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Raman investigation of the superconducting gap of $YBa_2Cu_3O_x$ for $6.85 < x < 7.0$

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The temperature dependences of the linewidth and frequency of the 340-cm^{-1} Raman-active phonon have been measured in five lightly twinned crystals of $YBa_2Cu_3O_x$ with different oxygen concentrations x. The observed changes in the linewidth and frequency that occur for temperatures below the critical temperature have been found to depend strongly on the value of x within the region $6.85 \lesssim x \lesssim 7.0$. The linewidth and frequency dependences for $T < T_c$ result in superconducting gap energy estimates which indicate that 2Δ decreases for oxygen concentrations $x > 6.95$ and remains approximately constant for $6.85 \lesssim x \lesssim 6.95$. Given the low level of impurities in these crystals these results are attributed to variations in the hole concentrations which arise primarily from variations in the oxygen content.

The temperature dependence of the Raman-active phonon at 340 cm^{-1} of $YBa_2Cu_3O_7$, which involves the out-of-phase vibration of the CuO_2-planar oxygen atoms, has been the subject of several studies.[1-5] The significant softening[1,2] of this phonon below T_c and its distinctive Fano line shape[3,4] provided evidence of strong electron-phonon coupling in this compound. The 340-cm^{-1} phonon was also found to broaden[3] below T_c, presumably because of the formation of a superconducting energy gap, 2Δ, where $2\Delta \approx 340$ cm^{-1}. Subsequently, it was found[6-9] that the Raman active phonons at 440 and 500 cm^{-1} also exhibited superconductivity induced changes in frequency and linewidth when the sample temperature was lowered below T_c.

Recently, several groups[8-15] have used the temperature dependences of the frequencies (ω_ν) and linewidths [full width at half maximum (FWHM) $=2\gamma_\nu$] of the Raman-active phonon modes at 340, 440, and 500 cm^{-1} to obtain estimates for 2Δ in $RBa_2Cu_3O_7$ compounds (where R designates a rare-earth atom). Qualitatively, one expects that phonons with energies less than the gap will narrow below T_c due to the removal of a decay channel, while those with energies greater than the gap broaden[16] as a result of scattering from superconducting pairs, as first observed in neutron scattering measurements in Nb_3Sn (Ref. 17) and Nb.[18] In addition, phonons with energies less than 2Δ should soften, while those with energies greater than 2Δ should harden.[16] An estimate for the gap energy 2Δ can thus be obtained by carrying out measurements on a set of phonons which have energies near the gap and which, ideally, bracket the gap.

Comparisons of the experimental measurements of $\Delta\omega_\nu$ and $2\Delta\gamma_\nu$ with the predictions of a strong coupling (ZZ) model[16] enable one to obtain a more quantitative estimate for 2Δ. Thomsen and co-workers[8,10] carried out measurements on several $RBa_2Cu_3O_7$ compounds and obtained a value for the gap of $2\Delta=(4.95\pm0.1)kT_c$. More recently, McCarty *et al.*,[14] in experiments carried out on untwinned crystals, observed linewidth dependences for the 340- and 440-cm^{-1} modes which implied a gap energy in the range $6.8kT_c \le 2\Delta \le 7.7kT_c$. Altendorf *et al.*,[11] from experiments on twinned single crystals of $YBa_2Cu_3O_7$, obtained a value of $2\Delta/kT_c=5.9\pm0.3$ for the gap, a value intermediate between the above determinations. Thomsen *et al.*[15] have attributed the differences in the above measurements to differences in sample quality. In particular, the crystals of McCarty *et al.*[14] contained some Au, and those of Altendorf *et al.*[11] contained 2.5 at.% Th. It was suggested[15] that these impurity concentrations led to a symmetrization of the gap around the Fermi surface and, under appropriate circumstances, to larger values for 2Δ. However, more recent investigations by Altendorf *et al.*[13] and McCarty *et al.*[19] have demonstrated that a narrowing of the 340-cm^{-1} mode occurs below T_c even in high-quality crystals with low impurity concentrations.

In an attempt to gain further insight into the reason for these apparently contradictory results we have carried out experiments on crystals with differing levels of oxygenation and hence different hole concentrations. More specifically this paper presents the results of measurements carried out on single crystals of $YBa_2Cu_3O_x$, where $6.85 \lesssim x \lesssim 7.0$. In a previous investigation[20] it was found that the critical temperature of single crystals of $YBa_2Cu_3O_x$ attained a maximum value for $x \cong 6.95$ and hereafter we will refer to $x=6.95$ as the optimal level of oxygenation. For $x \le 6.95$, the 340-cm^{-1} mode is observed to narrow below T_c, while for the crystals with $x > 6.95$, the 340-cm^{-1} mode broadens. From these results it is apparent that small changes in oxygenation away from an optimal value[20] can dramatically influence the linewidth behavior of the 340-cm^{-1} phonon. Since the hole concentration in RBaCuO compounds depends critically on annealing conditions and small impurity concentrations, these results could explain the different

Raman results that have been obtained by different groups.[10,11,14]

The five twinned crystals studied in this work (named *A*, *B*, *C*, *D*, and *E*) were grown in Zirconia crucibles by a flux method in a manner similar to that described previously.[11] Crystal *C* was annealed in 1 atm of flowing O_2 for two days at 860 °C, and the temperature was then reduced to 450 °C at a rate of 18 °C/h. The crystal was then further annealed at 450 °C for a further 6 days, and then quickly cooled to room temperature (i.e., in a few minutes). This resulted in a high-quality crystal[13] with a transition temperature (onset) of 93.7 ± 0.1 K and transition width less than 0.2 K (10%–90%) as determined by dc magnetization measurements (0.05 Oe applied field, parallel to c axis). Considering the transition temperature and annealing conditions,[20,21] the oxygen content (x in $YBa_2Cu_3O_x$) was estimated to be 6.95.

Crystal *D* was obtained from the same batch as crystal *C* and was annealed in the same way. It was then further annealed for 2 days at 510 °C in pure flowing O_2 at 1 atm followed by rapid cooling, in order to reduce the oxygen concentration. This resulted in a reduced transition temperature (onset) of 92.5 ± 0.1 K and transition width of 0.4 K (10%–90%) as determined by ac susceptibility measurements (0.1 Oe applied field, parallel to c axis). The oxygen content was estimated to be $x = 6.9$ by comparison with the known oxygen content of ceramic $YBa_2Cu_3O_x$ samples annealed under similar conditions.[21]

Crystal *E* was not taken from the same batch as crystal *C* and *D* but was grown and annealed under identical conditions. Crystal *E* was then further annealed for 72 h at 550 °C in flowing O_2 at 1 atm followed by rapid cooling. This resulted in a crystal with a transition temperature (onset) of 88.0 ± 0.2 K and transition width of 1.3 K (10%–90%) as determined by dc magnetization measurements (0.05 Oe applied field, parallel to c axis). The resulting oxygen content was estimated to be $x = 6.85$ by once again comparing with the known oxygen content of ceramic samples annealed under similar conditions.[21]

Crystal *B* was also grown and annealed at high temperatures under identical conditions as crystal *C*, but was further annealed under high pressure in the following way. The crystal was heated at 50 °C/h under 31.6 atm of pure O_2 up to a temperature of 450 °C. The crystal was then kept at 450 °C for 24 h under 39.5 atm of pressure. It was then cooled at 3 °C/h to 350 °C, kept at 350 °C and 37.5 atm of pressure for 48 h and finally cooled at 100 °C/h and 31.6 atm of pressure. This resulted in a crystal with a transition temperature (onset) of 93.0 ± 0.1 K, a transition width of 0.5 K (10%–90%) as determined by dc magnetization measurements (0.1 Oe applied field, parallel to c axis), and an oxygen content x estimated to be greater than 6.95. Chemical analysis[22] indicated that samples *B*, *C*, *D*, and *E* contained only small amounts of metal impurities (<50 ppm by weight of Zn, Al, Fe, and K).

Crystal *A* was grown in the same manner as *B*, *C*, *D*, and *E*, but was annealed by heating at 50 °C/h under 32.6 atm of pure oxygen to a maximum temperature of 500 °C, held at 500 °C and 32.6 atm for 24 h, after which it was cooled at 3 °C/h to 350 °C and kept at 350 °C and 32.6 atm for 48 h. Finally, crystal *A* was cooled at 100 °C/h and 32.6 atm. This crystal had a transition temperature (onset) of 89.8 ± 0.2 K, a transition width of 2.0 K (10%–90%) as determined by a dc magnetization measurement (10.0 Oe applied field, parallel to c axis), and an oxygen content x, estimated to be greater than 6.95. Chemical analysis[22] of this crystal indicated about 500 ppm (by weight) of potassium, in contrast with the previous four crystals. The source of this potassium was the fire brick used in the oven. It has been found that the initial high temperature (860 °C) anneal used for crystals *B*, *C*, *D*, and *E* ensures that the potassium concentration in these crystals is less than 50 ppm by weight. Although the amount of potassium in crystal *A* is still small (0.05% by weight), it does act as an acceptor impurity by substituting for barium and may thus enhance the hole concentration in the crystal. Raman spectra from the faces of crystals *A*, *B*, *C*, *D*, and *E* with the incident and scattered light polarized in the a-b plane were obtained with the 514.5-nm line of an argon ion laser.[13] A comparison of the Raman spectra, obtained from as grown crystals, and from crystals etched in a 1% Br/ethanol solution[23] for up to 1.5 h, did not indicate any significant differences. In this paper we will focus on the 340 cm^{-1} mode since its behavior below T_c is controversial[10,13–15,19] and also central to all gap determinations. The temperature dependences of the linewidths of the 340-cm^{-1} mode are shown in Fig. 1 for crystals *A*, *B*, *C*, *D*, and *E*. All linewidths are determined from fits to a Fano profile[10] with a linear background. The solid lines in Fig. 1 indicate a fit of the experimental points above T_c to a model of anharmonic decay.[10] Crystal *C* ($T_c = 93.7$ K) shows an overall narrowing below T_c of approximately 2 cm^{-1} as indicated by the departure of the experimental data points from the anharmonic decay curve. Similarly, crystals *D* and *E* indicate that a reduction in oxygen content from $x = 6.95$ to 6.85 increases the degree of narrowing by approximately 1 cm^{-1}. Finally, linewidth broadening below T_c in a manner similar to that reported by other groups[2,3,10] is observed in the high-pressure annealed crystals *A* and *B*. It therefore appears that the oxygen content or more generally the hole concentration is a dominant factor in determining the nature of the superconductivity induced linewidth shifts of the 340-cm^{-1} mode in these crystals. The enhanced broadening observed in crystal *A* is perhaps 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 crystal.

In Fig. 2 the temperature dependences of the frequencies of the 340-cm^{-1} mode for crystals *A*, *B*, *C*, *D*, and *E* are plotted. All five crystals indicate a softening in the frequency near T_c in accordance with the observations of other groups.[1–5] 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, the smallest being 1.5 cm^{-1} in crystal *E*. Such a diminished softening has also been observed in deoxygenated samples by Krantz *et al.*[2]

A comparison of the results shown in Figs. 1 and 2 with the strong coupling calculations[16] suggests that, since the linewidths narrow below T_c for crystals *C*, *D*, and *E* and

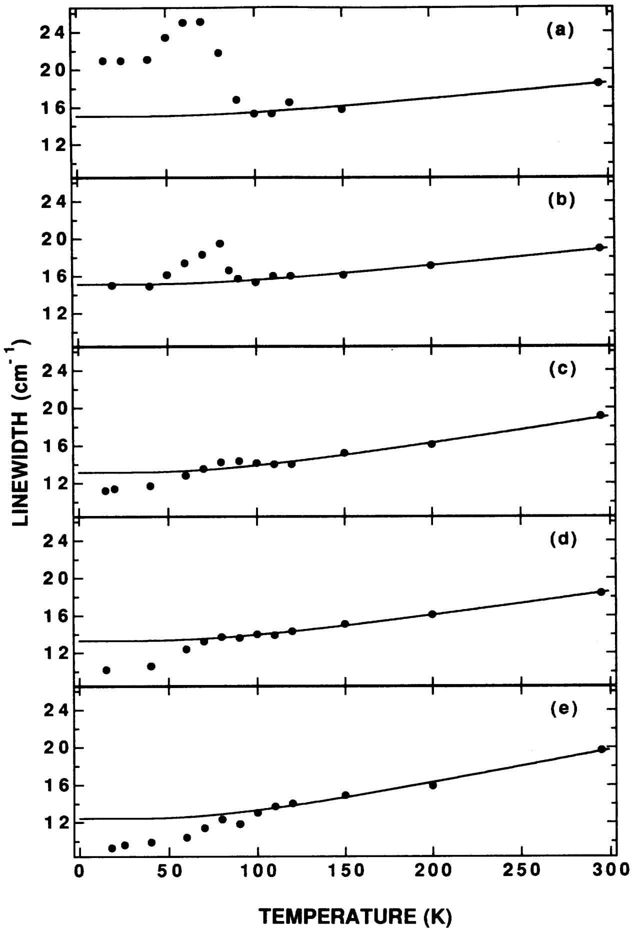

FIG. 1. Linewidths of the 340-cm^{-1} phonon as a function of temperature, for (a) crystal A ($x \cong 7.0$), (b) crystal B ($x \cong 7.0$), (c) crystal C ($x = 6.95$), (d) crystal D ($x = 6.9$), and (e) crystal E ($x = 6.85$). Linewidths were determined by numerical fits to Fano (Ref. 10) profiles with a linear background. The solid lines are fits of the data above T_c to a model of anharmonic decay (Ref. 10).

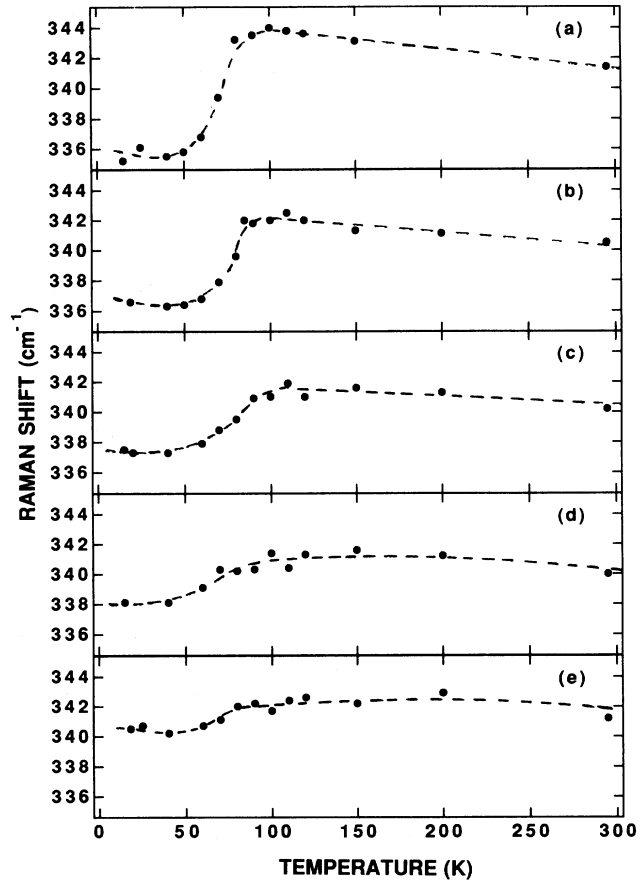

FIG. 2. Frequencies of the 340-cm^{-1} phonon as a function of temperature for (a) crystal A ($x \cong 7.0$), (b) crystal B ($x \cong 7.0$), (c) crystal C ($x = 6.95$), (d) crystal D ($x = 6.9$), and (e) crystal E ($x = 6.85$). The dashed lines are only intended to serve as guides to the eye.

broaden for crystals A and B, 2Δ should be greater than 340 cm^{-1} for crystals C, D, and E and less than 340 cm^{-1} for crystals A and B. The observed narrowing of the 340-cm^{-1} line [Figs. 1(d) and 1(e)] below T_c for crystals D and E is not predicted by the ZZ model.[16] Marsiglio, Akis, and Carbotte,[24] however, have recently shown that the presence of impurities can lead to a narrowing of the phonon linewidth, and a reduction in frequency shift, below T_c. Thus the increased number of oxygen vacancies in crystals D and E could act as impurity scattering centers, and contribute to the enhanced line narrowing [Figs. 1(d) and 1(e)]. One might then conclude that the gap energy is approximately the same in samples C, D, and E, and based upon the temperature dependence behavior of the 340-cm^{-1} mode in crystal C we estimate that $2\Delta \cong (6.75 \pm 0.25) kT_c$.

These results suggest that the different 340-cm^{-1} phonon linewidth behaviors observed by different groups[2,4,10–14] might be attributed to relatively small variations in oxygen concentration or impurity (e.g., Na, K) concentrations. In particular the present results can be compared to those of Krantz *et al.*[2] who measured the frequency and linewidth of the 340-cm^{-1} mode as a function of oxygen concentration in polycrystalline samples. Their findings can be considered to be consistent with the results presented here if experimental uncertainties and differing methods of linewidth determination are taken into consideration. In addition the presence of Au or Th, with oxidation states of 3 and 4, respectively, could reduce the hole concentration to a level near the optimal value and hence result in line narrowing, a prediction which is in agreement with previously published results.[11,14] It should be noted that this interpretation is different than that obtained from neutron experiments[25] on ceramic samples in which the addition of gold was accompanied by an increase in the oxygen content. The present and previous Raman results[14,15] imply that, in gold-doped single crystals, the corresponding increase in oxygen concentration is much smaller than it is in polycrystalline samples. Finally, qualitative estimates for 2Δ obtained from comparisons with the ZZ strong coupling model[16] do not appear to be correlated with the critical temperatures of these crystals. This lack of correlation between 2Δ and T_c suggests that the observed changes in phonon linewidth and frequency below T_c may be associated with a redistribution of electronic states that is not directly related to the superconducting gap formation.

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[1] R. M. Macfarlane, H. J. Rosen, and H. Seki, Solid State Commun. **63**, 831 (1987).

[2] M. Krantz, H. J. Rosen, R. M. Macfarlane, and V. Y. Lee, Phys. Rev. B **38**, 4992 (1988).

[3] 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).

[4] S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **37**, 5920 (1988).

[5] C. Thomsen and M. Cardona, in *Physical Properties of High Temperature Superconductors I*, edited by D. M. Ginsberg (World Scientific, Singapore, 1989).

[6] E. Altendorf, J. Chrzanowski, J. C. Irwin, and J. P. Franck, Solid State Commun. **76**, 391 (1990).

[7] K. F. McCarty, J. Z. Liu, R. N. Shelton, and H. B. Radousky, Phys. Rev. B **42**, 9973 (1990).

[8] C. Thomsen, M. Cardona, B. Friedl, C. O. Rodriguez, I. I. Mazin, and O. K. Andersen, Solid State Commun. **75**, 219 (1990).

[9] B. Friedl, C. Thomsen, E. Schönherr, and M. Cardona, Solid State Commun. **76**, 1107 (1990).

[10] B. Friedl, C. Thomsen, and M. Cardona, Phys. Rev. Lett. **65**, 915 (1990).

[11] E. Altendorf, J. Chrzanowski, J. C. Irwin, A. O'Reilly, and W. N. Hardy, Physica C **175**, 47 (1991).

[12] E. Altendorf, J. C. Irwin, W. N. Hardy, and R. Liang, Physica C **185–189**, 1375 (1991).

[13] E. Altendorf, J. C. Irwin, R. Liang, and W. N. Hardy, Solid State Commun. **80**, 627 (1991).

[14] K. F. McCarty, H. B. Radousky, J. Z. Liu, and R. N. Shelton, Phys. Rev. B **43**, 13751 (1991).

[15] C. Thomsen, B. Friedl, M. Cieplak, and M. Cardona, Solid State Commun. **78**, 727 (1991).

[16] R. Zeyher and G. Zwicknagl, Z. Phys. B Conden. Matter **78**, 175 (1990).

[17] J. D. Axe and G. Shirane, Phys. Rev. B **8**, 1965 (1973).

[18] S. M. Shapiro, G. Shirane, and J. D. Axe, Phys. Rev. B **12**, 4899 (1975).

[19] K. F. McCarty, J. Z. Liu, Y. X. Jia, R. N. Shelton, and H. B. Radousky, Solid State Commun. **79**, 359 (1991).

[20] R. Liang, T. Nakamura, H. Kawaji, M. Itoh, and T. Nakamura, Physica C **170**, 307 (1990).

[21] P. Schleger, W. N. Hardy, and B. X. Yang, Physica C **176**, 261 (1991).

[22] Quanta Trace Laboratories, Inc., Burnaby, British Columbia, Canada V5G 4M1.

[23] D. J. Werder, G. H. Chen, M. Gurvitch, B. Miller, L. F. Schneemeyer, and J. V. Waszczak, Physica C **160**, 411 (1989).

[24] F. Marsiglio, R. Akis, and J. P. Carbotte (unpublished).

[25] M. Z. Cieplak, G. Xiao, C. L. Chien, A. Bakhshai, D. Artymowicz, W. Bryden, J. K. Stalick, and J. J. Rhyne, Phys. Rev. B **42**, 6200 (1991).