150 200 250 TEMPERATURE (K)

FIG. 4. Frequencies of the 340-cm^{-1} phonon as a function of temperature for (a) crystal A, (b) crystal B, (c) crystal C, (d) crystal D, (e) crystal E, (f) crystal F, and (g) crystal G. The solid lines are only intended to serve as guides to the eye.

FIG. 5. Linewidths of the 340-cm⁻¹ phonon as a function of temperature for (a) crystal A, (b) crystal B, (c) crystal C, (d) crystal D, (e) crystal E, (f) crystal F, and (g) crystal G as determined by numerical fits to Fano profiles (Ref. 18) with a linear background. The solid lines are fits of the data above T_c to a model of anharmonic decay (Ref. 18).

(a)



FIG. 6. Inverse Fano parameters (-10/q) of the 340-cm⁻¹ phonon as a function of temperature for (a) crystal A, (b) crystal B, (c) crystal C, (d) crystal D, (e) crystal E, (f) crystal F, and (g) crystal G as determined by numerical fits to Fano profiles (Ref. 18) with a linear background. The solid lines are only intended to serve as guides to the eye.

be plotted on a convenient scale, with values close to zero indicating a very symmetric line profile. Figure 6 therefore implies that the 340-cm⁻¹ phonon peak becomes increasingly more symmetric as the oxygen concentration is reduced in the crystals. This suggests that there may be a reduction in the amount of interaction between the 340cm⁻¹ phonon and the carriers in the deoxygenated crystals. Furthermore, it is clear from Figs. 6(a)-6(d) that there is a maximum asymmetry (-10/q) in the 340cm⁻¹ peak which moves to higher temperatures as y is reduced from 7.0 to about 6.9. If it is assumed that this minimum in |q| occurs when the phonon energy coincides with a peak in the pair-breaking distribution, then we must conclude that this peak moves to higher energies as oxygen is removed from the crystals.

B. The 440- and 500-cm $^{-1}$ phonons

All measurements of these phonons were carried out with the incident light polarized parallel to the c axis of the crystals in the (zz) geometry. Values for the frequencies and linewidths of the 440- and 500-cm^{-1} phonons were obtained by fitting the corresponding Raman peaks to the combination of two profiles, a Lorentzian for the 440-cm⁻¹ phonon and a Fano profile¹⁸ for the 500-cm⁻¹ phonon; thus,

$$I = \frac{I_{440}}{1 + \varepsilon_{440}^2} + I_{500} \frac{(\varepsilon_{500} + q)^2}{1 + \varepsilon_{500}^2} + B , \qquad (2)$$

where $\varepsilon_{\nu} = (\omega - \omega_{\nu}) / \gamma_{\nu}$, ω_{ν} are the frequencies, γ_{ν} are the linewidths, B is a linear background term, and q is the Fano asymmetry parameter for the 500-cm^{-1} phonon peak. It should be noted that the 440-cm⁻¹ Raman peak is relatively weak in all spectra and also is located on the wings of the dominant feature at 500 cm⁻¹. We have adopted the combined fitting procedure (2) in an attempt to account for any mutual interference between the two peaks. This has resulted in a smaller estimate for $\Delta 2\gamma_{440}$ than was obtained⁸ by fitting this phonon in isolation. An example of such a combined Lorentz-Fano profile is shown in Fig. 7 superimposed on the experimental data for crystal A at 40 K. A Fano profile was used for the 500-cm^{-1} phonon since, although the Raman peak is symmetric in most of the cases, spectra of crystal G with the lowest oxygen concentration (y = 6.68) show a distinctly asymmetric 500-cm⁻¹ peak. Furthermore, McCarty *et al.*²³ have used a Fano profile in fitting the 500-cm⁻¹ phonon and it is interesting to compare their results for q to those here. The 440- and 500-cm⁻¹ peaks corresponding to the 40-K spectra of crystal G are shown in Fig. 8 along with the fitted Lorentz-Fano profile.

In Fig. 9, the temperature dependences of the frequencies of the 440-cm⁻¹ mode are plotted. As first observed by Thomsen *et al.*,¹¹ the frequency of this phonon hardens below T_c for crystals *A*, *B*, *C*, *D*, *E*, and *F* and softens marginally in crystal *G*. The largest shift in fre-



FIG. 7. The 440- and 500-cm^{-1} peaks obtained at 40 K in the (zz) geometry from crystal A (dots). The solid line represents a fit of the data to the combination of two profiles, a Lorentzian for the 440-cm⁻¹ phonon, and a Fano profile (Ref. 18) for the 500-cm^{-1} phonon, plus a linear background.



FIG. 8. The 440- and 500-cm^{-1} peaks obtained at 40 K in the (zz) geometry from crystal G (dots). The solid line represents a fit of the data to the combination of two profiles, a Lorentzian for the 440-cm⁻¹ phonon, and a Fano profile (Ref. 18) for the 500-cm^{-1} phonon, plus a linear background.

quency is again observed in crystal A while the amount of hardening is gradually reduced in the deoxygenated crystals. In Fig. 10, the temperature dependence of the 500-cm^{-1} mode frequency is plotted for each crystal. As with the 440-cm $^{-1}$ phonon, and as observed by other groups,^{9,14,23} hardening of the 500-cm^{-1} phonon is observed below T_c for crystals A, B, C, D, E, and F. The greatest frequency shift is observed in crystal C which hardens by about 4 cm^{-1} . In contrast to these results a softening of about 2 cm^{-1} is observed in crystal G. It should be noted that this softening [Fig. 10(g)] has an onset at approximately 80 K which is well above the critical temperature of this crystal ($T_c \approx 60$ K). This suggests that the softening in this crystal is not superconductivity induced.

In Fig. 11, the temperature dependence of the linewidth of the 440-cm⁻¹ mode is plotted for each crystal. In each case the departure of the experimental data points from the anharmonic decay curve¹⁸ below T_c is approximately equal to the experimental uncertainties. This is not the case for the temperature dependences of the linewidths of the 500-cm⁻¹ mode shown in Fig. 12 for all seven crystals. The 500-cm⁻¹ phonon linewidth



FIG. 9. Frequencies of the 440-cm⁻¹ phonon as a function of temperature for (a) crystal A, (b) crystal B, (c) crystal C, (d) crystal D, (e) crystal E, (f) crystal F, and (g) crystal G. The solid lines are only intended to serve as guides to the eye.



FIG. 10. Frequencies of the 500-cm⁻¹ phonon as a function of temperature for (a) crystal A, (b) crystal B, (c) crystal C, (d) crystal D, (e) crystal E, (f) crystal F, and (g) crystal G. The solid lines are only intended to serve as guides to the eye.



FIG. 11. Linewidths of the 440-cm⁻¹ phonon as a function of temperature for (a) crystal A, (b) crystal B, (c) crystal C, (d) crystal D, (e) crystal E, (f) crystal F, and (g) crystal G as determined by numerical fits of the 440- and 500-cm⁻¹ Raman peaks to combined Lorentz-Fano (Ref. 18) profiles with a linear background. The solid lines are fits to the data above T_c to a model of anharmonic decay (Ref. 18).

broadens by approximately 4 cm^{-1} in crystals A, B, and C as shown by the departure of the experimental data points from the anharmonic decay curve¹⁸ at 15 K and in a manner similar to that reported by other groups.^{9,14,23} Crystals D, E, and F show a diminished broadening in the 500-cm⁻¹ phonon linewidth of between 1 and 2 cm⁻¹ and a narrowing in the 500-cm⁻¹ phonon linewidth by about 3 cm^{-1} is observed in crystal G. Finally, the value of the Fano parameter q, for the 500-cm⁻¹ phonon peak in crystals A, B, C, D, E, and F varied from about 100 to about 2500 indicating that the 500-cm⁻¹ Raman peak in these crystals was highly symmetric and essentially Lorentzian. The value of the Fano parameter q, for the 500-cm⁻¹ phonon of crystal G, however, varied between 3 and 5 indicating a highly asymmetric peak. These results differ from those of McCarty et al.²³ which give relatively small negative values for the Fano parameter even in highly oxygenated crystals.

IV. DISCUSSION

Figures 13 and 14 summarize the observed superconductivity-induced shifts in frequency $(\Delta \omega_{\nu})$ and linewidth $(\Delta 2\gamma_{\nu})$, respectively, as a function of oxygen



FIG. 12. Linewidths of the 500-cm⁻¹ phonon as a function of temperature for (a) crystal A, (b) crystal B, (c) crystal C, (d) crystal D, (e) crystal E, (f) crystal F, and (g) crystal G as determined by numerical fits of the 440- and 500-cm⁻¹ Raman peaks to combined Lorentz-Fano (Ref. 18) profiles with a linear background. The solid lines are fits of the data above T_c to a model of anharmonic decay (Ref. 18).

concentration y, for all the crystals studied and for all three phonons. Shifts in linewidth $\Delta 2\gamma_{\nu}$ are taken between the experimental data points and the anharmonic decay curve¹⁸ at 15 K while shifts in frequency $\Delta \omega_{\nu}$ are taken as the difference in the phonon frequencies at 15 and 100 K. It is evident from these figures that, although there are variations in the 440- and 500-cm⁻¹ frequency and linewidth shifts over the range $6.93 \leq y \leq 7.0$ of oxygen concentrations, they are not as dramatic as the corresponding behavior of the 340-cm⁻¹ mode.

It is of interest to compare the observed superconductivity-induced changes in frequency and linewidth to the predictions of strong-coupling models^{17,25} in an attempt to obtain an estimate for 2Δ in each of the different samples. That is, for a given sample the values of $\Delta \omega_{\nu}$ and $\Delta 2\gamma_{\nu}$ for all three phonons should define a single value for the gap, as found previously.^{8,11,18} If we first examine the behavior of the 340-cm⁻¹ phonon, comparisons with calculations suggest that $2\Delta \approx 340\pm20$ cm⁻¹ ($\approx 5.4kT_c$) for crystal A (y = 7.0). The smaller values of $\Delta \omega$ and $\Delta 2\gamma$ obtained for crystals B(y = 6.99) and C (y = 6.93) further suggest that the gap is becoming larger as oxygen is removed from the sample and reaches a value of about $2\Delta \approx 440\pm50$ cm⁻¹



FIG. 13. Superconductivity-induced frequency shifts between 15 and 100 K for the 340-, 440-, and 500-cm⁻¹ phonons as a function of oxygen concentration. Data points with error bars correspond to crystals A, B, C, D, E, F, and G. The dashed lines are only intended to serve as guides to the eye.

 $(\approx 7.0 kT_c)$ for y = 6.90. The values for the gap were determined in the clean limit using the curves presented in Figs. 3 and 4 of Ref. 17, and a coupling constant,³⁷ $\lambda = 0.02$. Both the linewidth and frequency shifts are consistent with the ZZ model. It should be noted that increasing defect or impurity concentrations could also result^{17,25} in reductions of $\Delta \omega_{\nu}$ and $\Delta 2\gamma_{\nu}$ similar to those observed in Figs. 4, 5, and 9-12. However, impurity scattering does not appear to be playing an important role here, at least for crystals with $y \gtrsim 6.9$. In support of this statement one can note the dramatic changes in $\Delta 2\gamma_{\nu}$ that occur between samples A and B where $\Delta y \approx 0.01$, the relatively narrow phonon linewidths in crystals with $6.9 \leq y \leq 7.0$, and measurements of the surface resistance,³⁸ scattering rate,³⁸ and specific-heat jump²⁶ for crystal C with y = 6.93, the results of which are indicative of high-quality crystals.

From Fig. 5 it is also evident that for crystals A, B, and C, $\Delta 2\gamma_{340}$ exhibits a maximum relative to the anharmonic curve as the temperature is reduced below T_c . This maximum can be interpreted⁴⁰ as a resonance between the phonon frequency and a peak in the pairbreaking distribution density of states which is moving to higher energies as the temperature is decreased. The maximum broadening occurs at about 65, 80, and 85 K for samples A, B, and C, respectively, and if the peak in the density of states is associated with the opening of a gap then these results also suggest that the gap is increas-



FIG. 14. Superconductivity-induced linewidth shifts at 15 K for the 340-, 440-, and 500-cm⁻¹ phonons as a function of oxygen concentration. Data points with error bars correspond to crystals A, B, C, D, E, F, and G. The dashed lines are only intended to serve as guides to the eye.

ing in energy as y is decreased from 7.0 to 6.93. It should also be noted that the observed peak in the broadening is correlated with the maximum in -10/q (Fig. 6) for the same samples.

Interestingly, an increase in the ratio $2\Delta/kT_c$ from 5.8 for y = 7.0 to 6.8 for y = 6.63 has recently been predicted in a theoretical paper by Monthoux et al.³⁹ in which magnetic interactions constitute the pairing mechanism. This result thus perhaps provides some plausibility for the increasing gap behavior we have deduced from the 340-cm⁻¹ phonon renormalization. It should be noted that the negative values of $\Delta 2\gamma_{340}$ shown in Fig. 5 cannot be reconciled with the strong-coupling models because rigorous k-vector conservation would normally preclude the normal-state decay of a $k \approx 0$ phonon into an electron-hole pair.²⁵ However, in spectra obtained from the cuprates in the normal state $(T > T_c)$ the 340-cm⁻¹ phonon has a Fano profile which indicates the presence of an electron-phonon interaction, and thus implies that the usual k-vector selection rule must be broken in some manner. As previously suggested by Hadjiev et al.,²⁴ since the quasiparticle density is reduced dramatically when the sample is cooled below T_c , this decay channel is lost and line narrowing could be observed if the phonon energy is less than 2Δ and hence decay by a pair-breaking mechanism is impossible.

As the oxygen content in the crystals (D, E, F, G) is reduced below 6.93, $\Delta \omega_{340}$ continues to decrease [Figs.

4(d)-4(g)] and reaches zero at y = 6.68 while $\Delta 2\gamma_{340}$ remains negative. These results could be interpreted in terms of the strong-coupling models^{17,25} as implying further increases in gap energy. However, as y decreases the defect concentration in the crystals can be expected to increase with a corresponding increase in the scattering rate $1/\tau$. As pointed out in Refs. 17 and 25, large scattering rates tend to "wash out" observable phonon renormalization effects and can also lead to linewidth narrowing in the weak-coupling limit. Thus, the observed results for the frequency and linewidth behavior in crystals E to G could be explained by any, or all, of an increasing gap, an increase in the scattering rate, or a reduction in the carrier concentration and hence a smaller coupling constant, which would tend to diminish the strength of the effects.

If we now examine the behavior of the 500-cm^{-1} mode in terms of the above we find that its behavior is qualitatively consistent with the above interpretation in that the phonon both hardens and broadens for all crystals with y > 6.8 implying that $\omega_{500} > 2\Delta$. The magnitude of the hardening and broadening both decrease as y decreases below 6.9 which could result from a reduced hole concentration and hence smaller coupling constant or from an increase in the scattering rate $1/\tau$. In crystal G (y=6.68) the 500-cm⁻¹ phonon is observed to both soften and narrow with an onset temperature (≈ 80 K) that is significantly greater than the critical temperature $(\approx 60 \text{ K})$ of this sample and thus these changes are difficult to associate with the onset of superconductivity. It is interesting that Slakey et al.,⁴¹ in a study of the electronic scattering in a 60 K crystal, also found that the peak in the B_{1g} continuum was observable at temperatures well above T_c . It should also be noted that Litvinchuk, Thomsen, and Cardona⁴² observed a broadening of the 500-cm⁻¹ phonon in experiments carried out on crystals with y = 6.57, a result that is in sharp contrast to our results in crystal $G(y \approx 6.7)$.

The behavior of the 440 mode is, however, anomalous in that $\Delta 2\gamma_{440} \approx 0$ for all crystals and yet $\Delta \omega_{440} > 0$ for crystals *A*, *B*, and *C*. McCarty *et al.*⁹ obtained similar results for the 440 mode and used the linewidth change to estimate the gap value on the assumption that it was a more sensitive measure than was the frequency shift which was inconsistent with the value of the gap thus determined.

If one attempts a more quantitative comparison of $\Delta \omega_{\nu}$ and $\Delta 2\gamma_{\nu}$ for the 440- and 500-cm⁻¹ modes with the strong-coupling models,^{17,25} however, it becomes clear that neither of these two modes responds in a manner that is completely consistent with a gap that is increasing from 340 cm⁻¹ (y = 7.0) to 440 cm⁻¹ (y = 6.90) as is implied by the 340-cm⁻¹ mode. It is perhaps more realistic to assume that the 440- and 500-cm⁻¹ modes interact with a different set of electrons than does the 340-cm⁻¹ mode as has been suggested previously.¹¹ For example, one might assume that the 340-cm⁻¹ mode would interact most strongly with the B_{1g} continuum and the 440and 500-cm⁻¹ modes with the A_g continuum.^{6,7,12} It might then be possible to obtain the temperature variation of $\Delta 2\gamma_{\nu}$, for example, in a manner similar to that used by Klein *et al.*⁴³ in an investigation of the 115-cm⁻¹ mode.

V. CONCLUSIONS

The superconductivity-induced changes $\Delta \omega_{\nu}$ and $\Delta 2 \gamma_{\nu}$ have been measured for the Raman-active phonons at 340, 440, and 500 cm⁻¹, for crystals with seven different oxygen concentrations. The values of $\Delta\omega_{340}$ and $\Delta 2\gamma_{340}$ have been found to be very sensitive to small changes in the oxygen concentration. The previous controversy^{6,8,9,18,20,23} concerning the broadening of this mode can thus be reconciled in terms of small differences in the oxygen or hole concentrations in the samples used by different groups. We would argue²¹ that it is, in fact, the hole concentration which determines the behavior of this phonon. Hadjiev *et al.*²⁴ have correlated a lack of broadening of the 340-cm^{-1} mode with the appearance of features at 232 and 598 cm⁻¹. They have further attributed these modes to forbidden (ir active) vibrations of the chain atoms which become Raman active because of defect-induced disorder in the chains of oxygen-depleted samples. Our results are consistent with this interpretation in that we also observe these modes in oxygendepleted, and hence chain disordered, samples. However, we have also observed⁸ a lack of broadening of the 340 cm^{-1} mode in samples containing Th, and yet there was no indication of the features at 232 and 598 cm^{-1} in the spectra. Since Th^{4+} substitutes for Y^{3+} and hence reduces the hole concentration we thus conclude that the broadening of the 340-cm⁻¹ mode is determined by the hole concentration. The modes at 232 and 598 cm^{-1} will be correlated with a lack of broadening only if the hole concentration is reduced by chain defects created by oxygen removal or impurity substitution on the chain sites. In this regard it should be noted that our interpretation differs from that of Thomsen et al.¹⁹ who suggested that the presence of impurities led to a symmetrization or smearing of the Fermi surface and, under certain circumstances, to a larger effective gap.

Comparisons of the superconductivity-induced changes, $\Delta \omega_{\nu}$ and $\Delta 2\gamma_{\nu}$ with strong-coupling models^{17,25} suggest that the superconducting gap increases from about $2\Delta/kT_c \approx 5.4\pm0.3$ for y=7.0 to $2\Delta/kT_c \approx 7.0\pm0.7$ for samples with $y\approx6.9$. There is some ambiguity between the results obtained with the different phonons, however, and this perhaps implies that consistency in this approach would require the existence of two or more gaps with different symmetries.

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