Phonon renormalizations in $Y_{0.90}Ca_{0.10}Ba_2Cu_3O_{7-\delta}$ and $Y_{0.90}Ca_{0.10}Ba_2Cu_4O_8$ observed by Raman scattering

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We present the results of temperature-dependent Raman measurements of ceramic samples of calcium substituted $Y_{0.90}Ca_{0.10}Ba_2Cu_3O_{7-\delta}$ (Y123) and $Y_{0.90}Ca_{0.10}Ba_2Cu_4O_8$ (Y124). In overdoped Y123 a softening of the 340 cm^{-1} phonon frequency by 4 ± 2 cm^{-1} was seen below T_c, reducing to 1.1 ± 0.6 cm^{-1} at optimal doping. In the Y124 sample, the 340 cm^{-1} phonon was seen to soften by 1.0 ± 0.6 cm^{-1}. No anomalous change in the 340 cm^{-1} linewidth below T_c was discernible in the spectra from either material. The results from calcium substituted Y123 disagree with results from pure samples at similar hole concentrations, but agree with pure Y123 results at similar δ. Meanwhile the substitution of calcium in Y124 has no significant effect on the observed phonon renormalizations. We conclude that the phonon renormalizations in these materials are not solely governed by the planar hole concentration.

I. INTRODUCTION

For conventional superconductors there is a well understood relationship between the superconducting gap energy Δ_0 and the critical temperature T_c, but in high-temperature superconductors the exact relationship between Δ_0 and T_c is not well established. In high-T_c materials the critical temperature shows a strong dependence on the doping state, and a generic relationship between T_c and hole concentration p has been empirically established.[1] However, measurements of the superconducting gap have produced a large number of differing, sometimes contradictory, results—due in large part to the complications of strong gap anisotropy and the presence of the pseudogap in the normal state of underdoped materials. Evidence from NMR and heat capacity measurements suggest that for a large number of cuprate superconductors the pseudogap energy E_g rises rapidly from zero for $p\lesssim0.19$ and at $p\approx0.1$ is comparable with Δ_0. Compared to the pseudogap the superconducting gap energy on the underdoped side is relatively independent of p, while on the overdoped side it appears to scale with T_c.[2–5]

Raman studies of Y-Ba-Cu-O superconductors aimed at measuring the magnitude of the superconducting gap by observation of superconductivity induced phonon renormalizations have revealed a number of interesting features. Measurements as a function of oxygen deficiency δ in $YBa_2Cu_3O_{7-\delta}$ show that the character and magnitude of the phonon renormalizations depend on both δ and phonon symmetry.[6] The B_{1g}-like 340 cm^{-1} phonon renormalizations were found to be extremely sensitive to δ and show a doping dependence indicative of a gap energy which rises with increasing δ. In contrast, the A_g symmetry phonons at 440 and 500 cm^{-1} both show a superconductivity induced renormalization which, for small δ, is independent of δ and consistent with a constant gap. These results were corroborated by electronic Raman measurements.[7] A number of phonons are seen to undergo a similar superconductivity induced renormalization in the related $YBa_2Cu_4O_8$ superconductor.[8,9] In this system there is evidence of phonon anomalies above T_c, and the below T_c renormalizations are best accounted for by phonon self-energy models which consider an anisotropic superconducting gap with nodes.[9]

Interpretation of phonon frequency and width changes below T_c in terms of interaction with a gap is less straightforward than early models[10,11] indicated. Superconducting gap anisotropy, the presence of nodes in the gap, and various impurity scattering effects all exert a strong influence on the predicted phonon behavior in the superconducting state.[12–16] In addition, the presence of the pseudogap in underdoped Y123 and Y124 samples introduces another influence on the phonon self-energy both above and below T_c. Indeed, questions regarding the role played by the pseudogap in the observed phonon renormalizations have been raised for both Y123 and Y124 superconductors.[6,9] In Y123 particularly, the behavior of the B_{1g}-like phonon at 340 cm^{-1} as a function of doping suggests phonon-pseudogap rather than phonon-superconducting-gap interaction.[6] Electronic Raman measurements of the B_{1g} symmetry continuum also suggest that scattering from this symmetry is dominated by pseudogap excitations in underdoped materials.[7,4]

The overdoped side of the doping curve, where the pseudogap is absent, is therefore of some interest. Stoichiometric $YBa_2Cu_3O_7$ is already slightly overdoped,[17] but the remainder of the overdoped regime is normally inaccessible as the oxygen concentration cannot be increased further in this material. The related compound $YBa_2Cu_4O_8$ always has an oxygen concentration very close to stoichiometric and is underdoped in the pure state.[18] In both these compounds, altervalent interplanar substitution of Ca^{2+} for Y^{3+} increases p and provides a convenient alternate means of manipulating the doping state without substantially affecting the structural or superconducting properties of the materials.[19,20] In stoichiometric Y123 ($\delta=0$) an increase in p takes the material further into the overdoped regime, decreasing T_c. For Y124 the opposite effect is seen, the increase in p bringing the material closer to a state of optimal doping and increasing T_c.[18]

We have studied samples of calcium substituted Y123 and

Y124 to investigate superconductivity induced phonon anomalies in doping regions where pseudogap interference is expected to be small or absent. We observe phonon renormalizations similar to those seen in unsubstituted materials and discuss the observed dependence of these renormalizations on δ and p.

II. EXPERIMENT

Polycrystalline samples of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and $Y_{1-x}Ca_xBa_2Cu_4O_8$ were prepared by the common sintering method described in the literature[1,18] and the results presented here were obtained from samples with moderate calcium concentrations of $x=0.10$. The Raman spectra of the these samples showed no evidence of $BaCuO_2$ or other impurities associated with the partial substitution of Ca for Ba, which are usually seen for calcium concentrations $x>0.15$.[21] The oxygen stoichiometry of the Y123 sample was varied to alter the doping state from overdoped ($\delta\approx0.03$) to optimal doping ($\delta\approx0.22$), the oxygen concentration being estimated from previously determined T_c vs δ curves for calcium substituted Y123.[22] We use Eq. (1) of Tallon *et al.*[1]

$$T_c/T_{c,\max}=1-82.6(p-0.16)^2 \quad (1)$$

to estimate p for the calcium substituted Y123 sample. Measurement of the T_c for each sample was performed by either ac or magnetic susceptibility measurements (Y123 sample) or resistance measurements (Y124 sample). The $x=0.10$ Y123 sample had an overdoped T_c of 75 K, while at optimal doping $T_c=85$ K, which we use as $T_{c,\max}$ when estimating p. The T_c of the underdoped $x=0.10$ Y124 sample with was 85 K. The superconducting transition width, measured as the temperature difference between the 10 and 90 % points of the transition curve, was around 4 K for the Y124 sample and around 3.5 K for the Y123 sample when overdoped and optimally doped.

All Raman spectra were obtained in backscattering geometry with the sample mounted inside the cold head of a closed cycle refrigerator. A Jobin Yvon U1000 double monochromator with either a photomultiplier tube (PMT) or charge coupled device (CCD) was used to measure the spectra shown here. The spectral resolution was 5 and 2.5 cm^{-1} for measurements made with the PMT and CCD, respectively, fully resolving the spectral features studied here. An argon ion laser provided an excitation wavelength of 514.5 nm with a typical laser power of 50 mW incident on the sample surface and a line focused spot area of 0.025 cm^2. Measurements using low laser powers indicated that the sample was heated locally by less than 10 K at 50 mW incident power. This minimal sample heating will be ignored when sample temperatures are quoted.

In common with prior measurements of phonon line shapes in the high-T_c materials, phonon peaks were fitted with either a Lorentzian or a Fano line shape superimposed on a linear background.[23] As the phonon widths were usually small on the scale of any nonlinear background, this approximation yielded acceptable results. However, due to the covariance between the frequency, width, and asymmetry in the Fano equation[23] it was found for the spectra from some samples that the noise in the fitted parameters was exaggerated when the asymmetry parameter q was permitted to vary.

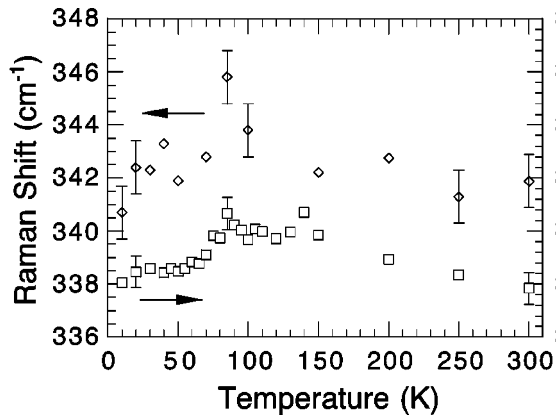

FIG. 1. The frequency of the 340 cm^{-1} phonon of $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ as a function of temperature when optimally doped ($T_c\approx85$ K, open squares) and overdoped ($T_c\approx75$ K, open diamonds). The Raman intensities were measured with the CCD and PMT detectors, respectively, and the spectral lines were fitted with Lorentzian and Fano equations, as noted in the text.

Fano fits with various fixed q values exhibited substantially reduced noise and indicated that the results do not depend strongly on the q value chosen. When fixed q Fano fit results are presented here, the q value which produced the least scatter in the fit results, and was consistent with both plain Fano fits and previous measurements,[6] was selected.

Uncertainties in the fitted line width and frequency were determined from the spread of values from fits of multiple spectra and by varying the width and frequency parameters until the agreement with the spectrum deteriorated noticeably, a technique used previously in the literature.[24] The fit region was also varied to confirm that effects from the nonlinear background were making no contribution to the fitted parameters. As the quoted renormalization magnitudes are the difference between measurements taken at 10 K and T_c, all quoted uncertainties are the sum of the fit uncertainty at these two temperatures.

III. RESULTS

A. Calcium substituted Y123

Spectra measured from the $x=0.10$ sample were consistent with previous Raman studies of calcium substituted Y123 (Refs. 25,26) and displayed the phonon modes at 340, 440, and 500 cm^{-1} which are known to exhibit superconductivity induced renormalization.[6,23]

For this sample in the overdoped state, the 340 cm^{-1} phonon line shape exhibited the strong asymmetry characteristic of this mode in pure Y123. A Fano equation was used to fit the spectral line shape, with a fixed q value of -3.5 used in order to reduce the effects of noise in the spectra on the fitted widths and frequencies. A fit of an anharmonic decay model[23] to the resulting line width data above T_c showed no deviation in the superconducting state from simple thermal narrowing, within a total uncertainty of ±3 cm^{-1}. In contrast, a dramatic softening of fitted line frequency by 4 ±2 cm^{-1} was clearly visible, the onset of which occurred directly at T_c, as shown in Fig. 1 (open diamonds, left axis). In this and subsequent plots of phonon temperature dependence, uncertainties will be shown for only a representative set of points. Uncertainties for data to the left of marked points are identical to the marked uncertainty. The observation that the softening of the 340 cm^{-1} phonon occurred at T_c verified that the laser power incident on the sample did not produce appreciable local heating.

The $x=0.10$ sample was then treated to optimize T_c at 85 K and Raman spectra at a range of temperatures obtained. It was found that a Lorentzian line shape more appropriately described the 340 cm^{-1} phonon line shape in this sample, and phonon frequency fit results using a Lorentzian equation are shown in Fig. 1 (open squares, right axis). An abrupt softening of the mode by 1.1 ± 0.6 cm^{-1} below T_c is observed—similar to, but weaker than, the softening seen when the sample was overdoped. Again, the onset of softening is seen to coincide with T_c, arguing against significant laser heating of the sample. The phonon line width exhibited no superconductivity induced renormalization within the uncertainty of ±1 cm^{-1} when compared to the predictions of the anharmonic decay model.

The phonon modes at 440 and 500 cm^{-1} were measured from the sample at optimal doping ($\delta\approx0.22$). Reliable fits to the 440 cm^{-1} spectral peak were difficult to obtain and the results were inconclusive for this phonon. The temperature dependence of the 500 cm^{-1} phonon line shape showed no anomalous line frequency or width behavior below T_c within uncertainties of ±2 and ±3 cm^{-1}, respectively. We note that essentially no renormalization of these phonon modes was observed by Altendorf *et al.*[6] in unsubstituted Y123 crystals with $\delta<0.1$.

B. Calcium substituted Y124

The temperature dependence of the Raman spectrum of a polycrystalline sample of $Y_{0.90}Ca_{0.10}Ba_2Cu_4O_8$ with $x=0.10$ was measured for similar reasons motivating the measurements of the calcium substituted Y123 materials. In contrast to the stoichiometric Y123 system, calcium substitution in Y124 raises T_c and brings the material's doping state towards optimal, but underdoped.[17]

Typical data for the 340 cm^{-1} phonon at 300 and 10 K are shown in Fig. 2. A single Lorentzian equation fitted to the 340 cm^{-1} peak over a restricted set of wave numbers was found to best reduce the effects of overlapping spectral lines and the nonlinear background below T_c. Plots of the 340 cm^{-1} phonon frequency as a function of temperature are shown in Fig. 3, showing the frequency undergoing a moderate softening of 1.0 ± 0.6 cm^{-1} as the temperature is reduced below T_c. In common with the data collected for the calcium substituted Y123 materials, the renormalization onset temperature is seen to coincide with T_c of the sample, in this case 85 K, indicating minimal surface heating by the laser. The linewidth in the superconducting state showed no deviation from the expected anharmonic decay curve calculated from fits to the measured width above T_c, within an uncertainty of ±1 cm^{-1}.

A number of phonons other than the 340 cm^{-1} mode are known to undergo renormalization in Y124,[8,9] however the results of fits to these other phonons in this calcium substituted sample were either ambiguous (315, 440, and 615 cm^{-1} phonons) or showed no renormalization within

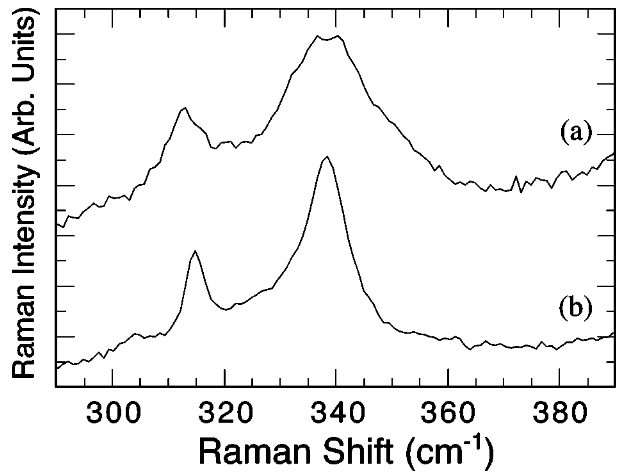

FIG. 2. Raman spectra from $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ showing the 315 and 340 cm^{-1} phonons measured with the CCD detector. Spectrum (a) was taken at 300 K, while spectrum (b) was taken at 10 K.

the measurement uncertainties (500 cm^{-1} phonon, with uncertainties of ±2 and ±3 cm^{-1} in frequency and width, respectively). Phonons of frequency lower than the 315 cm^{-1} phonon were not fitted.

IV. DISCUSSION

We begin the discussion of superconductivity induced phonon renormalizations with the 340 cm^{-1} mode of $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ and compare our results with data published in the literature for unsubstituted Y123. As the magnitude of phonon renormalization in Y123 shows a strong dependence on δ we restrict our comparison to data for which the oxygen content was strictly controlled and measured.

Figure 4 shows the magnitude of softening $\Delta\omega$ of the 340 cm^{-1} mode as a function of δ from polycrystalline samples measured by Krantz *et al.*[27] (open triangles), single crystals measured by Altendorf *et al.*[6] (open squares), and the $x=0.10$ sample renormalizations from the present study (filled circles). The calcium doped materials show a strong

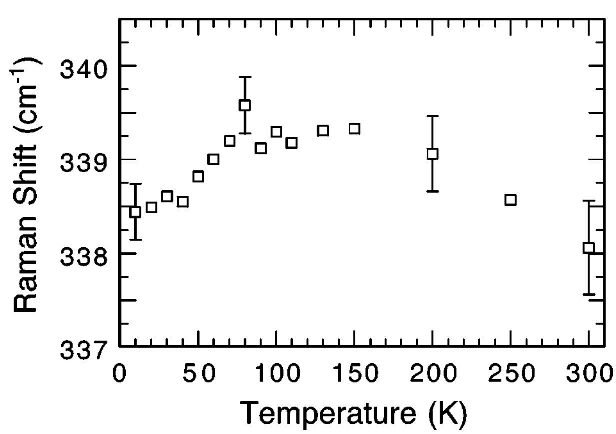

FIG. 3. The frequency of the 340 cm^{-1} phonon as a function of temperature in $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ ($T_c\approx85$ K). The Raman intensity was measured with the CCD detector and the spectral line shape was fitted with a Lorentzian equation.

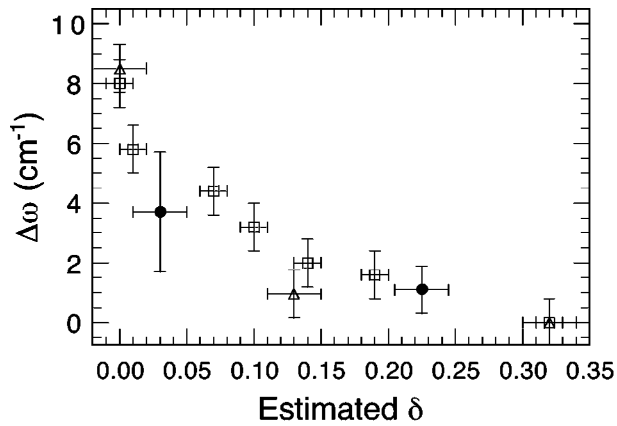

FIG. 4. The magnitude of softening of the 340 cm^{-1} phonon frequency below T_c as a function of δ in $Y_{0.90}Ca_{0.10}Ba_2Cu_3O_{7-\delta}$. Filled data points are for the samples measured here, while the unfilled data points represent measurements on pure ($x=0$) samples replotted from Ref. 6 (open triangles) and Ref. 27 (open squares).

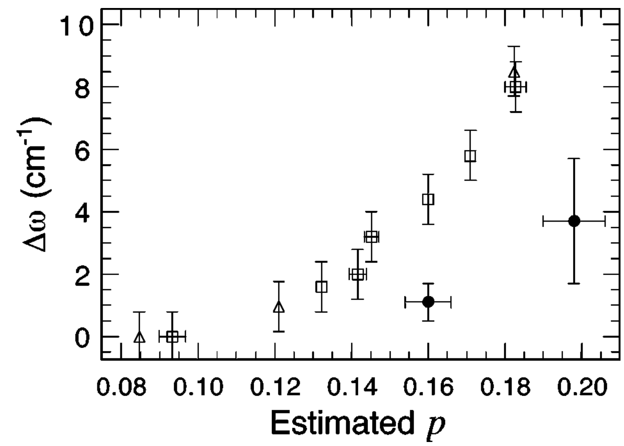

FIG. 5. The magnitude of softening of the 340 cm^{-1} phonon frequency below T_c as a function of p in $Y_{0.90}Ca_{0.10}Ba_2Cu_3O_{7-\delta}$. Filled data points are for the $x=0.10$ samples measured here, while the unfilled data points represent measurements on pure ($x=0$) samples replotted from Ref. 6 (open triangles) and Ref. 27 (open squares).

dependence on δ similar to that seen in pure Y123. Indeed, the magnitude of softening seen in the $x=0.10$ sample agrees within the uncertainties with the softening that might be expected from a pure sample of Y123 with identical δ. The doping dependence of the 340 cm^{-1} phonon width renormalization finds less agreement in the literature than does frequency, due to the strong dependence of the character of the width renormalization on disorder and impurity effects.[28,6] However, it is expected that for pure Y123 samples with $\delta \gtrsim 0.03$ the magnitude of width renormalization below T_c will be of the order of 2 cm^{-1} or less.[6,27] Recalling that the uncertainty in the 340 cm^{-1} linewidth measured for the $x=0.10$ sample was around ± 3 cm^{-1} the observed lack of anomalous change below T_c in this sample is both unsurprising and consistent with unsubstituted Y123. There is also good qualitative agreement between the pure and calcium substituted materials when phonon asymmetry is considered. In both pure[6] and substituted materials the measured asymmetry of the 340 cm^{-1} mode decreases as δ is increased.

These results argue that the strong δ and temperature dependence of the 340 cm^{-1} line shape seen in unsubstituted Y123 are largely unchanged by the substitution of calcium for yttrium in this material. A change in the phonon renormalizations might be expected simply because the physical and superconducting properties of the sample, the hole concentration p in particular, have been altered by the substitution of calcium.[18–20] We recall that p in the pure Y123 single crystal and polycrystal samples studied by Altendorf *et al.*[6] and Krantz *et al.*[27] was manipulated solely via oxygen stoichiometry which allows p to be increased only moderately above optimal when $\delta=0$. By contrast, p in the calcium substituted Y123 polycrystals of this study is determined by both the oxygen stoichiometry and the calcium concentration, allowing p to be increased significantly past optimal when $\delta=0$.

In order to clarify the relationship between p and the observed phonon renormalizations we replot the softenings from Fig. 4 as a function of p. We use Eq (1) to estimate p for each sample, given T_c and $T_{c,\max}$. For the the data of Altendorf *et al.*[6] we use the maximum T_c observed in their series of samples (93.7 K) as $T_{c,\max}$; however, the data of Krantz *et al.*[27] show no sample near optimal doping whose T_c might be taken as $T_{c,\max}$. By assuming that the p of their $\delta=0.00$ polycrystalline sample is similar to that of the $\delta=0.00$ single crystal of Altendorf *et al.*[6] we may use Eq. (1) to estimate a $T_{c,\max}$ of around 96 K for their series of polycrystal samples. For the calcium substituted Y123 polycrystals measured in the present study we take $T_{c,\max}=85$ K.

Figure 5 shows the magnitude of softening $\Delta\omega$ of the 340 cm^{-1} mode plotted against the hole concentration p, calculated using Eq. (1) from the quoted sample T_c and estimated $T_{c,\max}$ described above. As in Fig. 4, the data of Altendorf *et al.*[6] are represented by open squares, the data of Krantz *et al.*[27] by open triangles, and the $x=0.10$ sample renormalizations from the present study by filled circles. The uncertainty in p is the propagated uncertainty in T_c and $T_{c,\max}$, taken to be the quoted superconducting transition widths. Uncertainties are not shown on data points where the uncertainty is small ($<\pm 0.001$) nor for the data of Krantz, where no T_c uncertainty or transition width was quoted.

It is clear from Fig. 5 that the softenings measured from single-crystal and ceramic samples of pure ($x=0$) Y123 form a single curve as a function of p. The agreement between the data of Altendorf *et al.* and Krantz *et al.* is most satisfactory, despite the somewhat arbitrary determination of $T_{c,\max}$ for the latter data. Notably, the softenings measured from the calcium substituted sample do not agree with those of pure Y123, even when the samples have identical hole concentrations at $p=0.16$. Taken together, Figs. 4 and 5 argue that the magnitude of softening seen in the Y123 system is not solely dependent on the planar hole concentration p but rather depends on the total doping state of the sample. A recent x-ray absorption spectroscopy study of calcium substituted Y123 concluded that $T_{c,\max}$ in the Y123 system depends on the hole concentration associated with *both* the chains and planes.[20] Our data indicate similar behavior for the magnitude of 340 cm^{-1} phonon renormalization. We also note that the room-temperature phonon line-shape dependence on calcium substitution in Y123 led the authors of Ref. 26 to argue similarly that the phonon behavior in this system cannot be exclusively identified with the carrier concentration on the planes.

Despite a considerable theoretical effort that has been devoted to the phonon self-energy effects in high-temperature superconductors[10–16] the exact relationship between phonon renormalization and the superconducting gap Δ_0 remains unclear in these materials. Considering these various models it is apparent, from both previous studies and the results presented here, that the 340 cm^{-1} phonon in Y123 and Y124 has less energy than the weight of the gap distribution to which it couples. However, the origin and nature of this gap lie at the center of the continuing debate over the mechanism of high-temperature superconductivity itself.

The anomalous δ dependence of the 340 cm^{-1} phonon renormalization below T_c in pure Y123 is well known. To this we add the observation that the magnitude of the softening of this mode is not solely dependent on hole concentration p, contradicting the common assumption that the δ and p dependence of the 340 cm^{-1} phonon self-energy are identical. In Y124 we find a similar result—the substitution of calcium into the material, raising p, has no appreciable effect on the temperature dependence of the 340 and 500 cm^{-1} phonons, consistent with prior measurements of pure and Zn substituted Y124.[8,9] As the Y124 oxygen stoichiometry is fixed in Y124, this result reveals common behavior in both the Y123 and Y124 systems with regard to the oxygen stoichiometry (δ) and p dependence of the 340 cm^{-1} phonon self-energy.

V. CONCLUSIONS

The substitution of calcium for yttrium in $Y_{0.90}Ca_{0.10}Ba_2Cu_3O_{7-\delta}$ does not significantly alter the 340 cm^{-1} phonon line shape and renormalization as a function of δ compared to data from pure Y123. When considered as a function of hole concentration p we find that the renormalizations differ between calcium substituted and pure materials for identical hole concentrations. We therefore conclude that the observed renormalizations are not solely determined by p in this material. Similarly, the substitution of calcium into the Y124 superconductor, where the oxygen concentration is always very close to stoichiometric, does not appear to affect the 340 or 500 cm^{-1} phonon temperature dependence. These results show that the planar hole concentration p, which is commonly believed to determine a number of superconducting properties in the high-T_c materials, does not uniquely determine the magnitude of 340 cm^{-1} phonon softening in Y123 nor does it affect the renormalization of the 340 and 500 cm^{-1} phonons in Y124. We conclude that it is the oxygen stoichiometry which determines the magnitude of renormalization seen in our calcium substituted Y123 and Y124 samples.

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