

HIGH TEMPERATURE STUDY OF THE RAMAN-ACTIVE PHONON MODES OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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We have accomplished Raman scattering measurements on a polycrystalline sample of YBCO in the temperature range 25-600°C and in oxygen atmosphere. In the spectra at high temperature, we observe, new vibrational structures at 360, 585, and 605 cm^{-1} . The usual Raman modes at 335, 440, and 500 cm^{-1} showed a trend to broaden and flatten with increasing temperature. We attribute the peaks observed at high temperature to IR-active vibrational modes which become Raman-active as a result of temperature induced disorder in the YBCO unit cell. In this perspective, we discuss how the migration of oxygen atoms might account for the observed phenomena.

Keywords: A. high T_c superconductors, E. inelastic light scattering

Introduction - Raman scattering is a sensitive tool for determining the oxygen content in the copper oxide superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO).^{1,2} The oxygen content, i.e. the value of the parameter δ , influences many of the physical properties of the compounds of the YBCO family.^{3,4} Even the superconductive characteristics of YBCO depend on δ : for instance, the critical temperature T_c decreases with δ and presents two characteristic plateaux at 90 K (for $0 < \delta < 0.2$) and 60 K (for $0.3 < \delta < 0.5$).⁵ Despite these observations, the average value of δ is not the only parameter influencing T_c : the distribution of δ in the compound is of great importance too. It was recently demonstrated that samples with the same average value of δ , but different distributions of oxygen vacancies, show critical temperatures which differ by as much as 30 K.⁶ This observation has prompted us to perform Raman scattering experiments on polycrystalline YBCO samples to investigate the effects of temperature on the measured spectra. We have analyzed a frequency region, ranging from 260 to 670 cm^{-1} , where the phonon modes are mainly due to vibrations of the oxygen atoms. Processes of migration and diffusion of oxygen atoms within the sample are then expected to affect the observed Raman spectra.

Our study relies on the fact that if the point group of the crystal has a center of inversion, parity is a good quantum number and the irreducible representations have odd or even parity. In this case, a necessary condition for the phonons to be Raman-active is that they have even parity.⁷ Now, the point group of the crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has a center of inversion only in the case of ordering of the

oxygen vacancies and in the absence of defects. This fact implies that the appearance of IR-active modes in the Raman spectra can be associated with a lowering of symmetry. Furthermore, the specific Raman modes which disappear from the spectra, and the IR modes which appear in the spectra give information on the lattice sites involved in the process of symmetry lowering.

The Raman modes of YBCO are reliably assigned to the vibrations of specific ions in the unit cell. Specifically, the oxygen atom vibrations in which we are interested give rise to the Raman lines at 335, 440, and 500 cm^{-1} . Their position in frequency depends on the oxygen stoichiometry, and the 500 cm^{-1} mode is the most sensitive to the oxygen content shifting from 478 cm^{-1} in the tetragonal semiconducting $\text{YBa}_2\text{Cu}_3\text{O}_6$ to 502 cm^{-1} in the orthorhombic superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.² The 335 cm^{-1} mode is attributed to the off-phase vibration, along the *c*-axis, of the oxygen atoms O(2) and O(3), while their in-phase vibration originates the 440 cm^{-1} mode (here and in the following we label the atoms according to the conventions used in Ref. 8). The 500 cm^{-1} mode is determined by the vibration along the *c*-axis of the oxygen atoms O(4).⁹ The IR-active modes of YBCO have been studied on the basis of measurements done on single crystals¹⁰⁻¹³ and on a highly oriented multi-crystalline block.¹⁴ The three IR-active modes whose frequencies lie in the spectral range of interest are centered at about 360, 585, and 640 cm^{-1} . They have been assigned to the Cu(2)-O(2) bond bending parallel to the *ab* plane, to the Cu(2)-O(2) stretch mode, and to the Cu(1)-O(4) stretch along the *c*-axis, respectively.^{10,12,15}

The oxygen in-diffusion and out-diffusion processes in polycrystalline samples of YBCO can be obtained by heat treatments in controlled atmosphere. It is known that the onset temperature of the two processes is of the order of 450°C.^{8,16} The time required to change the bulk oxygen

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content in a ceramic sample is of the order of hours to tens of hours, whereas a monocrystal requires longer times.

Experimental details - The Raman measurements were carried out on a polycrystalline sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ positioned in a specially designed optical device which allowed us to perform spectroscopic measurement in conditions where both the atmosphere and the temperature of the sample were under control. The Ar+ laser line at 5145 Å (beam power 20 mW) was focused on the sample into a spot of about 50 μm in diameter. The same optics were used to focus the incoming laser radiation on the sample and to collect the scattered signal. No polarization analysis was carried out on the back scattered radiation which was dispersed by means of a triple-stage monochromator (Spex 1877 Triplemate). The instrumental resolution was 5 cm^{-1} . The signal was detected by an intensified 512-diode array detector OMA-III system, cooled at -20°C. The intrinsic noise of this detector, as well as its linearity range and long time stability, have been thoroughly analyzed as a function of the detector temperature and of the exposure time, and optimal working conditions for noise subtraction were determined.¹⁷ According to these results, many sampling cycles (involving signal accumulation and subsequent noise subtraction), each having a duration of a few minutes, were performed and accumulated into the memory of the acquisition electronics, for a total measuring time on the order of 1-3 hours per spectrum. The wavelength calibration of the spectrometer was periodically checked by means of an argon spectral lamp, which shows seven well defined lines in the range 5215-5330 Å.

In order to achieve a homogeneous temperature field on the whole sample, this was located in a quartz ampoule which was enclosed within a cavity of a copper block. This block formed the body of a specially designed optical oven. The temperature of the copper block was measured with a K-type thermocouple and stabilized by means of a triple action electronic temperature controller, which was interfaced with a computer. A pair of quartz pipes, sealed to the inner ampoule, allowed the flow of the controlled atmosphere. The quartz container was closed on the top by a spring loaded optical window, and a second quartz window was adjusted on top of the oven to prevent convective turbulence.

The polycrystalline sample was initially tested at room temperature and its oxygen content was determined by measuring the position in frequency of the apex oxygen phonon mode. This was centered at 481 cm^{-1} implying an oxygen content of about 6.3 per formula unit (p.f.u.). At this point the oven was closed, a constant flux of argon was established, and the sample temperature was increased at a rate of 8°C/min up to 600°C. The temperature was then stabilized at 600°C. This high value of T, and the argon atmosphere, made us confident that the sample was in the tetragonal phase with $\delta=1$. The argon cylinder was then closed and the oxygen flux was started. At this time the oxygen in-diffusion process began, causing a progressive occupation of the oxygen sites O(1).^{8,18} The sample was kept at a constant temperature of 600°C in a flowing oxygen atmosphere for a total time of 15 hours. Subsequently, the temperature was slowly lowered down to

25°C, over a period of more than 60 hours, still in flowing oxygen atmosphere.

During the whole thermal cycle, two series of spectra were collected. The first series refers to the sample kept at 600°C, in flowing oxygen atmosphere, and consists of six spectra taken at a constant time-interval starting from the time the oxygen flux was started. These spectra show the effect of the oxygen in-diffusion process at high temperature. The second series consists of 21 spectra, recorded during the cooling process, and each of them is relative to a constant intermediate temperature. These spectra allow us to study the temperature evolution of the Raman phonon modes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

This procedure allowed us to study *directly* the oxidation process of YBCO from the tetragonal (disordered) phase at 600°C to the orthorhombic (ordered) phase at room temperature.

Results - In the discussion of the results it is convenient to begin with the second series of spectra. Fig. 1 shows 9 of the 21 spectra acquired during the cooling process. The room temperature spectrum of Fig.1 shows the characteristic Raman bands of oxygen. In particular, the position of the band at 490 cm^{-1} implies a value of $\delta=0.3$. We remind that the initial calibration (481 cm^{-1}) provided for δ a value of 0.7. This is in rather good agreement with an independent determination, obtained by weighting the sample before and after the thermal process, which gave $\Delta\delta=0.35\pm 0.01$ and confirms a rather homogeneous oxidation of the sample.

At low temperature (<200°C), the familiar Raman modes at 335, 440, and 490 cm^{-1} are evident. At higher temperatures, these lines start to broaden and eventually disappear from the spectrum for a sample temperature

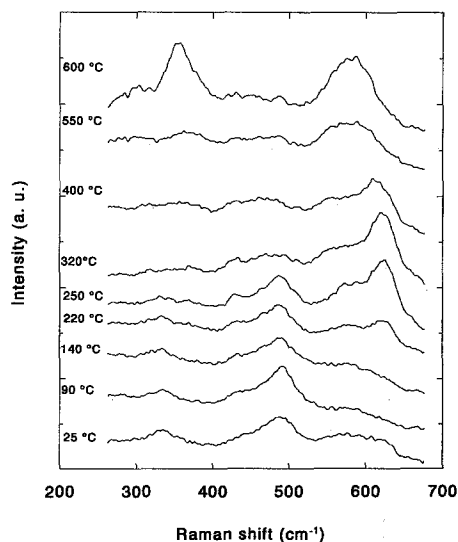


Fig. 1 - Raman spectra of YBCO acquired in the temperature range 25-600°C in an oxygen atmosphere. These spectra show the broadening and shifting of the room temperature Raman modes at 335, 440, and 490 cm^{-1} with increasing temperature. Also, we observe the build-up of the new structures around 360, 585, and 605 cm^{-1} which are discussed in the text. Linear offset is added for clarity.

around 300°C. We have analyzed the width and peak frequency of these Raman bands by fitting each of them with a Lorentzian line shape. The temperature behavior of the line centers of the three characteristic Raman modes is reported in Fig. 2a. We observe that the frequency of the modes decreases with increasing temperature. This fact can be attributed to the anharmonicity of the potential of the oxygen atoms.¹⁹

The two most striking features of the temperature behavior of this portion of the Raman spectrum are the progressive attenuation of the intensity of the Raman modes (which eventually merge in the background for temperatures higher than about 300°C), and the appearance of different structures at high temperature. The progressive disappearance of the mode at 490 cm⁻¹ can be attributed to a migration of the O(4) oxygen towards the empty sites at O(1) and O(5) positions on the Cu-O basal planes.²⁰ This migration could be induced by the high temperature, which makes accessible a second minimum in the potential of the apical oxygens O(4).²¹

In any case, defects in the lattice structure would destroy the inversion symmetry with respect to the central yttrium atom and would make some of the infrared modes Raman-active. The progressive disappearance of the characteristic Raman lines should be balanced by the simultaneous emergence of IR-active modes in the Raman spectra. In fact, there are three IR-active modes in the explored spectral region, centered at 360, 585, and 640 cm⁻¹,^{10-14,22,15} and we expect to observe structures centered around these frequency values. This is exactly what we observe in the spectra reported in Fig. 1, where three developing IR-active

modes are actually measured at the higher temperatures. The two lower modes (namely 360 and 585 cm⁻¹) characterize significantly the spectrum at the highest temperature, and are clearly detected starting from 400°C. The structure detected at high temperature, around 605 cm⁻¹, has been observed independently by Burns *et al.*,²³ and has been interpreted with the creation of new O-O bonds in the basal plane. However, observing Fig. 2b, where we report the temperature dependence of the peak frequency of the IR-active bands, we notice that the frequency of this peak approaches, with decreasing temperature, the value of 640 cm⁻¹ which has been measured in the IR spectra at room temperature. We therefore identify this structure with the 640 cm⁻¹ IR-active mode. The position of the 360 and 585 cm⁻¹ modes as a function of temperature are also reported in Fig. 2b. These frequencies also tend to decrease with increasing temperature, as a consequence of the anharmonicity of the potential. In particular, the peak position of the low frequency mode approaches 380 cm⁻¹ in the limit of room temperature, consistently with the reported results.¹⁵

We now move to discuss the first series of spectra taken during the oxygen in-diffusion process, which are reported in Fig. 3. These spectra were taken at 600°C, at three hour intervals starting from the moment the oxygen flux was started. It is interesting to comment on the different behavior with time, and therefore with oxygen content, of the two IR modes at 360 and 585 cm⁻¹. These two bands characterize the Raman spectrum at this temperature, as discussed above. First, we observe a progressive increase of the intensity of the two modes, more evident in the 360

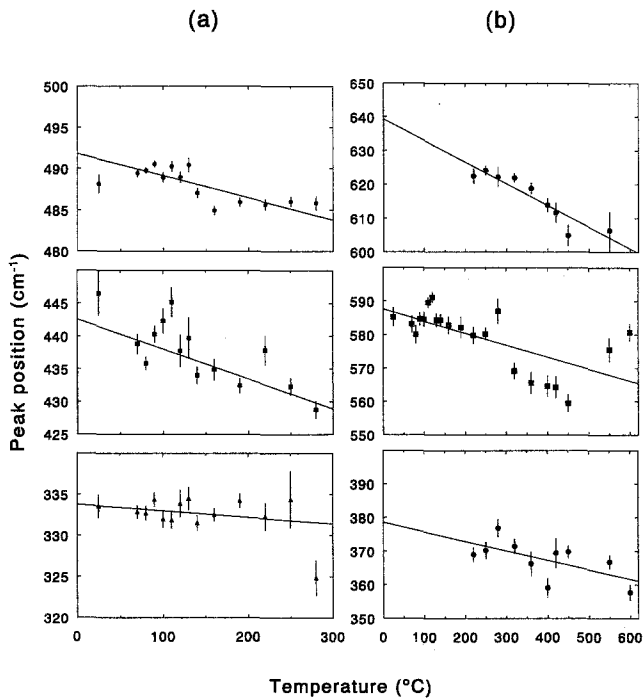


Fig. 2 - Temperature behavior of the line centers of the observed Raman (a) and IR (b) modes. The straight lines are obtained by a weighted least squares fit.

cm^{-1} peak, during the 15 hours of the duration of the measurement. Secondly, while the mode at 360 cm^{-1} shows a slight change in peak position from 362 cm^{-1} (at $t=0$ and low oxygen content) down to 356 cm^{-1} (at $t=15 \text{ h}$ and high oxygen content), the peak frequency of the mode at 585 cm^{-1} remains nearly constant. Also, the width of the two lines shows a different behavior. We conclude this section by reminding that the high frequency mode is related to the motion of the O(2) in the ab plane, while the 360 cm^{-1} IR mode is connected with the motion of O(4) in the same plane.¹⁵

Discussion - The time behavior of the Raman spectra at constant temperature (600°C , see Fig. 3) shows the spatial size and the time scale involved in the process. If we recall that Raman spectroscopy is sensitive to a superficial region of the sample extending for about $1000\text{-}2000 \text{ \AA}$ below the surface, we observe that the oxygen diffusion in this range of distances is characterized by a process of the order of a few hours (we remind that the total time spanned in Fig. 3 is 15 hours). The temperature behavior of the Raman spectra taken at fixed temperature ($T=600^\circ\text{C}$) and constant oxygen flux could be explained by the internal migration of the oxygen atoms. The relatively faster amplitude saturation of the 585 cm^{-1} band, with respect to the 360 cm^{-1} one, would indicate a faster migration to the basal sites which are followed by a slower occupation rate of the apical sites (cf. Fig. 3).

The progressive separation of the two IR-active bands in the region $585\text{-}640 \text{ cm}^{-1}$, which is observed by decreasing the temperature from 550°C to 220°C (cf. Fig. 1) points to the presence of a microscopic structure which disappears at still lower temperatures. As already mentioned, a jump between two different equilibrium sites of the O(4) oxygens is a good candidate for a possible explanation of this behavior. Beyond the appearance of IR modes in the Raman spectra, the migration of axial oxygen O(4) to a different site could account for the disappearance of the 490 cm^{-1} mode from the Raman spectra.²¹ However, this mechanism alone cannot account for the simultaneous disappearance of the 335 cm^{-1} peak which is driven by the off-phase vibrations of the O(2)-O(3) oxygen atoms.

The key for an interpretation of the temperature evolution of the Raman spectra is probably given by the different threshold temperatures which are necessary to start a diffusion process from the different oxygen sites.²⁴ When temperature is well below 300°C , only the O(1) oxygens can diffuse, which produces an increase in the 640

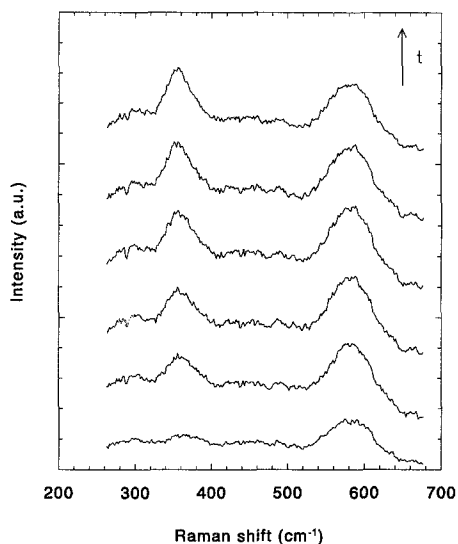


Fig. 3 - Raman spectra of YBCO acquired at a constant temperature of 600°C in an oxygen atmosphere. The six spectra were acquired at three hour intervals, starting from the onset of oxygen flux (15 hours total). Linear offset is added for clarity.

cm^{-1} IR band, but leaves almost unchanged the ordinary Raman modes at 335 and 490 cm^{-1} . As temperature grows above 300°C , also the O(4) oxygens are allowed to migrate and this deep disturbance of the elementary cell washes out the ordinary Raman spectrum. At still higher temperatures (beyond 400°C) also the O(2) and O(3) oxygens are interested by the diffusion process which becomes homogeneous over all oxygen positions in the structure.²⁴ Finally, at 600°C , the system becomes totally disordered, as far as the oxygen is concerned, and the Raman spectrum assumes a shape which is very dissimilar from the familiar picture. The three spectra at the highest temperatures reported in Fig. 1 reflect this situation.

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