Effect of oxygen stoichiometry on softening of Raman active lattice modes in $YBa_2Cu_3O_x$

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Temperature-dependent frequency-shift and linewidth data of the Raman active 337-cm^{-1} CuO_2 in-plane bond-bending mode have been measured for five different oxygen stoichiometries between $x=7.00$ and $x=6.14$ in polycrystalline samples. Softening and line-broadening effects observed for the $x=7.00$ sample are sharply reduced for $x=6.87$ even though the superconducting transition temperature is similar. With a further reduction of oxygen content below $x=6.68$ both the soft-mode behavior and the line-broadening effects completely disappear. These unexpected results could suggest a large variation in the interaction between the electronic system and the lattice as the oxygen content is varied.

I. INTRODUCTION

Raman scattering has played an important role in advancing our understanding of the $YBa_2Cu_3O_x$ class of high-temperature superconductors[1,2] by providing a sensitive probe of the microstructure of these materials[3–19] and probing excitations possibly involved in the superconducting pairing mechanism itself.[20–23] Several investigations have reported soft-mode behavior and line-shape changes in certain Raman active[6,7,23] and infrared active[7,24(a)] modes coinciding with or preceding the onset of superconductivity. Phonon self-energy effects due to superconductivity have been suggested to cause the observed softening of the 337-cm^{-1} Raman mode, thus pointing toward a strong coupling theory.[24(b)] Also soft-mode behavior has been observed in Mössbauer studies.[25,26] It is now widely believed that pairing and superconductivity take place in the Cu(2)-O(2,3) planes located between the yttrium and barium planes. Oxygen stoichiometry in the fence like ribbons formed by O(4) and the Cu(1)-O(1) chains between the barium planes strongly affects the structural properties of the material as a whole and the superconducting properties[27] of the adjacent Cu(2)-O(2,3) planes in particular. The prominent Raman mode with room-temperature peak at 337 cm^{-1} which has been assigned to bond-bending motion of A_g symmetry in the Cu(2)-O(2,3) planes with O(2) and O(3) oscillating out of phase[11] exhibits substantial softening[6] and broadening[23] below the superconducting transition temperature in fully oxygenated samples. In the following we present the results of a systematic study of these effects as a function of oxygen content. The frequency shifts and linewidths were measured for five different oxygen stoichiometries and seven different temperatures between $x=7.00$ and $x=6.14$ and 5 and 300 K, respectively, using polycrystalline samples that were independently characterized by chemical, x-ray, and magnetic measurements. The results are quite surprising and indicate that both the soft-mode behavior and line-broadening effects associated with the superconducting state depend critically on oxygen stoichiometry.

II. EXPERIMENTAL DETAILS

The preparation of $YBa_2Cu_3O_7$ from Y_2O_3, BaO, and CuO followed the procedure described elsewhere.[28] Finely ground starting materials were reacted in flowing oxygen for 12 h, pressed into pellets, and sintered for a further 12 h in oxygen at 950 °C. The oxygen content was varied by equilibrating a pellet of material of the $x=7.0$ compound in an argon atmosphere at various temperatures T. The samples were held at this temperature for 36 h and then slowly cooled over a period of 8 h to room temperature. Material prepared in this way is expected to have oxygens in the O(1) and O(5) positions in the Cu(1) planes more highly ordered than materials that are quenched rapidly from a given temperature, a method that has been used by several groups. This procedure made it possible to obtain a particular value of x by a choice of T. A final determination of x was made by thermogravimetric analysis, and by chemical titration which gave values of x agreeing within 5%. The values of x reported in this paper were determined by iodine titration and had a reproducibility of ± 0.02. The critical temperatures reported here are those at which the samples had zero resistance.

Raman scattering measurements were made on pressed pellets of finely ground material which had been annealed in argon, as described above, to produce material with different oxygen content. The samples were mounted in an Oxford Instruments flow cryostat under approximately 1 atm of helium exchange gas. Variation of the temperature between 4 and 300 K was achieved with a small heater mounted on the coldfinger. The temperature of the coldfinger was measured with a RhFe resistance sensor with an accuracy of ± 1 K. Approximately 100 mW of 514.4-nm Ar^+ laser light polarized in p direction was focused with a cylindrical lens to a line 6×0.5 mm^2 on the sample producing a power density of 3 W/cm^2. Laser heating of the sample in this configuration was previously measured[19] to be less than 10 K. The scattered light was collected at 90° and spectrally analyzed with a 1-m JY double monochromator using a spectral resolution of 4

cm^{-1} and single channel detection. Data aquisition time per run varied between 2 and 8 h due to the varying strength of the 337 cm^{-1} mode with oxygen content.[18] The peak positions and linewidths are accurate to 0.4 and 0.8 cm^{-1}, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the room-temperature Raman spectrum of $YBa_2Cu_3O_{7.00}$ with prominent lines at 151, 337, 433, and 501 cm^{-1}. Polarized single-crystal data have shown that these modes all have A_g symmetry.[9,11] Two of these modes correspond to bond-bending vibrations within the Cu(2)-O(2,3) planes with the O(2) and O(3) atoms oscillating out of phase and in phase. These normal modes have been assigned to the peaks at 337 and 433 cm^{-1}, respectively, using normal-mode calculations with empirical force constants.[29] The temperature dependence of the 337-cm^{-1} mode with $x=7.00$ is shown in the inset of Fig. 1 together with the atomic displacements for one of the two Cu(2)-O(2,3) planes in the unit cell. Between room temperature and 90 K this mode shifts to higher frequency by about 2 cm^{-1} as expected from a small hardening of the lattice. At the superconducting transition the frequency shift changes sign and softens by about 9 cm^{-1} at 5 K with most of the variation occurring between 90 and 50 K. This softening is accompanied by an increase in linewidth by 4 cm^{-1} between 90 and 30 K followed by a 2 cm^{-1} narrowing at 5 K. Although the 433-cm^{-1} mode involves similar bond-bending vibrations, no anomalous behavior at the superconducting transition has been observed for this mode. Figure 2 shows the detailed frequency shift and linewidth variations of the 337-cm^{-1} mode as a function of temperature for five different oxygen stoichiometries ($x=7.00$, 6.87, 6.68, 6.40, and $x=6.14$). These data show clearly that both the soft-mode behavior and line-broadening effects in the superconducting state depend critically on oxygen stoichiometry. This is most clearly illustrated by comparing the $x=7.00$ and $x=6.87$ data where both the mode frequency and the linewidth show a similar temperature dependence but the magnitude of the soft-mode behavior and the broadening effects are almost reduced by a factor of 10 (i.e., the overall softening has reduced from 9 to about 1 cm^{-1} and the maximum broadening effect has decreased from 4 cm^{-1} to approximately 0.6 cm^{-1}). As one reduces the oxygen content even further to $x=6.68$, 6.40, and 6.14 both the broadening and soft-mode behavior disappear within experimental error. These results are quite surprising. *A priori* one would have expected the soft-mode behavior and line broadening to be similar in the fully oxygenated sample and the $x=6.87$ one. The transition temperatures are very similar (i.e., $T_c=92$ K and $T_c=84$ K, respectively) and no large structural differences have been reported

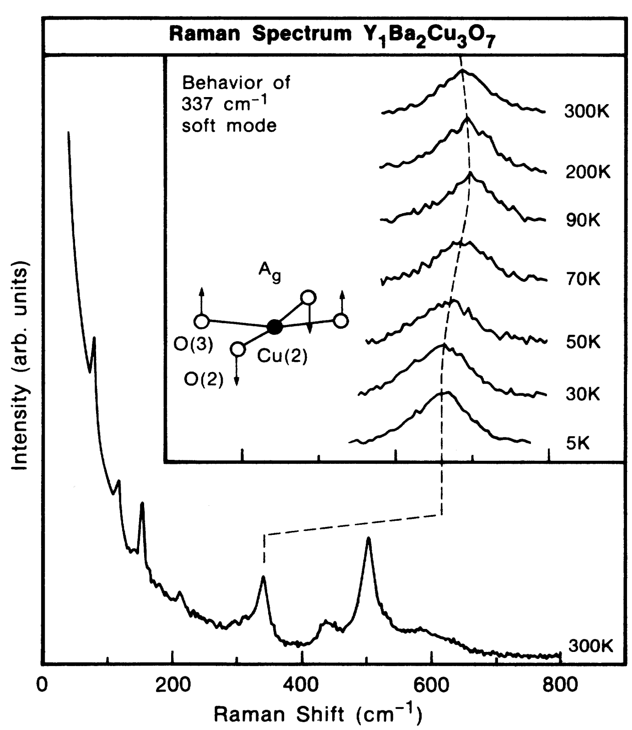

FIG. 1. First-order Raman spectrum of $YBa_2Cu_3O_{7.00}$ showing characteristic peaks with room-temperature positions at 155, 337, 433, and 502 cm^{-1} (the features at 79 and 117 cm^{-1} are due to plasma lines). The inset shows the temperature dependence and normal-mode displacements [only for one Cu(2)-O(2,3) plane] of the 337-cm^{-1} mode.

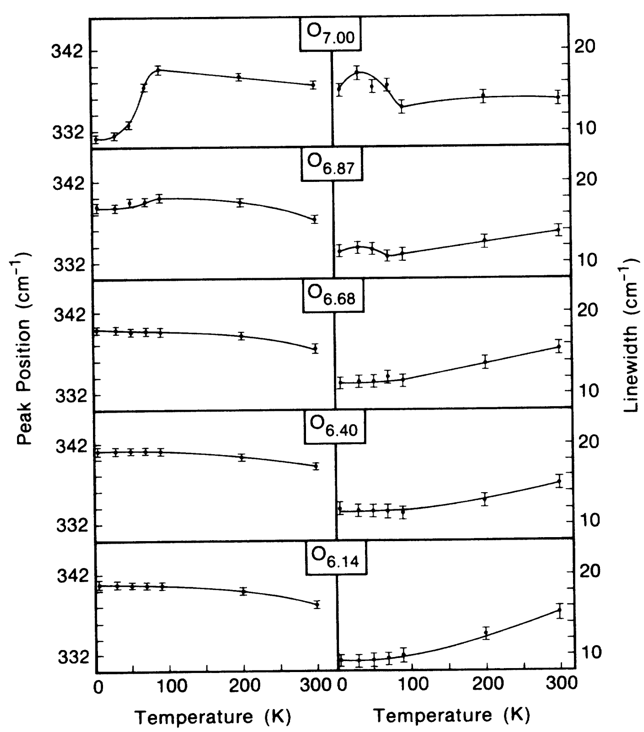

FIG. 2. Temperature-dependent peak positions and linewidths (full width at half maximum) of the 337-cm^{-1} mode in $YBa_2Cu_3O_x$ displayed for oxygen stoichiometries $x=7.00$, 6.87, 6.68 with respective superconducting transition temperatures of 92, 84, and 51 K and semiconducting samples with $x=6.40$ and 6.14.

between these samples at room temperature[30,31] and for $x=7.0$ between 5 and 300 K.[32] Indeed, the room-temperature Raman scattering data are almost identical for the 337-cm^{-1} mode and only very small shifts are observed for the other modes.[18] For oxygen content $x=6.68$, T_c is reduced to 51 K and one would have expected the onset of the soft-mode behavior to be shifted to the new critical temperature with possibly a reduction in the magnitude of the broadening and softening but not a complete disappearance of these effects. For the nonsuperconducting samples $x=6.40$ and $x=6.14$ the results are as expected with no soft-mode behavior or anomalous broadening.

Cooper *et al.* in a recent paper[23] have attributed the increase in linewidth of the 337-cm^{-1} mode below the superconducting transition for fully oxygenated samples to increased damping due to electronic continuum states which are redistributed by the opening of the energy gap. As the gap opens the density of electronic states at 337 cm^{-1} increases leading to Fano line shapes and increased damping. Our results for the $x=6.87$ sample show a similar temperature dependence below T_c but with a much reduced magnitude. In the framework of the Cooper *et al.* model these results suggest that the gap opens in a similar fashion to the fully oxygenated samples but that either the density of electronic states near 337 cm^{-1} or the coupling between the electronic states and the lattice is greatly reduced. The former result is consistent with the similar transition temperatures in the fully oxygenated and the $x=6.87$ samples but the large effect of oxygen stoichiometry on the interaction between the electronic system and the lattice is unexpected. As the oxygen stoichiometry is reduced further to $x=6.68$ the line-broadening effect below the superconducting transition completely disappears suggesting a further large reduction in the interaction between the lattice and the electronic continuum. Another interesting feature of this data is the differences in the temperature dependence of the linewidth above the superconducting transition for the various oxygen stoichiometries. The $x=7.00$ sample shows almost a flat behavior between 300 and 90 K while the other stoichiometries show a substantial reduction in linewidth as a function of temperature. This may indicate that phonon decay mechanisms play a much smaller role in the $x=7.00$ sample if its decay is dominated by electronic interactions. The soft-mode behavior below the superconducting transition, has been observed by several groups for the $x=7.00$ stoichiometry. The observed scaling of the maximum linewidth increases and the soft-mode frequency shifts below 90 K as one varies the oxygen stoichiometry suggests that a similar effect may be causing both phenomena. This effect may be due to a redistribution of the electronic states which not only modifies decay channels but the lattice dynamics as well. Such a model may help to explain the large dependence of these effects on oxygen stoichiometry. Recent Hall coefficient measurements[33] suggest that in-plane carrier densities vary strongly with oxygen stoichiometry near $x=7.0$ at 95 K. In particular, between $x=7.00$ and $x=6.90$ the carrier density decreases by more than a factor of 2. Similar strong oxygen stoichiometry dependence in this range has been reported for the 95 K resistivity.[27] Such an effect would influence the interaction between the lattice and the electronic states and should be included in any explanation of the strong oxygen dependence of our results.

In conclusion, we have measured the frequency shifts and linewidths of the 337-cm^{-1} A_g Raman mode between 300 and 5 K. Softening and line broadening observed below the superconducting transition temperature of 92 K sharply decreases between $x=7.00$ and $x=6.87$ with T_c undergoing only a small change. As the stoichiometry is further reduced to $x=6.68$, 6.40, and 6.14 both the soft-mode behavior and the broadening effects completely dissappear. The sensitivity of these effects to oxygen stoichiometry is surprising and needs further experimental and theoretical elucidation.

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