Raman study of the anomalous behavior of the 340-cm^{-1} CuO_2 planar-oxygen phonon in Ni-doped $YBa_2Cu_3O_{7-\delta}$ superconducting films

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The unusual softening of the B_{1g}-like phonon of $YBa_2Cu_3O_7$ is studied as a function of T_c by substituting up to 6% nickel for Cu. The abrupt onset and small temperature range over which the softening occurs in undoped $YBa_2Cu_3O_7$ are modified upon doping with the softening occurring well *above* T_c and continuing smoothly to 10 K when T_c is reduced to 71 K. The phonon linewidth in the doped films shows no anomalies, regardless of Ni concentration. In contrast, the self-energies of the A_g modes associated with the plane copper [Cu(2)] and bridging oxygen (O_4) atoms reveal normal thermal behavior for all films. We conclude that an additional mechanism, besides strong coupling of phonons to superconducting electrons, contributes to the B_{1g}-phonon anomalies.

I. INTRODUCTION

There is a large body of literature in which the anomalous temperature dependences below T_c of the frequencies and linewidths of various Raman- and infrared-active-zone-center phonons in $YBa_2Cu_3O_{7-\delta}$ (Refs. 1–12) and $YBa_2Cu_4O_8$ (Refs. 13–15) are interpreted as evidence[8,9,11–15] that, for that portion of the Fermi surface that couples to each of these phonons, there exists an inelastically rounded BCS-like superconducting density of states, i.e., $N_s(E)$ has a gap and a strong peak. In the most dramatic data,[3,4,10] the "340-cm^{-1}" phonon, which involves out-of-phase vibrations of the O(2) and O(3) oxygens in the CuO_2 planes, softens by 4–8 cm^{-1} and broadens by 7 cm^{-1} (from 13 to 20 cm^{-1}), as the sample is cooled from T_c($\approx$92 K) to about 70 K. Moreover, since application of a magnetic field for $T \lesssim T_c$ hardens this phonon,[5] the direct or indirect mediation of superconductivity seems destined in accounting for at least part of the phonon renormalization.

Calculations of Zeyher and Zwicknagl (ZZ),[16] who use the Eliashberg formulation of superconductivity to evaluate corrections to phonons due to electron-phonon coupling, are the primary theory invoked to explain the phonon anomalies. Substantial electron-phonon coupling is indeed indicated, even in the normal state, by the asymmetry of the Raman peak at 340 cm^{-1}. Underlying the ZZ theory is the repulsion between coupled quantum energy levels with similar energies; in this case the one-phonon, no quasiparticle state, [$E=\hbar\omega_{\rm ph}$, $\mathbf{q}=0$, spin$=0$], is pushed to lower or higher energy by coupling to the no-phonon, two-quasiparticle [$E_{\rm tot}\approx 2\Delta$, $(\mathbf{k}\uparrow;-\mathbf{k}\downarrow)$, spin$=0$] states. Phonon broadening reflects an increase in $N_s(E)$ at $E=\hbar\omega_{\rm ph}/2$, which increases the decay of the phonon into two $(\mathbf{k}\uparrow;-\mathbf{k}\downarrow)$ quasiparticles.

The important parameters of the ZZ theory are $\hbar\omega_\nu/2\Delta(0)$, the electron-phonon coupling strength Λ_ν for phonon ν in the pure material, and the normalized electron elastic-scattering rate, $\hbar/2\Delta(0)\tau$, which weakens electron-phonon coupling. An inelastically broadened BCS superconducting density of states is implicit in the theory. When reasonable values for these parameters are used, e.g., $\hbar\omega_\nu/2\Delta(0)\approx 1$, $\Lambda_\nu\approx 0.01-0.02$, and $\hbar/2\Delta(0)\tau \ll 1$,[17,18] renormalizations of the 340- and 440-cm^{-1} phonons are several times larger than are observed. This quantitative discrepancy leaves room for some broadening of the peak in the superconducting density of states from anisotropy or pair breaking, which would be present in a more realistic theory.

Qualitatively, the key prediction of the ZZ theory is that linewidth and frequency changes below T_c are correlated. Phonons with energies below $2\Delta(0)$ soften and sharpen; phonons with energies above $2\Delta(0)$ harden and broaden. The crossover from softening to hardening as $\hbar\omega_\nu/2\Delta(0)$ increases past about 1.1, with $\hbar\omega_\nu/2\Delta(0)$ varied by doping or oxygen depletion, for example, should be very rapid. A sample right at the crossover point should have no anomaly in its frequency but have the largest phonon broadening.

Observation of phonon anomalies below T_c and development of the ZZ theory led quickly to numerous doping studies in which ω_ν and/or T_c were varied systematically. In most studies, unlike the present investigation of Ni-doped $YBa_2Cu_3O_{7-\delta}$, $\hbar/2\Delta(0)\tau$ remained small. An early important success for the ZZ theory was the observation that the size of the hardening and softening as well as linewidth changes of the 340- and 440-cm^{-1} phonons varied more or less as predicted when $\omega_{\rm ph}$ was decreased by about 10% by replacing Y with rare-earth atoms and ^{16}O was replaced by ^{18}O.[8,9] These dopings did not change T_c or increase $1/\tau$ significantly. It was not possible to increase $\omega_{\rm ph}/2\Delta$ with these dopings to observe the crossover from softening to hardening.

There are other studies of doped $YBa_2Cu_3O_{7-\delta}$, including O-depleted $YBa_2Cu_3O_{7-\delta}$,[6,19] Au substituted for Cu atoms in the CuO chains,[20] and Pr doped for Y.[20,21] Au doping does not affect T_c, while O depletion and Pr doping decrease T_c. There is no evidence that any of these dopings increases $1/\tau$ substantially. In all cases, the renormalization of 340-cm^{-1} phonon linewidth disap-

pears quickly with doping. Phonon softening is only slightly less sensitive to doping; for example, it disappears completely when T_c decreases below 84 K with oxygen depletion and when T_c decreases below 60 K for Pr doping. Within the ZZ picture, the disappearance of linewidth effects means that the relevant gap increases, rather than decreases, with doping. As an explanation,[20] it has been suggested that different phonons couple most strongly to different portions of the Fermi surface, and that the energy gap is different on these different portions. Dopant-induced elastic scattering could reduce this gap anisotropy by increasing the smaller gaps toward a presumably larger average value. This then would increase the gap over the portion of the Fermi surface coupled to the 340-cm^{-1} phonon, even as T_c decreases. This is an interesting conjecture which needs further study because there is no evidence that elastic scattering is strong enough and because a reduction in gap anisotropy usually is accompanied by a sharp decrease in T_c, which certainly is not observed in the Au-doped samples.

Besides the ZZ theory, there is another, phenomenological, approach to understanding phonon anomalies.[4,10] In this approach, changes with temperature of the electronic continuum[10,14,22–28] from the Raman spectra are correlated with changes in the phonons, assuming some coupling between the two. This approach has some success, but cannot account for, e.g., the disappearance of renormalization of the 340-cm^{-1} phonon when oxygen depletion reduces T_c below 84 K. We will not consider this approach further in this paper.

We undertook this Raman study of Ni-doped $YBa_2Cu_3O_{7-\delta}$ to determine whether the phonon anomalies evolve according to ZZ theory as T_c, and presumably $2\Delta(0)$, are systematically suppressed with Ni. Ni is an excellent dopant for several reasons. It is found to substitute on all Cu sites including Cu(2) atoms on the CuO_2 planes where superconductivity is known to exist, and thus is expected to increase $1/\tau$, while having a minor effect on hole density. From a companion study of the infrared reflectance of our doped films[29] we indeed confirm that Ni increases $\hbar/2kT_c\tau$ to values near unity. One might hence expect Ni to reduce anisotropy of the gap and thereby sharpen the peak in the quasiparticle density of states, as conjectured in analyses of earlier doping studies of phonon anomalies.[20] $1/\tau$ has also been directly estimated from transport data for all films[30] and thus, at least, a qualitative evaluation of its role in the ZZ theory should be realized. Moreover, while Ni doping reduces T_c, it should hardly affect the frequency and linewidth of the O(2)-O(3) Raman phonons, since the short-range Cu-O and Ni-O overlap potentials are very close[31] and the lattice parameters are also hardly modified by doping. Such tunability of the superconducting properties with minimal changes to the vibrational characteristics could provide a means to isolate and study the influence of the ordered state on the phonons.

Our results below show that the abrupt onset and small temperature range over which the softening occurs in undoped $YBa_2Cu_3O_{7-\delta}$ are modified in the doped films where the softening occurs well above T_c and continues to 10 K when T_c is reduced to 71 K. The phonon linewidths show no anomalies regardless of Ni concentration. The expectations of the ZZ calculations, namely rapid suppression of the softening and the narrowing of the linewidths with reduced T_c are hence not realized. Feile *et al.*[7] and Cooper and Klein[10] discuss the possibility of other mechanisms, in addition to coupling of phonons to BCS-like superconducting electrons, to be in place. Our results provide evidence of another mechanism that can produce effects of the observed size in that they show an onset of softening of the 340-cm^{-1} phonon well above T_c, and that no additional anomaly occurs at T_c.

II. EXPERIMENTAL DETAILS

The samples are highly oriented, 3000 Å thick, epitaxial films of $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ on (100) $SrTiO_3$ substrates. The c axis is perpendicular to the substrate. They are fabricated by codeposition of Y, BaF_2, Cu, and Ni with an *ex situ* postanneal at 900 °C in oxygen bubbled through water, followed by 1 h at 500 °C in pure dry oxygen to oxygenate them as fully as possible.[30,32] Ni concentrations quoted are nominal values deduced from the deposition rates.

To confirm reproducibility of our results, two samples of the same nominal Ni concentration of 6 at. % were studied. These are labeled 6%-A and 6%-B. The transition widths are <3 K, as shown in Fig. 1, which displays the change in inductance of a flat coil pressed against a film as a function of T.[33] Our values for $T_c(x)$ are a little higher than bulk samples of Bridges *et al.*,[34] possibly due to more NiO precipitation than they encountered, which was about 50% for $x \gtrsim 0.05$, although there is no evidence for NiO in our x-ray measurements. Their x-ray-absorption fine structure (XAFS) data[34] indicate that Ni substitutes equally on all Cu sites, so roughly two-thirds of it goes into the CuO_2 planes.

Resistivity[30] and infrared reflectance measurements[29] provide estimates of $1/\tau$. We find that $1/\tau$ is roughly linear in Ni concentration, and it reaches

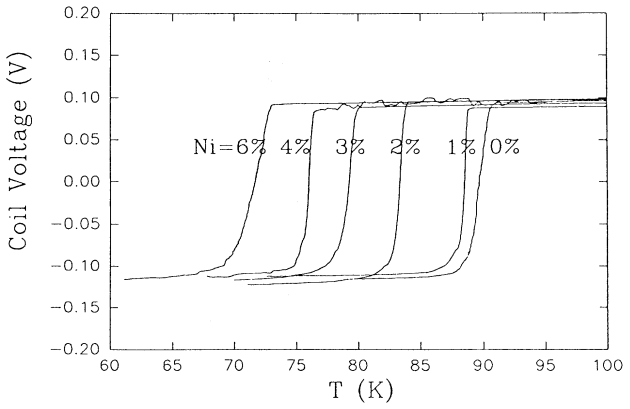

FIG. 1. Change in inductance of a flat coil pressed against the $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ film vs T to show the width and location of the superconducting transition. The 6% Ni-doped film shown is the 6%-A sample; 6%-B shows a very similar response.

2×10^{13}/s($\approx$140 K) at $x=4$ at. %, where $T_c\approx76$ K.

Raman measurements were made in backscattering with 150 mW of 5145 Å or 6471 Å photons and the radiation analyzed with a Spex double-grating spectrometer. The beam was focused to a line $\sim3\times0.5$ mm by a cylindrical lens to minimize heating. The temperatures quoted are those recorded near the sample. The films are close to being fully oxygenated ($\delta\approx0$), which is consistent with the O(4) Raman phonon occurring just above 500 cm^{-1} in all samples.[35]

III. RESULTS

Figure 2 shows Raman spectra excited at 5145 Å at 10 K from several films of $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ with varying x. The B_{1g} phonon at $\sim$340 cm^{-1} and the 500-cm^{-1} O(4) vibration are observed and occur within ±1 cm^{-1} for all films at 10 K, thus confirming that the introduction of Ni has a minimal effect on these vibrations. Because of the $c_\perp$ film orientation, the intensity of the in-phase O(2)-O(3) A_g phonon at 440 cm^{-1} is too weak to study accurately.[32] A broader peak centered around 590 cm^{-1} and a peak at $\sim$230 cm^{-1} that display sample dependent intensities are observed in certain films. These phonons have been previously identified[35,36] as group theoretically Raman-forbidden vibrations arising from the CuO chain and thus indicate the presence of some disorder in the chains. The two remaining A_g modes, at 116 cm^{-1} (Ba mode) and 150 cm^{-1} (Cu2 mode) are not clearly evident in the spectra of Fig. 2 because of parasitic Rayleigh scattering. However, as discussed below, they are observed under more resonant conditions when excited at 6471 Å.

Figures 3 and 4 show in more detail the temperature dependence of the 340-cm^{-1} vibration in the pure ($T_c=90$ K) and one of the 6 at. % Ni-doped films ($T_c=71$ K). Similar spectra were obtained from the other films. The solid line through each spectra is a fit based on a Fano line shape

$$I(\omega)=I_0(q+\varepsilon)^2/(1+\varepsilon^2)+C\ ,$$

with $I(\omega)$ being the intensity and $\varepsilon=(\omega-\omega_0)/\gamma$. Here ω_0 is the position of the uncoupled phonon, ω is the Raman shift, γ is the half-width of the peak, q is an asymmetry parameter, and C is a constant. The 340-cm^{-1} peak is asymmetric with $q\approx-6$ for all samples at 10 K. We summarize all results, as derived from the fits, for the frequency (ω_0) and half-width (γ) of the B_{1g}-like 340-cm^{-1} phonon in Figs. 5 and 6.

Figure 7 shows the temperature dependence of the Raman data in the vicinity of the 500-cm^{-1} O(4) Raman phonon for the 6%-A film; the other films yielded similar quality spectra. The solid line is a fit with a Lorentzian

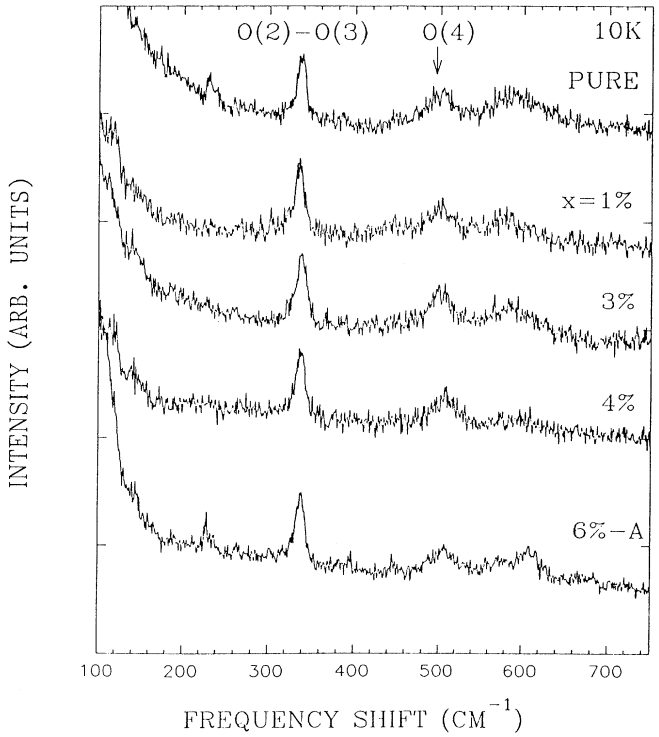

FIG. 2. Raman spectra excited with light at 5145 Å from pure and Ni-doped $YBa_2Cu_3O_{7-\delta}$ films at 10 K.

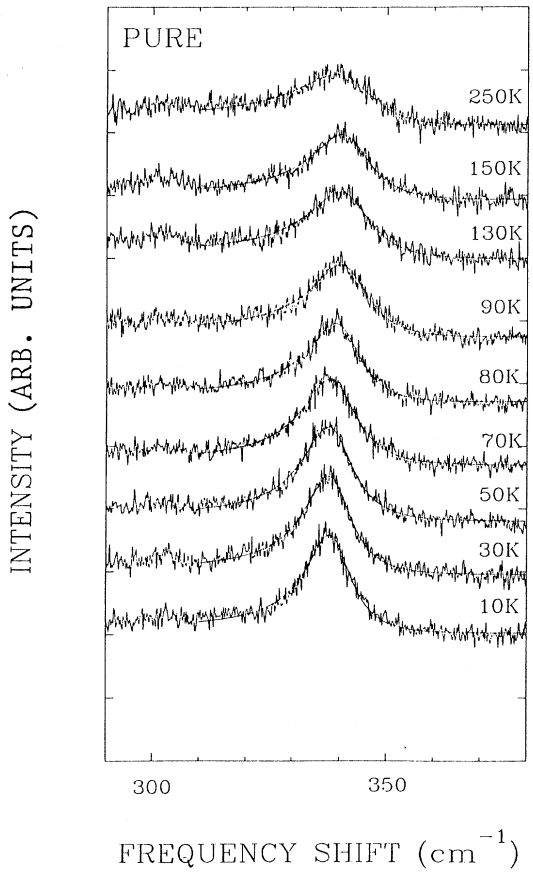

FIG. 3. Temperature dependence of the 340-cm^{-1} Raman phonon in pure $YBa_2Cu_3O_{7-\delta}$. The solid line through each spectrum shows fits based on Fano line shape analysis.

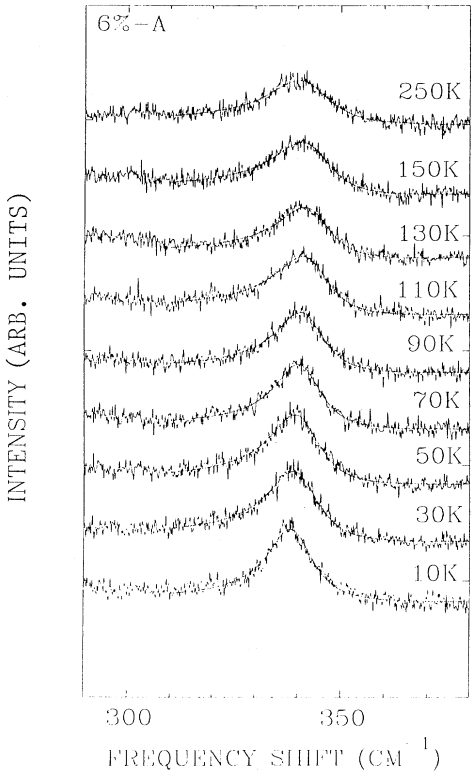

FIG. 4. Temperature dependence of the 340-cm^{-1} Raman phonon in sample 6%-A, the 6% nickel-doped $YBa_2Cu_3O_{7-\delta}$ film. The solid line through each spectrum shows fits based on Fano line shape analysis.

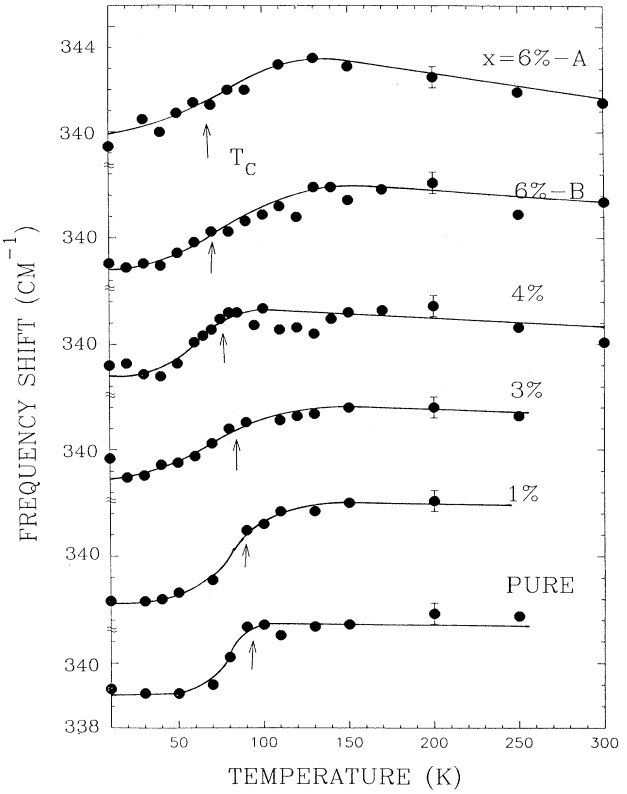

FIG. 5. Frequency ω of the 340-cm^{-1} O(2)-O(3) phonon vs T for films with Ni concentrations up to 6 at. %.

and a linear background. Since in this case the peaks are much more symmetric ($|q| \sim 30$) than the B_{1g} mode, a Fano analysis was not utilized. Because the frequency of this phonon diminishes with oxygen deficiency, its occurrence at 500 cm^{-1} indicates that the oxygen stoichiometry in our films is about $O_{6.95}$. Such an estimate of oxygen stoichiometry from the O(4) Raman frequency of the doped material is reasonable, since the incorporation of Ni hardly affects the original lattice parameters[37] nor changes the frequencies of the other Raman phonons. The frequency and width of this phonon in our films are consistent with measurements on fully oxygenated crystals.[11,12]

Figure 8 illustrates the temperature dependence of the low-frequency spectra recorded with the 6471 Å laser line from the 6%-B film. The spectra in this case are dominated by three main features: two relatively broad peaks centered at 116 and 143 cm^{-1} and the mode identified by arrows at 150 cm^{-1}. We identify the 116-cm^{-1} peak with the Ba atom vibration and its full line width (13 cm^{-1}) is comparable to that reported from pure single-crystal $YBa_2Cu_3O_{7-\delta}$.[38] The 150-cm^{-1} mode is associated with Cu(2) vibration. Consistent with single-crystal results, this mode is narrower than the 116-cm^{-1} Ba mode.[38] The vibration at 143 cm^{-1} is similar to that reported in some crystals, and the possibility of it arising from slight oxygen disorder has been proposed.[38] Although this mode lies very close in frequency to the B_{2g} and B_{3g} modes, its symmetry has been reported to be distinct from them.[38]

The temperature dependences of the 150-cm^{-1} Cu(2) mode and the 500-cm^{-1} O(4) mode in the 6% film are summarized in Fig. 9. In contrast to the 340-cm^{-1} phonon (Fig. 5), they show no unusual renormalization at T_c. The behavior of the O(4) vibration is similar to that reported in Ref. 2 for the undoped material, and does not reveal an anomaly at T_c in the frequency as observed[11] in an untwinned single crystal of $YBa_2Cu_3O_{7-\delta}$. The 150- and 500-cm^{-1} modes in our films show only normal hardening arising from anharmonicity of the crystal.

IV. DISCUSSION

We first focus on the temperature dependencies of the 340-cm^{-1} phonon in all of our films, shown in Figs. 5 and 6. Note that the frequency ω_{ph} and half-width γ at $T=100$ K, (338–339 cm^{-1} and 6–6.5 cm^{-1}, respectively), are the same in the undoped and doped films. γ is about the same as observed in single crystals at T_c. This is not surprising, since the masses and charge state (+2) of the Ni and Cu ions are about the same, as are the Ni-O and Cu-O short-range overlap potentials.[31] Also, no impurity phonons are observed in the Raman spectra. Al-

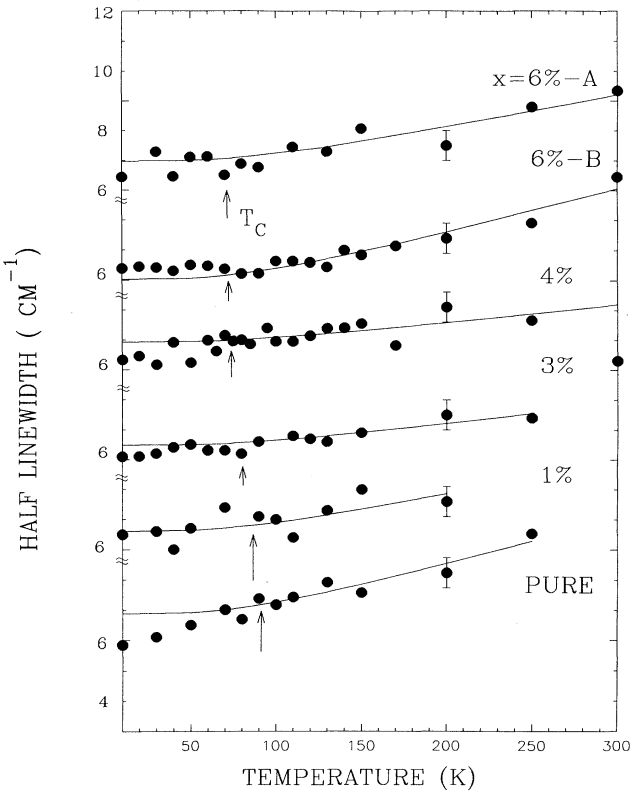

FIG. 6. Half-width γ of the 340-cm^{-1} O(2)-O(3) phonon vs T for films with Ni concentrations up to 6 at. %.

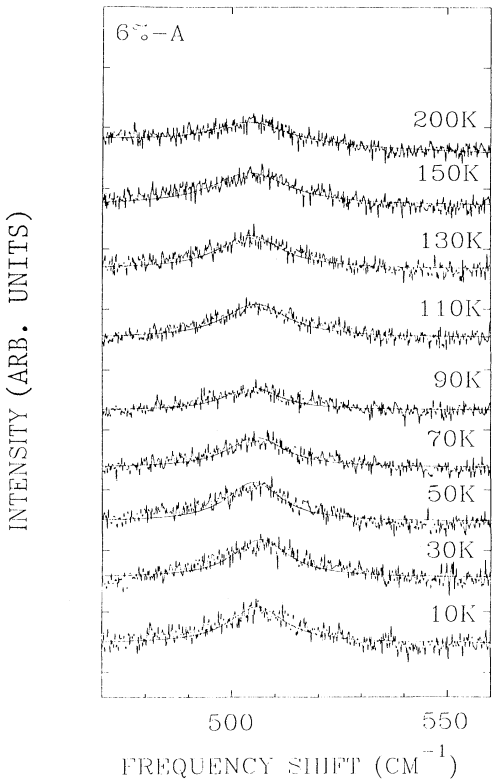

FIG. 7. Temperature dependence of the 500-cm^{-1} A_g phonon in sample 6%-A, the 6% nickel-doped $YBa_2Cu_3O_{7-\delta}$ film. The solid line through each spectrum shows fits based on Lorentzian line shape analysis.

though expected, these results give us confidence that doping changes the lattice chemistry without changing its structure significantly.

Now let us examine ω_{ph} vs T (Fig. 5). The undoped film shows the usual abrupt softening below T_c, with the softening occurring between T_c and $2T_c/3$. The total softening of 3.5 cm^{-1} is consistent with results on other $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_4O_8$ films,[7,13] and is as large as the softening in some crystals of $YBa_2Cu_3O_{7-\delta}$.[11,12] It is however smaller than that reported in some other studies.[2,6,20,38] Already with only 1 at. % Ni, there is some evidence that the abruptness of the softening is reduced with the softening extending down to about $T_c/2$. This is more clear in the 3 at. % Ni film when the softening prolongs to even lower temperatures and, in addition, it appears that the softening commences above T_c. At 4 at. % Ni, there is further evidence of softening above T_c with possibly a shallow dip around 120 K that recovers prior to softening by a further 3 cm^{-1} to 10 K. At 6 at. % Ni, the onset of the softening is now clearly above T_c and occurs at $\approx$130 K in both samples, almost double $T_c \approx 71$ K. The total softening from 130 to 4 K for 6 at. % Ni is about 5 cm^{-1}, comparable to the largest effects observed in high-quality crystals.[38] At 6% doping the softening continues to temperatures as low as 10 K. It is thus seen that the abruptness of the renormalization observed in the intrinsic film becomes progressively less pronounced with increasing x. In the 6% samples, at least, it is clear that there is no additional anomaly at T_c that is detected within the resolution of the measurements.

In contrast, the O(4) phonon (500 cm^{-1}) and the Cu(2) phonon (150 cm^{-1}) in the 6 at. % Ni film show normal thermal hardening (Fig. 9) between 300 and 4 K and hence reassure that the substrate does not influence the significant results of Fig. 5. Moreover, no dopant-induced structural transition, that may give rise to the observed phonon behavior, has been reported for the Ni concentrations we utilized.

As shown in Fig. 6, the half-width γ of the 340-cm^{-1} phonon in our doped films decreases smoothly with temperature. The solid lines indicate a fit to the experimental points above T_c to a model of anharmonic decay.[8] The pure film shows a slight narrowing below T_c as indicated by the departure of the data from the solid curve. Nothing unusual happens in the B_{1g} phonon linewidth either at the temperature where softening begins or at T_c for the other films. The lack of anomaly in γ at T_c has been observed also in a high-quality crystal, as well.[12]

Other dopants studied to date[20] show that a small amount of doping tends to reduce or eliminate linewidth effects of the B_{1g} phonon. Thus the absence, upon doping with Ni, of the slight narrowing of the 340-cm^{-1} mode below T_c observed in our pure film is consistent with this general pattern of behavior. Some caution is

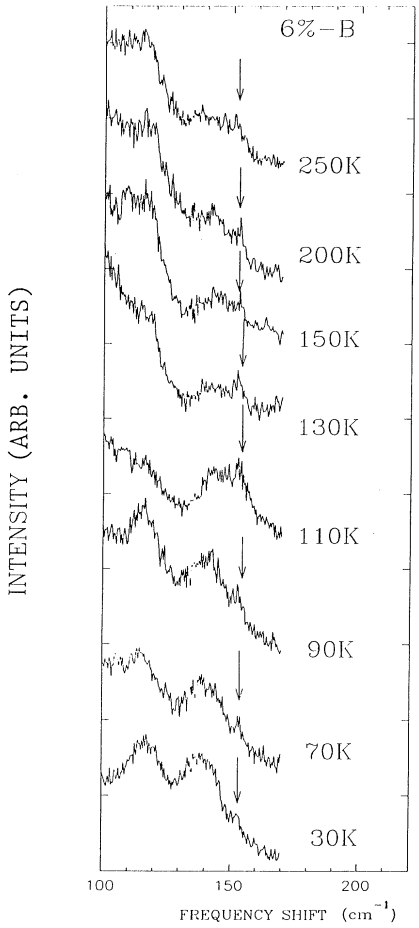

FIG. 8. Temperature dependence of Raman spectra excited with light at 6471 Å from sample 6%-*B*, the 6% Ni-doped $YBa_2Cu_3O_{7-\delta}$ film. Arrows indicate the mode close to 150 cm^{-1} identifying the Cu(2) A_g Raman vibration.

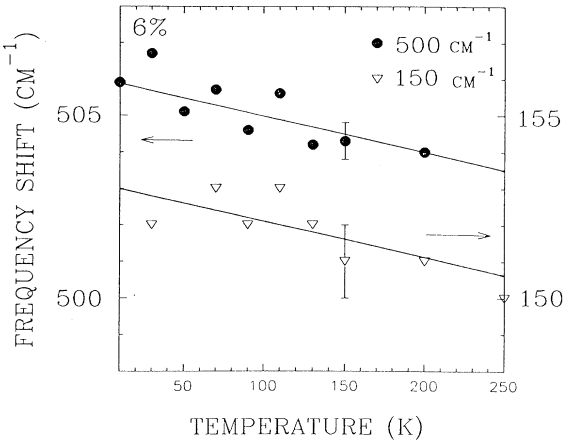

FIG. 9. Frequency ω of the 500-cm^{-1} O(4) phonon and 150-cm^{-1} Cu(2) phonon vs T for films with Ni concentrations up to 6 at. %.

needed here, as some oxygen disordering may accompany Ni doping and contribute to reducing linewidth effects as it appears in the case of our undoped film. The effect of Ni on renormalization of the phonon frequency is different from other dopants, especially in that it allows the phonon softening to commence above T_c. This effect cannot be due to oxygen disorder, since such disorder has no affect on the normal thermal response of the B_{1g} phonon self-energy above T_c.

What do we expect from the Zeyher and Zwicknagl theory? Taking $2\Delta(0)/kT_c=5$, $\hbar\omega/2\Delta$ for the B_{1g} phonon varies from 1.03 to 1.3 as x increases from 0 to 6%. As seen from Fig. 5 of Ref. 16, there is a rapid change in sign of the real part of the phonon self-energy as $\omega/2\Delta$ crosses beyond 1.08 that then asymptotically approaches the normal-state value depending on strength of the scattering rate $1/\tau$. The hardening that follows with the crossover for low impurity scattering rates is suppressed as $\hbar/\tau$ approaches 2Δ. Below T_c, ZZ theory hence predicts that softening in pure $YBa_2Cu_3O_{7-\delta}$ should change to hardening (by about the same amount as the 440-cm^{-1} A_g phonon hardens in pure $YBa_2Cu_3O_{7-\delta}$), as 2Δ decreases from about 320 to 250 cm^{-1}, if the scattering rate lies below 2Δ. The crossover to hardening is expected for a Ni concentration $x\approx 3\%$, where $2\Delta=280$ cm^{-1}. Based on our estimates of $1/\tau$ from resistivity[30] and infrared reflectance measurements,[29] softening should be virtually eliminated by 3 at. % Ni doping. The absence of such suppression, that would have otherwise tied the phonon softening and hardening observed in $YBa_2Cu_3O_7$ to the superconducting gap, hence suggests that the physics underlying the ZZ theory alone does not account for the observed phonon renormalizations.

The linewidth behavior summarized in Fig. 6 is also not in accord with the ZZ theory. In pure $YBa_2Cu_3O_{7-\delta}$, the line should broaden below T_c, and the broadening should decrease by a factor of 2–3 as x increases from 0 to 6%, and $\hbar\omega/2\Delta$ reaches 1.3. This behavior is likely related to oxygen disorder on the CuO chains,[36,39] although the physics of that behavior is not understood at present.

As mentioned above, gap anisotropy in pure $YBa_2Cu_3O_{7-\delta}$ is sometimes hypothesized to allow the ZZ theory to cover the effects of other dopants on phonon renormalizations at T_c, especially the rapid loss of linewidth effects with doping.[20] In this picture, dopant-induced elastic scattering reduces the anisotropy, and presumably sharpens the peak in the superconducting density of states. Although the gap may indeed be anisotropic in pure $YBa_2Cu_3O_{7-\delta}$, and the anisotropy may be affected by dopants, it is unlikely that this explanation accounts for the softening we have observed above T_c.

There have been, to our knowledge, no observations of softening above T_c of Raman-active phonons in pure or doped $YBa_2Cu_3O_{7-\delta}$. It was recently shown, however, that the 440-cm^{-1} mode in oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ ($\delta=0.43$) hardens above T_c.[19] Softening of some infrared-active phonons above T_c has been reported in $YBa_2Cu_3O_{7-\delta}$ systems when the Cu atoms have been partially substituted with Zn, Fe, and Co.[40–42] We

note that even in pure $YBa_2Cu_3O_{7-\delta}$, the infrared phonon at 285 cm^{-1}, which is the analog of the 340-cm^{-1} Raman phonon, softens smoothly from 300 to 10 K. Thus, it is significant that we observe softening above T_c in the 340-cm^{-1} Raman phonon, a mode that has been so heavily studied and, which shows such large anomalies.

Some models for phonon renormalizations above T_c have been put forward, including superconducting fluctuations,[42] dopant-enhanced screening of ionic charges in doped $YBa_2Cu_3O_{7-\delta}$, and microscopic inhomogeneities.[43] At present, the relative merits of these models are unclear. Our results demonstrate that the 340-cm^{-1} phonon responds to some additional mechanism not incorporated in the ZZ theory.

We finally note that the qualitative predictions of the ZZ theory, in particular the transition from softening to hardening as 2Δ is lowered below $\hbar\omega_{ph}$, remain valid and should be present in $YBa_2Cu_3O_{7-\delta}$, even if other influences on phonon frequencies and linewidths exist. For reasonable values of Λ_ν the resulting renormalization effects must be observable. The 340-cm^{-1} phonon in 6%-Ni films softens continuously through T_c; how much of the softening below T_c is from ZZ physics remains to be determined. The occurrence of phonon softening well above the onset of bulk superconductivity in the doped films is also intriguing. Indeed, an anomalous decrease of the planar Cu(2) spin relaxation has also been measured above T_c in NMR measurements[44] and a Raman feature persisting into the normal state[22] provide evidence that precursor effects may somehow precede the transition to bulk superconductivity in $YBa_2Cu_3O_{7-\delta}$.

V. CONCLUSIONS

The unusual softening of the B_{1g}-like phonon at 340 cm^{-1} in 6 at. % Ni-doped $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ films commences well above T_c and continues smoothly to about 10 K. This phonon does not broaden below T_c regardless of the concentration of nickel. The Raman-active A_g phonons associated with the plane copper Cu(2) and bridging oxygen O(4) atoms behave normally from 300 to 10 K, and thus establish that the behavior of the B_{1g} phonon is intrinsic and is not associated with the substrate, for example. The behavior of the 340-cm^{-1} phonon with Ni doping is not captured in the ZZ theory, and the deviations, particularly the softening above T_c, cannot be explained by invoking gap anisotropy or relating it to effects due to oxygen disorder. These results provide evidence that an additional mechanism, besides that of strong coupling to superconducting electrons, contributes to the phonon anomaly. The conditions giving rise to the phonon anomalies in the high-T_c superconductors are thus more intricate than is presently understood.

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[1]R. M. Macfarlane, H. J. Rosen, and H. Seki, Solid State Commun. **63**, 831 (1987).
[2]A. Wittlin, R. Liu, M. Cardona, L. Genzel, W. Konig, W. Bauhofer, Hj. Mattausch, and A. Simon, Solid State Commun. **64**, 477 (1987).
[3]C. Thomsen, M. Cardona, B. Gegenheimer, R. Liu, and A. Simon, Phys. Rev. B **37**, 9860 (1988).
[4]S. L. Cooper, F. Slakey, M. V. Klein, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **38**, 11 934 (1988).
[5]T. Ruf, C. Thomsen, R. Liu, and M. Cardona, Phys. Rev. B **38**, 11 985 (1988).
[6]M. Krantz, H. J. Rosen, R. M. Macfarlane, and V. Y. Lee, Phys. Rev. B **38**, 4992 (1988).
[7]R. Feile, P. Leiderer, J. Kowalewski, A. Assmus, J. Schubert, and U. Poppe, Z. Phys. B **73**, 155 (1988).
[8]B. Friedl, C. Thomsen, and M. Cardona, Phys. Rev. Lett. **65**, 915 (1990).
[9]C. Thomsen, M. Cardona, B. Friedl, I. I. Mazin, C. O. Rodriguez, and O. K. Anderson, Solid State Commun. **75**, 219 (1990).
[10]S. L. Cooper and M. V. Klein, Comments Condens. Matter Phys. **15**, 99 (1990).
[11]K. F. McCarty, H. B. Radousky, J. Z. Liu, and R. N. Shelton, Phys. Rev. B **43**, 13 751 (1991).
[12]E. Altendorf, J. Chrzanowski, J. C. Irwin, A. O'Reilly, and W. N. Hardy, Physica C **175**, 47 (1991).
[13]Y. Liu, J. Y. Lee, M. J. Sumner, R. Sooryakumar, and T. R. Lemberger, Phys. Rev. B **42**, 2643 (1990).
[14]E. T. Heyen, M. Cardona, J. Karpinski, E. Kaldis, and S. Rusiecki, Phys. Rev. B **43**, 12 958 (1991).
[15]A. P. Litvinchuk, C. Thomsen, P. Murugaraj, and M. Cardona, Z. Phys. B **86**, 329 (1992).
[16]R. Zeyher and G. Zwicknagl, Z. Phys. B **78**, 175 (1990).
[17]M. C. Nuss, P. M. Mankiewich, M. L. O'Malley, E. H. Westerwick, and P. B. Littlewood, Phys. Rev. Lett. **66**, 3305 (1991).
[18]D. A. Bonn, P. Dosanjh, R. Liang, and W. N. Hardy, Phys. Rev. Lett. **68**, 2390 (1992).
[19]A. P. Litvinchuk, C. Thomsen, and M. Cardona, Solid State Commun. **83**, 343 (1992).
[20]C. Thomsen, B. Friedl, M. Cieplak, and M. Cardona, Solid State Commun. **78**, 727 (1991).
[21]K.-M. Ham, R. Sooryakumar, and M. B. Maple (unpublished).
[22]F. Slakey, M. V. Klein, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **42**, 2643 (1990).
[23]S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Rice, and D. M. Ginsberg, Phys. Rev. **37**, 5920 (1988).
[24]F. Slakey, S. L. Cooper, M. V. Klein, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **39**, 2781 (1989).
[25]F. Slakey, M. V. Klein, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **43**, 3764 (1991).
[26]K. F. McCarty, J. Z. Liu, R. N. Sheltin, and H. B. Radousky, Phys. Rev. B **42**, 9973 (1990).
[27]R. Hackl, W. Glaser, P. Muller, D. Einzel, and K. Andres,

Phys. Rev. B **38**, 7133 (1988).
[28]D. Kirillov, C. B. Eom, and T. H. Geballe, Phys. Rev. B **43**, 3752 (1991).
[29]M. J. Sumner, J.-T. Kim, and T. R. Lemberger, Phys. Rev. B (to be published).
[30]J.-T. Kim, D. G. Xenikos, A. Thorns, and T. R. Lemberger, J. Appl. Phys. **72**, 803 (1992).
[31]W. Kress, U. Schroder, J. Prade, A. D. Kulkarni, and F. W. de Wette, Phys. Rev. B **38**, 2906 (1988).
[32]Y. Liu, G. Pangilinan, R. Sooryakumar, M. J. Sumner, and T. R. Lemberger, J. Appl. Phys. **64**, 3598 (1988).
[33]D. G. Xenikos and T. R. Lemberger, Rev. Sci. Instrum. **60**, 831 (1989).
[34]F. Bridges, J. B. Boyce, T. Claeson, T. H. Geballe, and J. M. Tarascon, Phys. Rev. B **42**, 2137 (1990).
[35]C. Thomsen and M. Cardona, in *Physical Properties of High-Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, New York, 1989), Vol. I.
[36]V. G. Hadjiev, C. Thomsen, A. Erb, G. Muller-Vogt, M. R. Koblischka, and M. Cardona, Solid State Commun. **80**, 643 (1991).
[37]J. F. Bringley, T.-M. Chen, B. A. Averill, K. M. Wong, and S. J. Poon, Phys. Rev. B **38**, 2432 (1988).
[38]K. F. McCarty, J. Z. Liu, Y. X. Jia, R. N. Shelton, and H. B. Radousky, Physica C **192**, 331 (1992).
[39]E. Altendorf, J. C. Irwin, R. Liang, and W. N. Hardy, Phys. Rev. B **45**, 7551 (1992).
[40]R. Gajic, J. Schutzmann, J. Betz, T. Zetterer, H. Otto, P. E. Obermayer, and K. F. Renk, Solid State Commun. **78**, 65 (1991).
[41]R. Gajic, M. J. Konstantinovic, Z. V. Popovic, W. Konig, S. Zec, and I. Bradaric, Solid State Commun. **81**, 85 (1992).
[42]H. S. Obhi and E. K. H. Slaje, J. Phys.: Condens. Matter **4**, 195 (1992).
[43]J. C. Phillips, Phys. Rev. Lett. **64**, 1605 (1990); Solid State Commun. **81**, 497 (1992).
[44]W. W. Warren, R. Walstedt, G. Brennert, R. J. Cava, R. Tycko, R. F. Bell, and G. Dabbagh, Phys. Rev. Lett. **62**, 1193 (1989).