

Raman scattering on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals with variable oxygen content

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Abstract

Light scattering investigations have been performed on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal with $0 < \delta < 1$. Softening and the stiffening in frequency of the 5 A_g normal modes originating from the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure have been observed as the oxygen content decreases. Moreover, for intermediate oxygen content : $0.4 \leq \delta \leq 0.5$, the existence of a new structural phase, the Ortho II phase, has been detected. This new phase is defined by the double elemental unit cell $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$ and establishes the connection between the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ metallic phase related to the D_{2h}^1 space group and the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ insulator phase related to the D_{4h}^1 space group.

1. Introduction

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds have received a considerable amount of interest because of their high temperature superconducting properties. Superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds occurs near the orthorhombic / tetragonal structural change as well as the metallic / insulator phase transition, both controlled by the oxygen stoichiometry. The metallic superconducting phase appears for $0 \leq \delta < 0.35$ whereas the insulator non superconducting phase occurs for $0.35 < \delta \leq 1$. Increasing δ from 0 to 1 in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds corresponds to removing oxygen atoms from the Cu-O chain (1). In the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure the O1 sites are fully occupied as illustrated in Figure 1.a whereas, in the $\text{YBa}_2\text{Cu}_3\text{O}_6$ structure the O1 sites are all empty as represented in Figure 1.b. In the past few years, several Raman scattering investigations have been performed on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds as δ increases. In particular studies have been focused on the frequency shifts of the 5 A_g Raman active modes related to the D_{2h}^1 space group of the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure which decompose, as the oxygen content decreases, into the 4 A_{1g} and 1 B_{1g} modes related to the D_{4h}^1 space group of the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ structure. The normal modes at 147 cm^{-1} in $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure, attributed (2-7) to the vertical motions along the c axis of the Cu2 atoms soften, whereas, the normal modes at 336 cm^{-1} and 437 cm^{-1} , respectively assigned (2-7) to the

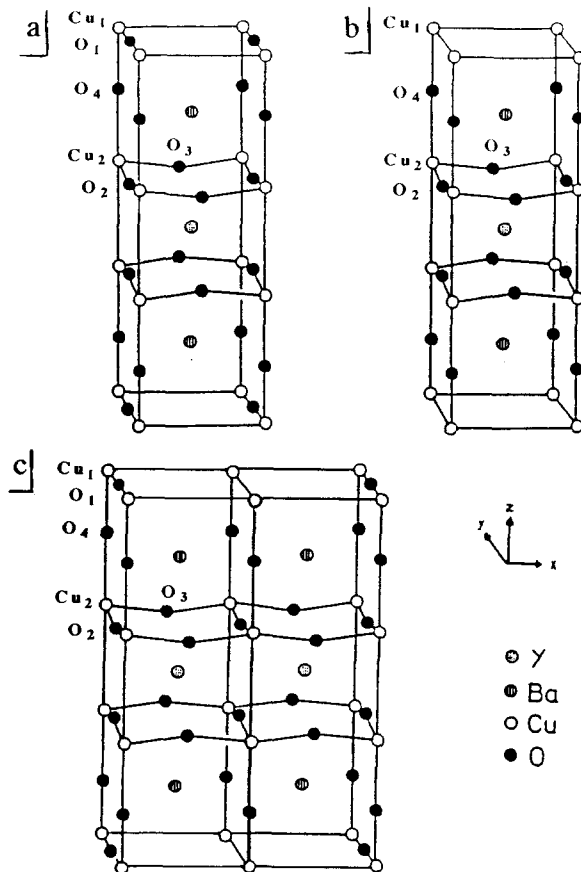


Figure 1. Elemental unit cells of a) $\text{YBa}_2\text{Cu}_3\text{O}_7$, b) $\text{YBa}_2\text{Cu}_3\text{O}_6$ and c) $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$

vertical motion of the O2-O3 oxygen atoms vibrating out of phase and in phase, harden when the oxygen concentration decreases. However, the situation is still confused concerning the normal modes at 117 cm^{-1} and 499 cm^{-1} respectively assigned to the Ba atoms and the O4 apical oxygen atoms vibrating along the *c* axis. The frequency shift of the Ba normal mode is not yet clearly detected and some authors report ⁽²⁻⁶⁾ a regular softening of the O4 normal mode from $\delta = 0$ to 1, whereas others ⁽⁷⁾, show its softening for $\delta \leq 0.6$ and its sudden hardening for $\delta > 0.6$. In order to clarify the situation, the study of the frequency shifts, presented here, has been focused on the $5 A_g$ normal mode as δ increases in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals. On the other hand, most of the Raman measurements mentioned above ^(2-4,6-8) report the existence of new peaks for intermediate oxygen contents which are not yet well identified. As a second step in this work, we have clearly detected and assigned these new peaks. It then appears that these new modes belong neither to the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ nor to the $\text{YBa}_2\text{Cu}_3\text{O}_6$ tetragonal structures but can be attributed to the normal modes of the "Ortho II" phase defined by the $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$ unit cell where oxygen ordering appears, i.e every other Cu-O chain is empty of oxygen as illustrated in Figure 1.c.

2. Experimental set up

Light scattering measurements have been performed on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals with variable oxygen content δ . Crystals were grown in a gold crucible using the self-flux method ⁽⁹⁾. Their typical size is $(1 \times 0.5 \times 0.1\text{ mm}^3)$. The compositions of $\delta = 0.5$, $\delta = 0.4$, $\delta = 0.2$ and $\delta = 0$ have been respectively obtained by a final annealing in oxygen atmosphere at 740, 600, 500 and 350°C according to previously reported composition versus temperature relations ⁽¹⁰⁾, whereas the $\delta = 0.7$ composition was obtained by a heat treatment at 850°C under an oxygen-argon gas mixture. The oxygen concentrations have been controlled by x-ray diffraction measurements of the structural parameters ⁽¹⁾ and by iodometric titration ⁽⁶⁾. For $\delta = 0, 0.2, 0.4$ and 0.5 , the critical temperatures are $T_c \approx 92\text{ K}, 80\text{ K}, 60\text{ K}$ and 60 K respectively. Micro-Raman studies have been carried out at room temperature with a U 1000 Jobin-Yvon double monochromator using the 514.52 nm laser line. A photomultiplier tube was connected to a micro computer for data collection. The microprobe produced a laser spot of few square micrometers. The incident and scattered light was emitted and collected by the microprobe objective. We had therefore a perfect 180° back scattering geometry

allowing analyses in $Z(xx)Z^*$, $Y(zz)Y$ and $Z(x,y)Z$ configurations. The intensity was maintained below 10 W/cm^2 in order to minimize possible thermal damage.

3. Results and discussion

Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal with variable oxygen content in the $Y(zz)Y$, $Z(xx)Z$ and in the $Z(x,y)Z$ configurations are displayed in Figures 2.a, b and c respectively. We can notice that most of the phonons existing in the orthorhombic phase are still present in the tetragonal phase shifting in frequency and varying in intensity. However for intermediate oxygen content, typically : $\delta = 0.4$ and $\delta = 0.5$, new peaks appear.

3.1 Analysis of the frequency shifts

The frequency shifts of the normal modes related to the vibrations of the O4 apical oxygens, the O2-O3 oxygens in phase and out of phase motions, in $Y(zz)Y$, $Y(zz)Z$ and $Z(xx)Z$ configurations are shown in Figures 3. a, b and c respectively. The frequency shifts of the normal modes related to the Barium ions and the Cu2 atoms in the $Y(zz)Y$ and $Z(xx)Z$ configurations respectively, are illustrated in Figures 3.d and 3.e. No evidence of a new peak position ⁽⁷⁾ for the O4 normal mode at 600 cm^{-1} when $\delta > 0.6$ has been detected. The interpretation of these frequency shifts is not obvious and is not well understood. The Cu2-O4 bonds being mostly ionic ⁽¹¹⁾ the softening of the Cu2 normal mode as δ increases can be explained by the increase of the Cu2-O4 inter-atomic distance ⁽¹⁾ which reduces the Coulomb interaction, in $1/r^2$, between the two ions. In the same way the shift to low energy of the Ba normal mode can be understood by the disappearance of the Coulomb forces coming from the interaction between the O1 and the Ba ions as the O1 oxygens are removed from the Cu-O chains. On the contrary, Coulomb interaction arguments do not permit to explain the softening of the O4 normal mode which do not correspond to the reduction of the Cu1-O4 distance ⁽¹⁾. And finally, the hardening of the O2-O3 normal mode can be understood by the decrease of the free carriers in the Cu-O2 planes, as δ increases, which reduces the screening between the Cu-O2 layers and yields more efficient inter-layers Coulomb interactions ^(4,5).

* *x, y, z* indicate respectively the unit vector parallel to the *a, b, c* axes of the crystal. The first term into the bracket indicates the electric field direction of the incident light and the second one the electric field direction of the scattered light. The left term out of the bracket indicates the direction of the incident wave vector and the right term out of the bracket, the direction of the scattered wave vector.

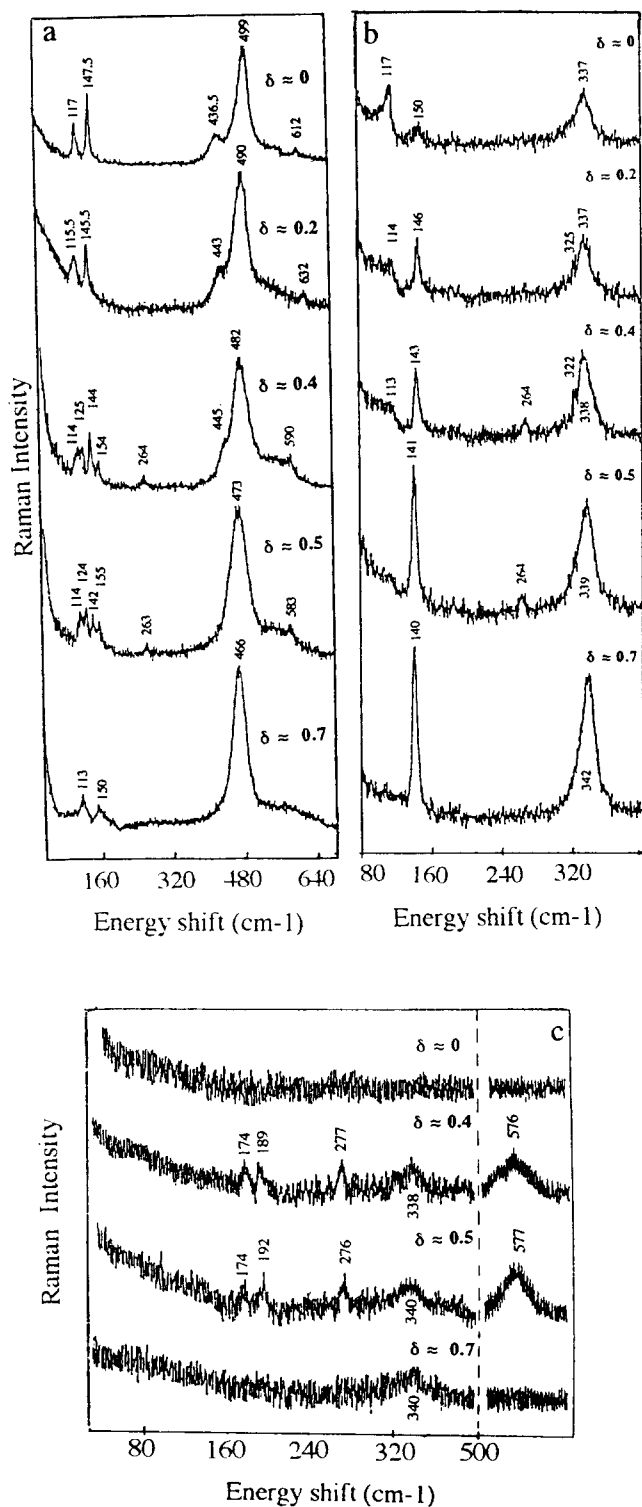


Figure 2. Raman spectra as a function of oxygen content in the a) Y(zz)Y, b) Z(xx)Z and c) Z(xy)Z configurations.

3.2 Assignment of the new peaks

For intermediate oxygen concentrations new modes appear on the Raman spectra, which belong neither to the

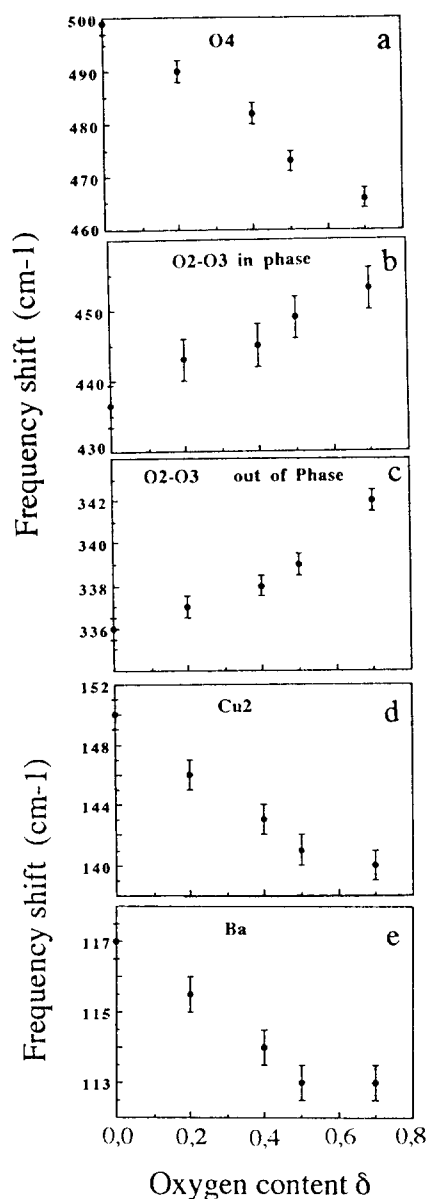


Figure 3. Frequency shifts of the 5Ag normal modes with variable oxygen content.

orthorhombic $YBa_2Cu_3O_7$ nor to the $YBa_2Cu_3O_6$ tetragonal structures. Some of them have been already detected by earlier Raman scattering studies (2-4,6-8), but, not clearly identified. The frequencies of these extra modes are listed in Table 1.

Table 1. Frequencies of the new peaks

Configurations	Frequencies in cm^{-1}				
Y(zz)Y	125	154	264	583	
Z(xx)Z	154	264	322	585	
Z(x,y)Z	174	190	276	335	576

It has been shown by neutron⁽¹²⁾ and electron^(13,14) diffraction measurements that for δ near 0.5, ordering of oxygen vacancies appears in the Cu-O chains. A doubling of the a axis has then been observed and indicate that one Cu-O chain out of two is empty of oxygen. This new phase, represented in Figure 1.c, is called the Ortho II phase. Its structure is orthorhombic and related to the D_{2h}^1 space group. Group theoretical analysis has been performed⁽¹⁵⁾ on the $Y_2Ba_4Cu_6O_{13}$ structure. The 72 optical modes and their symmetry are given by the decomposition of the mechanical representation Γ as follows :

$$\Gamma = 11A_g + 3B_{1g} + 11B_{2g} + 8B_{3g} + 2A_u + 13B_{1u} + 11B_{2u} + 13B_{3u}$$

Due to the existence of an inversion center, the Raman active modes are even and are 33 in number :

$$11A_g + 3B_{1g} + 11B_{2g} + 8B_{3g}$$

The new modes listed in Table 1 can then be attributed, using symmetry considerations⁽¹⁵⁾ and earlier dynamical calculations^(4,5), to the A_g and B_{1g} normal modes related to the $Y_2Ba_4Cu_6O_{13}$ structure. The A_g and B_{1g} normal modes detected at 125 and 174 cm^{-1} correspond respectively to the out of phase motion of the barium atoms along the a and b axis. The A_g mode at 154 cm^{-1} detected in both $Z(xx)Z$ and $Y(xx)Y$ configurations has been assigned to the out of phase motion of the Cu2 atoms in the Cu-O2 planes along the c axis. The A_g and B_{1g} modes detected at 264 cm^{-1} and 276 cm^{-1} in the $Y(zz)Y$ and $Z(xy)Z$ configurations can be assigned to the out of phase motion of the yttrium atoms along the a and b axis respectively. The peaks at 322 cm^{-1} of A_g symmetry is attributed to the out of phase motion of the O2 oxygen in the Cu-O2 planes. Finally the A_g and B_{1g} normal modes detected at 585 cm^{-1} and 576 cm^{-1} have been assigned to the O2-O3 atoms in out of phase motion along the a and b axis respectively. Finally two peaks have not been clearly identified at 335 cm^{-1} and 190 cm^{-1} in the $Z(x,y)Z$ configuration. The first could be attributed to the reminiscence of the B_{1g} normal mode related to the tetragonal structure, whereas, the second could be originating from defects of oxygen ordering in the $Y_2Ba_4Cu_6O_{13}$ structure.

4. Conclusion

The softening in frequency of the normal modes related to the Barium, the Cu2 copper and the O4 oxygen atoms vibrations have been clearly detected as well as the stiffening of the O2-O3 oxygen atoms in phase and out of phase motions when the oxygen content decreases. Moreover for intermediate oxygen concentrations

$0.4 \leq \delta \leq 0.5$, new peaks appear in the Raman spectra of $YBa_2Cu_3O_{7-\delta}$ in the $Y(zz)Y$, $Z(xx)Z$ and $Z(x,y)Z$ configurations which can be assigned to the A_g and B_{1g} normal mode of the $Y_2Ba_4Cu_6O_{13}$ structure, called the Ortho II phase. This new phase establishes the connection between the Ortho I, $YBa_2Cu_3O_7$ metallic superconducting phase and the Tetra I, $YBa_2Cu_3O_6$ insulating non superconducting phase, and reveals ordering of the oxygen vacancies for $0.4 \leq \delta \leq 0.5$ which can be correlated to the "plateau" at $T_c = 60$ K that shows⁽¹⁶⁾ the critical temperature versus δ .

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