Phase separation and softening of the $O2,3$ in-phase mode in the YBa$_2$Cu$_3$O$_x$ superconductors

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Systematic Raman measurements have been carried out on the YBa$_2$Cu$_3$O$_x$ superconductors with very well-defined oxygen concentration $6.4 < x < 7.0$. In contrast to the literature, the frequencies of some of the phonons do not vary linearly with the oxygen content. The variation of the phonon characteristics of the apex oxygen mode with doping is consistent with the development of superstructures. A softening of the phonon due to the in-phase vibrations (A_g mode) of the plane oxygen atoms takes place in the overdoped region.

There is experimental evidence that the removal of oxygen and the variation of the transition temperature are related to the coexistence of various ordered and/or disordered configurations of the chain oxygens.[1] It is well known that the position of the apex oxygen phonon band depends on the oxygen content x,[2] while its shape is stated to be affected by the ordering pattern and range of the chain oxygens.[3] From the other two mostly studied modes due to the vibrations of oxygens, the (A_g) in-phase vibrations of the plane oxygens decrease in frequency almost smoothly from $x=7$ to $x=6$.[2] Unlike the apex oxygen case, this mode has not been investigated in detail. On the other hand, the B_{1g} out-of-phase plane oxygen phonon seems insensitive to the oxygen concentration.

The main idea of this work is to revise the Raman investigations of 123 which have been performed mainly with samples of an appreciably less sophisticated perfection and purity grade than those used here. In view of the structural and chemical complexities of YBa$_2$Cu$_3$O$_x$ and their influence on its physical properties, it is very important to have very carefully synthesized and characterized materials. The present Raman study is actually a spin-off of the systematic characterization of the YBa$_2$Cu$_3$O$_x$ series using as a parameter the oxygen nonstoichiometry and the conditions of synthesis. The latter include the various starting materials and the conditions of oxygen equilibration and annealing. Two groups of samples have been synthesized, differing in the source of Ba used. Some results gained with samples using directly oxidized Ba metal as starting material have been already published.[4,5] In order to be able to make direct comparison with the Raman measurements of the literature, we have used here samples which have been synthesized by the conventional barium carbonate method. Careful characterization by magnetization[5,6] and Raman measurements,[6] x rays, and chemical analysis has shown that although such samples might be relatively less pure (containing possibly some traces of carbonate which cannot be detected with standard analytical techniques) are more homogeneous than the ones synthesized with oxidized Ba.

Oxides of Y and Cu of $5N$ purities, and barium carbonate Puratronic grade with total impurity metal content 20 ppm (including 10 ppm strontium) were fired two times in air at 860 and 880 °C for 50 and 70 h, respectively, and then four times in flowing oxygen at 900, 930, 945, and 935 °C (40 h for each sintering) with intermediate grindings in a glove box. No pressing into pellets took place at any time to ensure, as far as possible, similar conditions for all parts of the powders. The total amount of annealing was of the order of 280 h, and after the last annealing the equilibrium with oxygen took place with a cooling rate of 1 °C/min. In this way powders of oxygen content $x=6.984$ were synthesized. Lower oxygen contents down to $x=6.4$ were achieved by annealing the samples with the necessary amounts of yttrium metal at 600 °C (15 h, cooling rate 10 °C/h) in sealed ampoules. Through the exact measurement of the yttrium weight an adjustment of the oxygen content within $x=0.01$ was possible.

In investigations as a function of nonstoichiometry it is important to use a method of chemical analysis as exact as possible. Using the volumetric method reported in the past[7] we could determine the oxygen content with an accuracy of $\Delta x = \pm 0.001$ in the oxygen stoichiometry coefficient of the orthorhombic samples. We note, however, that this very high accuracy is possible only for phase-pure samples. An impurity phase of 1 wt % would increase the error up to $\Delta x = 0.005$. The phase purity of the samples was examined with a STOE powder diffractometer. No other phases apart from 123 were found. The sensitivity of the instrument for impurity phases was determined to 0.5 wt %, using a calibration with standards containing different amounts of BaCuO$_2$, the most common impurity in 123.

The Raman spectra were obtained mainly at room temperature and some at 77 K with a T64000 Jobin-Yvon triple spectrometer equipped with a liquid-nitrogen-cooled CCD detector and a microscope. The 514.5 and 488.0 nm lines of an Ar$^+$ laser were used for excitation at low power which was kept fixed during the measurements at the level of 0.1–0.2 mW. The spectra were measured not on polycrystals but on individual microcrystallites in the scattering configura-
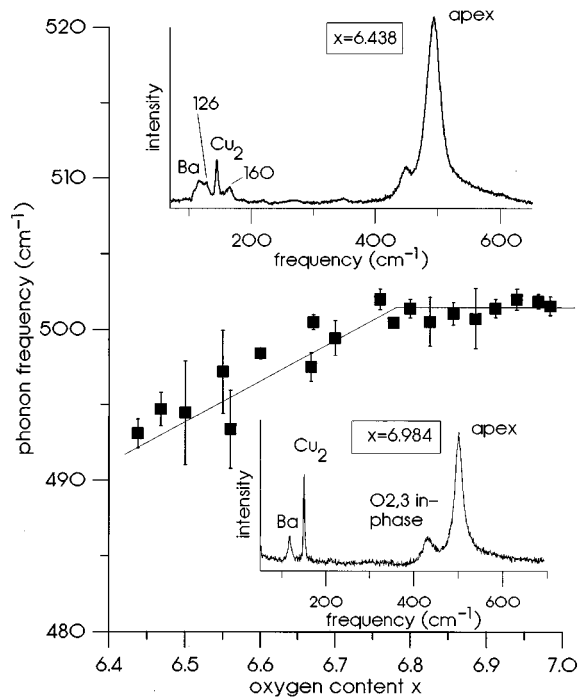
FIG. 1. Frequency vs oxygen concentration x of the apex phonon band. The continuous lines are guides to the eye. (inserts): Raman spectra of 123 for the $y(zz)\bar{y}$ scattering configuration for the two extreme concentrations $x=6.438$ and $x=6.984$.

FIG. 2. The width of the apex and in-phase modes. The continuous lines are guides to the eye.

tions $y(zz)\bar{y}$ and $y(xx)\bar{y}$, where the z axis coincides with the c axis and is assumed to be perpendicular to the long dimension of the microcrystallite. By studying a variety of microcrystals under the microscope the most favorable orientation was chosen for the c axis but there always was an uncertainty on the orientation of the other two axes which were located in the xy plane. Accumulation times were of the order of 1–1.5 h and a number of microcrystallites (seven to ten) were studied for each oxygen concentration for better statistics (error bars in Figs. 1–4). Both laser lines were used for each concentration and the spectra acquired looked practically identical. The spectrometer was calibrated just before and right after each measurement by using a standard material (a silicon wafer) and a low-frequency plasma line as a reference. In most of the cases the shift in the phonon frequencies was less than 0.1 cm^{-1} but when necessary the spectra have been corrected accordingly. The possibility of a local heating of the samples by the applied laser beam was excluded by studying the spectra on various power densities.

Typical spectra for the two extreme dopings are presented in the inserts of Fig. 1 for the $y(zz)\bar{y}$ polarization. In the low-frequency region, the relative intensity of the Ba ($\sim$118 cm^{-1}) and Cu2 ($\sim$150 cm^{-1}) phonons decreases as the oxygen content decreases and two other disorder-induced modes appear at 126 and 160 cm^{-1}.[8] By fitting the low-frequency part of the spectra with four Lorentzians we have seen that the frequency of the Ba mode does not change with x, while the Cu2 phonon frequency shows a slight linear increase from 144 cm^{-1} for $x=6.438$ to 150 cm^{-1} for $x=6.984$. The two impurity modes remain at almost constant frequencies without any changes in the width,[8] while the linewidth of the
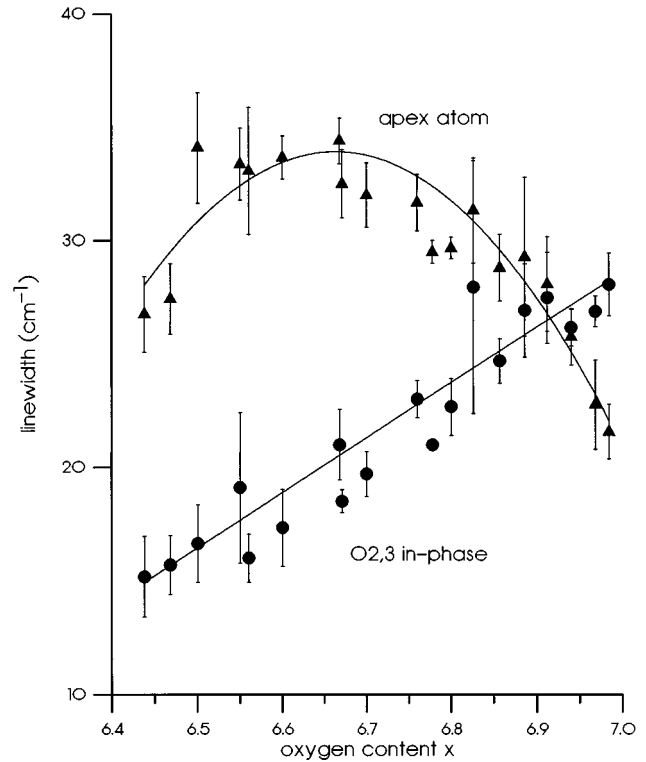
Cu2 peak remains small ($\sim$4 cm^{-1}) with an increase of $\sim$2 cm^{-1} towards the lowest oxygen content.

In the high-frequency part of the spectra, the apex frequency increases linearly with x up to $\sim$6.75, but then remains almost unchanged (Fig. 1), the pronounced nonlinear change of the apex phonon band with oxygen content being in contradiction with previously reported Raman works (for a review see Ref. 2). On the other hand the width of this band (Fig. 2) is considerably narrow ($\sim$22 cm^{-1}) near the ends of the oxygen concentration region, while it broadens by about 10 cm^{-1} at the intermediate concentrations. In Ref. 3 the apex mode had shown a pronounced structure for $x=6.4$. This mode has been decomposed into three peaks of which one at 470 cm^{-1} was associated with the tetragonal (T) phase. For similar oxygen concentration our spectra do not have much resemblance to those of Ref. 3, as there is no trace of the 470 cm^{-1} peak (insert in Fig. 1). On the other hand, the assumption of another mode at about 486 cm^{-1} turns out to be necessary for a proper fit with symmetric bands of the high-frequency part of the spectra. A fit with four peaks (one for the in-phase, two for the apex, and a wide disorder induced peak at $\sim$555 cm^{-1}) allowed to vary freely in frequency and width shows an apex mode at rather constant frequency 486 cm^{-1} and another apex mode at higher frequency (502 cm^{-1} for $x>6.9$) that softens with decreasing x. The width of these two apex modes reveals that the high-frequency apex mode broadens by 10 cm^{-1} as x decreases from 6.984 to 6.56, but at lower concentration it narrows considerably and at $x=6.438$ it has almost the same width (22 cm^{-1}) as for $x=6.984$. If we assume that this is due to the appearance of another mode, there is an excellent fit of the apex mode with three peaks centered at around 486, 493, and 502 cm^{-1} (varying within ± 1 cm^{-1}) with constant

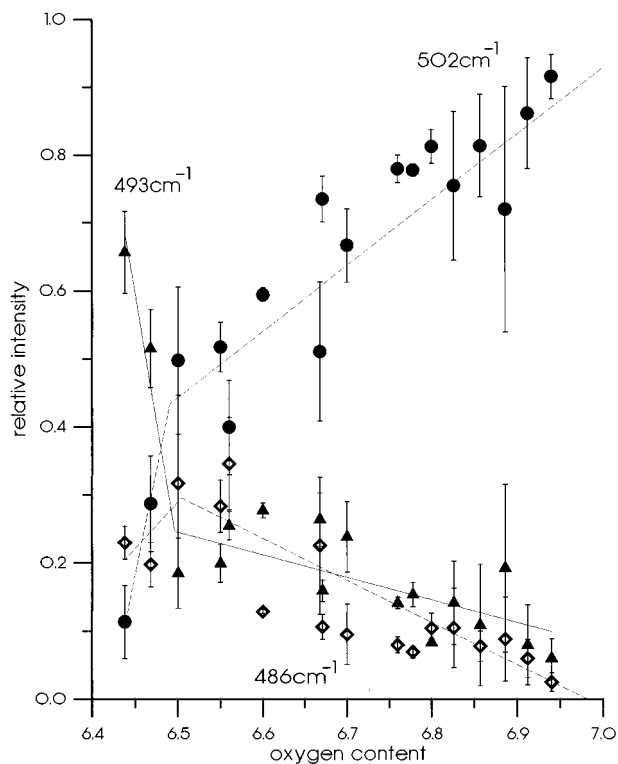FIG. 3. The relative intensities of the three apex modes as a function of x. The lines are again guides to the eye.
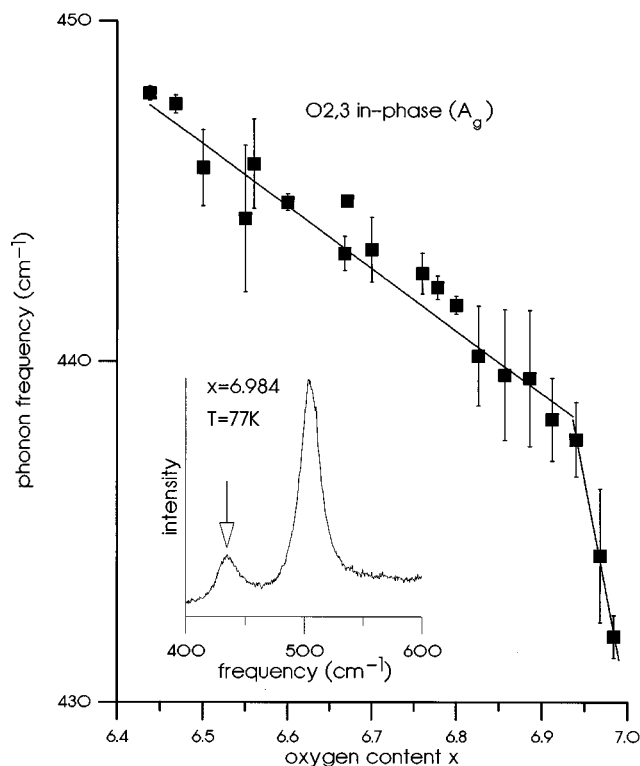

FIG. 4. Variation of the frequency of the in-phase phonon with oxygen content. The continuous lines are linear best fits for the under- and overdoped regions. The insert shows the spectrum for the $x=6.984$ sample at $T=77$ K.

width (22 cm^{-1} ±1 cm^{-1}) for the whole range of the oxygen concentration. Concerning the relative intensities of the above three apex modes the one at 502 cm^{-1} dominates near $x=6.984$, where the other two disappear, and it reduces to very low intensity with decreasing x, at approximately 6.4 (Fig. 3). For $x=6.984$ the intensity of both 486 and 493 cm^{-1} modes is practically zero and then increases with decreasing x. At $x\simeq6.5$ an appreciable change of slope takes place, resulting in an abrupt increase of the intensity of the 493 cm^{-1} mode and a maximum of the 486 cm^{-1}. It should also be noted that while at $x=6.984$ the narrow apex band consists almost completely of the 502 cm^{-1} peak; at the other end $x=6.438$, although still narrow, consists mainly of the 493 cm^{-1} but also contains a considerable amount of the 486 cm^{-1} mode. The appreciable dependence of the apex mode intensities on the oxygen concentration is supporting rather a chemically induced phase separation, than a dissociation under the energy of the laser beam.

One may assume that the first two of these modes at 502 and 493 cm^{-1} correspond to the long-range ortho-I and ortho-II phases, respectively, while the third peak may come from regions with different oxygen ordering. It should be also remarked that the intensities of Fig. 3 show a certain similarity to the estimated volumes of the three stable states found with inelastic neutron scattering,[9] pointing to a phase separation phenomenon.

The behavior of the total width of the apex band is different from the change in the width of the diamagnetic transition, which has been shown to fluctuate as a function of the nonstoichiometry[6] with maxima at $x=6.50$ and 6.80. Actually, whereas the diamagnetic transition broadens at the transitions from the ortho I to ortho II and from the ortho II to

the T, possibly due to the decrease of the chain ordering, the width of the Raman peak becomes narrow at the phase boundaries ($x>6.90$ and $x<6.50$) where the chains are nearly full or nearly empty (minimal concentration of chain ends).

Concerning the B_{1g} mode, it remains practically unaffected both in frequency and width by the changes in the oxygen content, contrary to the behavior of the A_g mode of the same atoms, as will be discussed below. The B_{1g} mode has been proven to be sensitive upon Y and Ba substitution by ions of different ionic radii.[10,11] More specifically, in the series $Pr_{0.5}R_{0.5}Ba_2Cu_3O_y$ it has been found that this mode suffers an overall softening by 30 cm^{-1} upon increasing the average rare-earth (R) ionic radius from Lu to La[10] and also broadens in the same direction. In the series $SmBa_{2-x}Sr_xCu_3O_y$ the B_{1g} mode softens by 10 cm^{-1} with increasing concentration x of Sr.[11] At the same time, the in-phase phonon of A_g symmetry of the same atoms is only slightly affected by these substitutions.

The variation of the frequency of the A_g in-phase oxygen phonon as a function of x (Fig. 4), shows that the phonon peak decreases almost linearly by 9 cm^{-1} from $x=6.438$ to 6.94. Above this concentration an abrupt shift appears from 440 cm^{-1} at $x=6.94$ to 432 cm^{-1} at $x=6.984$. This sudden change of the phonon frequency beyond the point of the optimum doping, i.e., $x\sim6.92$ does not seem to be correlated with any changes in all other phonon modes, which remain constant in this range. The absence of such correlation does not seem to support the assumption of a very strong coupling of the in phase with other modes. The width of this phonon

increases almost linearly with the oxygen content (Fig. 2) without any observable asymmetric changes or splitting of the peak, even at $x=6.984$.

The indications from the magnetization measurements for the development of another phase in the overdoped region,[5] led us to try to fit the in-phase mode by two peaks representative of the two phases. Contrary to the case of the apex phonon, in the case of the in-phase phonon a double fit could not work out in the same way and the two peaks were now varying in frequency, width, and relative intensity. Besides, the spectrum of the sample with $x=6.984$ taken at liquid-nitrogen temperature, does not show the existence of two peaks with the 440 cm^{-1} line being narrow and symmetric (insert in Fig. 4).

The question arises if this oxygen-content-dependent softening of the A_g phonon (Fig. 4) has to some degree structural origin. A recent very careful structural investigation[12] of the materials used in this work, synthesized with barium carbonate, shows that, in contrast to the literature, the lattice parameters do not change linearly with oxygen content. This is in general agreement with previous findings.[5] In particular, the a axis (decreasing with increasing oxygen content) remains larger than expected from the linear extrapolation above $x=6.70$, whereas the b axis (increasing with increasing oxygen content) stays lower than expected from the linear extrapolation and with increasing oxygen content saturates with a maximum at $x=6.85-6.90$. The same is true for the orthorhombicity, with the maximum shifted to $x=6.94$, exactly the concentration at which the A_g phonon starts softening. At approximately this concentration the volume also starts decreasing more rapidly with oxygen content (overdoped region). These structural data in the overdoped region show a clear contraction of the b axis and an appreciable decrease of the orthorhombicity with increasing oxygen content. This contraction appears first at $x=6.7$.

Hereupon effects related to the hole concentration changes in the CuO$_2$ plane and their influence on the in-phase vibrational mode should be examined. The continuous reduction of frequency of this mode from low oxygen content towards fully oxygenated (Fig. 4) seems to be correlated with the redistribution of carriers from chains to the planes which happens with increasing amount of doping. In the overdoped region the acceleration of this softening might come from an abrupt change in the hole concentration and in this way it has the same origin with the anomalous behavior of the CuO$_2$ plane buckling, beyond $x=6.94$,[5] if one thinks that this later crystallographic parameter is indicative of the Cu2 valence state. It is nevertheless unclear how the carrier concentration changes affect the in-phase mode. Screening effects have been indicated as a candidate.[2] Screening becomes stronger as the metallic character of the material emerges upon doping. According to a recent theoretical model[13] the coupling with the carriers of the in-phase phonon, contrary to the out-of-phase one, is strongly screened. In this case the renormalization (softening) and narrowing of the in-phase phonon with increasing doping is expected due to the reduction of its interaction with the carriers.[13] However, this comes in contradiction to the observed widening of the peak as x increases (Fig. 2), making the screening effects to be a hardly convincing scenario for the in-phase phonon behavior. It should be noted also that, as mentioned above, the magnetization vs x curves show at this oxygen content range ($x>6.95$) an anomaly due to a broadening and that the T_c slightly decreases due to repulsive interaction of the holes (overdoped region). [5,6]

In conclusion, the variation of the spectral characteristics of the apex phonon supports the assumption of the development of three phases in the superconducting region $6.44<x<7.0$. The in-phase phonon shows a characteristic softening at the optimum doping, where some of us proposed phase separation in the past.[5] Presently, it seems that this effect can be correlated with structural changes and/or redistribution of carriers. From the point of view of the phase separation we note that anomalies appear near both phase boundaries of the superconducting YBa$_2$Cu$_3$O$_x$. The present Raman investigation shows anomalies in the overdoped region (oxygen-rich phase boundary), but also brings important evidence for the coexistence of more than one apical oxygen mode near the oxygen-poor phase boundary.

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