

Hydrostatic-pressure-induced phase separation in the $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconductor

D. Lampakis,¹ D. Palles,¹ E. Liarokapis,¹ S. M. Kazakov,² and J. Karpinski²

¹*Department of Physics, National Technical University of Athens, GR-15780 Athens, Greece*

²*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, 8093 Zurich, Switzerland*

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A micro-Raman study under high hydrostatic pressure (up to ~ 7.5 GPa) has been carried out on $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconducting single crystals at room and low temperatures down to 77 K. Seven strong modes of A_g symmetry, two of weak B_{2g} and B_{3g} symmetry, and another mode at ~ 431 cm^{-1} have been investigated. With increasing hydrostatic pressure the first nine phonons shift to higher energies while the latter is independent of pressure. A splitting of the mode attributed to the in-phase vibrations of the plane O oxygen atoms has been observed. Besides, anomalous nonlinear pressure behavior has been observed for the other A_g phonons, which is correlated with the splitting of the in-phase mode and the pressure dependence of the superconducting transition temperature of this compound. The results indicate a pressure-induced phase separation, which is related with a lattice distortion from the tilting of the CuO_6 octahedra.

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INTRODUCTION

Hydrostatic pressure effects in the oxide superconductors have been studied extensively.^{1,2} For these materials, the dependence of the superconducting transition temperature (T_c) on pressure (dT_c/dP) varies in a large range of values and it provides indications that a material may reach higher T_c values at ambient pressure by suitably modifying its structure with atomic substitutions creating an internal *chemical pressure*. Therefore, the high-pressure experiments are of primary interest.^{1,2}

The $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y124) compound was first detected as a lattice defect in $\text{YBa}_2\text{Cu}_3\text{O}_x$ (Y123) powders.³ The structural difference between Y123 and Y124 is the doubling of the $\text{Cu}_{ch}\text{-O}_{ch}$ chains along the b axis and between the Ba-O_{ap} planes, which gives a stronger bond between the oxygen O_{ch} and copper Cu_{ch} atoms at the chain sites leading to the absence of the oxygen defects. This is in contrast to the Y123 case in which the $\text{Cu}_{ch}\text{-O}_{ch}$ chains become easily oxygen deficient.⁴ Although the crystal structure and the values of the critical temperature, T_c , of both doped Y123 and Y124 compounds are very similar ($T_c \sim 92$ K and 80 K, respectively), their behavior under pressure is different. In particular, while the pressure dependence of T_c in Y123 is relatively low, with dT_c/dP from ~ 1 to ~ 2.5 K/GPa,⁵ the pressure dependence of T_c in Y124 shows a large positive derivative, with $dT_c/dP = 5.5$ K/GPa up to 4 GPa and exceeds 100 K above 5 GPa.⁶⁻¹¹

Detailed Raman studies of the Y123 compound at ambient pressure have shown that the five strong phonons in the energy region below ~ 500 cm^{-1} are of A_g symmetry with eigenvectors along the c axis. These modes are attributed to the vibrations of the Ba atom, the Cu_{pl} , the in-phase and out-of-phase (B_{1g} -like) vibrations of the O_{pl} oxygen atoms of the CuO_2 planes, and the apical O_{ap} oxygen. In the case of Y124 the phonons involving vibrations of the Cu_{ch} and O_{ch} atoms are also Raman active.¹² It is known that the ion distances in the unit cell of Y124 do not change considerably with respect to the Y123 system,^{13,14} and the energies of the

Cu_{pl} and O_{pl} (in-phase and out-of-phase vibrations) phonons are similar to the corresponding ones of Y123 while those of the Ba and O_{ap} atoms soften slightly.¹² In previously reported measurements four out of the six Raman-allowed modes of the double $\text{Cu}_{ch}\text{-O}_{ch}$ chains have been detected. The chain modes of A_g symmetry at ~ 250 and 600 cm^{-1} were assigned to the vibrations along the c axis of the Cu_{ch} and O_{ch} atoms, respectively,^{12,15} while the peaks at ~ 210 and 315 cm^{-1} to the motion of the O_{ch} and Cu_{ch} atoms along the a (B_{2g} symmetry) and b (B_{3g} symmetry) axes, respectively.¹² It should be noticed that in the case of the Y124 compound, the intensity of the B_{2g} , B_{3g} modes is high (even higher than the intensity of some A_g phonons).

While there are several hydrostatic pressure studies of the transition temperature, the structure, and the electronic properties of the cuprate superconductors, the high-pressure Raman investigations on these compounds are limited. The main reason is the difficulty of studying the very weak phonons of the superconducting materials inside the high-pressure diamond anvil cell. According to previous studies^{16,17} the energy of most of the Raman active phonons of Y124 increases almost linearly with pressure. Nonlinear pressure dependence has been observed for the energy shift of the A_g symmetry in-phase vibrations of the O_{pl} atoms.¹⁶ Additionally, an anomalous pressure dependence has been detected for the energy of the A_g mode of the Cu_{pl} atoms at ~ 150 cm^{-1} , which deviates from linearity at pressures exceeding ~ 6 GPa.¹⁷ Besides, Kakihana *et al.* have noticed that the pressure dependencies of this mode energy and of the critical temperature for the compound are similar.¹⁷

Several studies have been reported up to now concerning the appearance of local lattice distortions with doping in cuprates and their possible correlation with the superconducting critical temperature. In particular, for the $\text{YBa}_2\text{Cu}_3\text{O}_x$ compound the room temperature Raman study has shown that the energy of the in-phase O_{pl} mode decreases with increasing x and, then, softens strongly and two phases separate around the optimal doping ($x \sim 6.92$).¹⁸⁻²⁰ This anomalous softening has been associated with the increase of the

dimpling in the CuO_2 planes, supporting the idea that local coherent distortions of the CuO_2 planes and transition temperature are related.²¹ Concerning the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) superconductor, a correlation has been found between the spectral characteristics at room temperature for some of the phonons and the superconducting transition temperature, for the $0 \leq x \leq 0.45$ doping range.²² This result seems to be connected with the presence of local lattice distortions as those detected in doped LSCO samples,²⁵ which activate symmetry forbidden IR modes in the Raman spectra.^{22–24}

Both in Y123 and the LSCO compounds the lattice distortions are induced by chemical doping, which usually incorporates lattice defects. An alternative and *cleaner* way to modify the doping is by applying a hydrostatic pressure. For the hole-doped superconductors, it has been claimed that chemical doping and the application of hydrostatic pressure affect the superconducting properties in a similar way.^{1,2} In the cases of the Y123 and Y124 compounds T_c measurements as a function of doping or pressure confirm these results.^{5–11} Besides, a direct correlation between T_c and the density of the hole concentration in the two CuO_2 planes has been found.^{26–28} Surprisingly, the spectral characteristics of the apex and CuO_2 plane phonons, as a function of doping in Y123, and as a function of pressure in Y124, presented in this article, vary in a similar way. This result probably denotes that the redistribution of carriers induced by doping is similar to that induced by the application of hydrostatic pressure.

In this work, high-pressure Raman measurements of superconducting single crystals of Y124 have been carried out aiming to investigate the appearance of structural defects. The results indicate that the application of a critical hydrostatic pressure (~ 2.5 – 3.0 GPa) on Y124 induces such lattice distortions and furthermore a coexistence of phases.

EXPERIMENTAL

The preparation conditions of the Y124 samples used in this work have been described elsewhere.²⁹

The Raman spectra were obtained at high hydrostatic pressures with a T64000 Jobin-Yvon triple spectrometer equipped with a liquid-nitrogen-cooled charge coupled device (CCD) and a microscope lens of magnification $\times 100$ ($\times 40$ for the hydrostatic pressure measurements), in the temperature range 77–295 K. A Merrill-Bassett-type diamond anvil cell (DAC) was used for the high-pressure measurements (up to 7.5 GPa), which has allowed the Raman studies to be carried out in a backscattering geometry. The pressure-transmitting medium was a mixture of methanol-ethanol. Silicon single crystals distributed around the sample were used for calibration of the pressure and for monitoring the hydrostatic conditions. The excitation was obtained with the 514.5 nm line of an Ar^+ laser, which produced the lowest luminescence from the diamonds. Low temperature measurements were carried out in a pseudo-hydrostatic environment by incorporating the small DAC into an Oxford cryostat suitable to reach temperatures down to 5 K and appropriately modified for the incorporation of the DAC and the application of the selection rules. By including two more small sili-

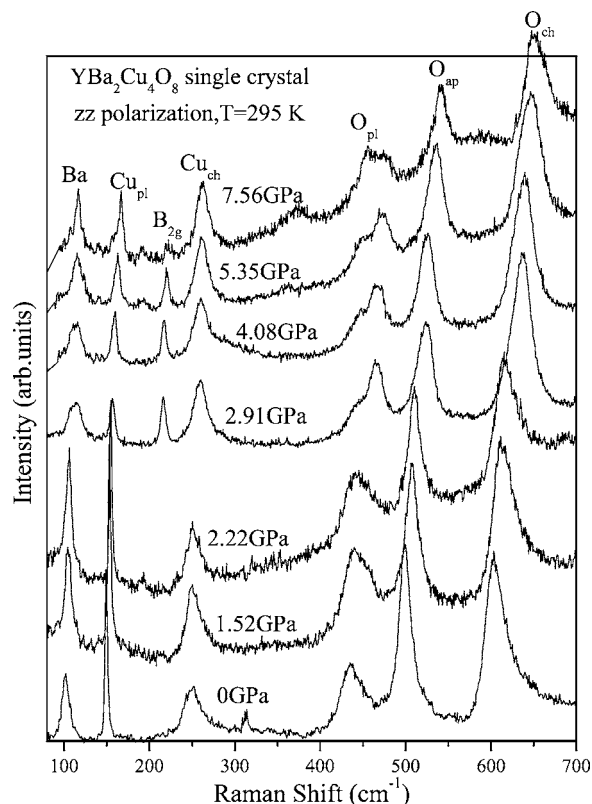


FIG. 1. Typical room temperature Raman spectra of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ compound for selected hydrostatic pressures. The almost complete absence of the B_{1g} -like mode of the O_{pl} atoms denotes the nearly pure zz scattering geometry (Ref. 12). The splitting of the in-phase O_{pl} mode is obvious at high pressures.

con crystals, one outside the DAC but inside the Oxford cryostat and another in the open air, the effect of pressure could be discriminated from that induced by the low temperature and any miscalibration of the spectrometer during the measurement. The laser beam was focused on the sample at a spot of diameter 1 – $2 \mu\text{m}$ ($\times 100$ lens) or 3 – $5 \mu\text{m}$ ($\times 40$ lens), while the power level was kept below 0.20 mW for the ambient conditions measurements or 0.40 mW for the high-pressure measurements, in order to avoid local heating effects. In the previous high pressure Raman studies^{16,17} the selection rules could not be applied and the presented Raman spectra were mainly acquired in mixed polarization geometries. In this work, tiny pieces from the single crystals were freshly cut before the measurements in the appropriate direction to allow the study of pure $y(zz)\bar{y}$ [or $x(zz)\bar{x}$] and $y(xx)\bar{y}$ [or $x(yy)\bar{x}$] (the x and y axis could not be discriminated) scattering geometries. Typical accumulation times were 1 – 2 h (room temperature) or 2 – 6 h (high pressure) depending on the scattering polarization, and all modes of A_g symmetry and the $\text{Cu}_{ch} B_{3g}$ and $\text{O}_{ch} B_{2g}$ modes have been examined.

RESULTS

Figure 1 presents characteristic Raman spectra of the Y124 compound in the zz scattering polarization for

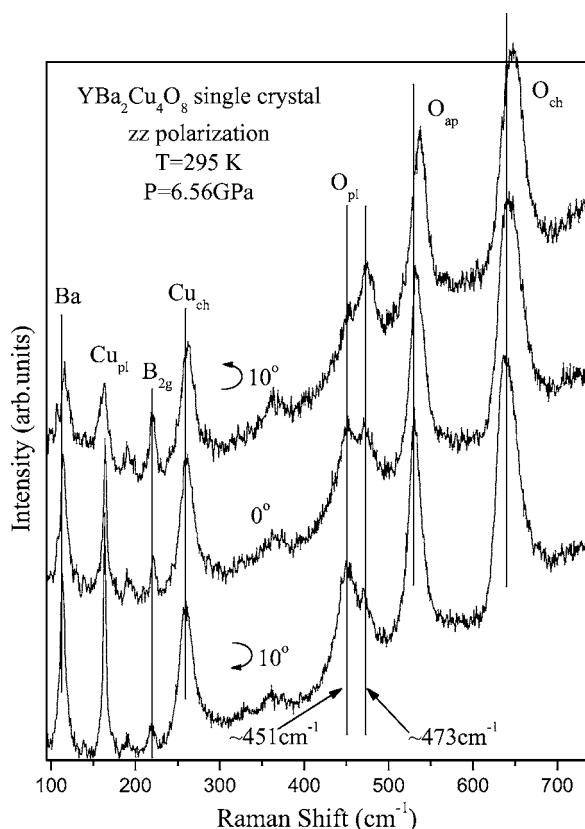


FIG. 2. Room temperature Raman spectra from the same crystallite shown in Fig. 1, at ~ 6.56 GPa. When the splitting of the in-phase mode takes place, the relative intensity of the two in-phase components is modified by slightly rotating the sample orientation for the approximate zz polarization.

selected hydrostatic pressures at room temperature. In all pressures studied the spectra are of similar quality with those obtained outside the DAC. The six strong modes of A_g symmetry are clearly observed even at the highest pressure studied. These modes are assigned to the vibrations along the z axis of the Ba atoms (100.7 ± 1.0 cm^{-1}), the Cu_{pl} atoms (148.4 ± 1.0 cm^{-1}), the Cu_{ch} atoms (245.5 ± 1.6 cm^{-1}), the in-phase vibrations of the O_{pl} atoms of the CuO_2 planes (434.9 ± 1.4 cm^{-1}), the apex O_{ap} atoms (498.3 ± 1.0 cm^{-1}), and the chain O_{ch} atoms (599.1 ± 1.1 cm^{-1}). At high pressures (above ~ 2.5 GPa) the in-phase mode appears as a double peak with energy difference ~ 20 cm^{-1} . The relative intensity of the two in-phase components is strongly modified by slightly rotating by a few degrees the sample orientation, as shown in Fig. 2 for the approximate zz polarization and $P = 6.56$ GPa. At ambient pressures this effect is absent and appears only at high hydrostatic pressures (roughly above 2.5 GPa). We have observed that when the intensity of the high-energy component of the in-phase mode increases, then (a) the intensity of one of the B_{2g} or B_{3g} modes (attributed to the vibrations of the O_{ch} atoms along the x axis or of the Cu_{ch} atoms along the y axis) simultaneously increases, (b) the intensity of the other A_g symmetry modes decreases, while (c) the Cu_{pl} and the Ba modes become broader (Fig. 2).

For further examination of this effect high-pressure measurements have been carried out at low temperatures. Figure

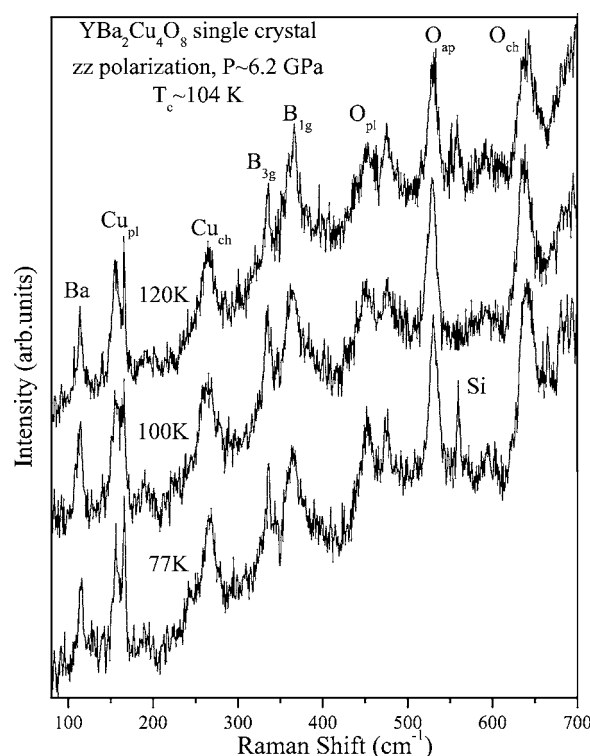


FIG. 3. Typical low temperature Raman spectra from a crystallite of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ sample at ~ 6.2 GPa, where the splitting of the two A_g phonons of the CuO_2 plane is observed. No significant changes in the Raman spectra occur below and above T_c , as expected.

3 presents Raman spectra at ~ 6.2 GPa, from the same single crystal spot as in Fig. 1. The expected superconducting critical temperature at this pressure is ~ 104 K (according to the data of Refs. 6–11). As seen in Fig. 3, the energy splitting of the in-phase phonon is not modified at low temperatures while the relative intensity of the two components changes by slightly rotating the polarization, just like at room temperature (see Fig. 2). The spectra acquired above and below T_c are similar, denoting that no structural changes are taking place in crossing from the normal to the superconducting phase.

Any connection of the in-phase phonon splitting with a loss of hydrostaticity (appearance of uniaxial or biaxial components or an inhomogeneous distribution of strains) can be excluded for various reasons. The in-phase phonon has A_g symmetry and is not a degenerate mode to split under a uniaxial or biaxial strain. On the other hand, an inhomogeneous distribution of strains should induce a splitting in proportion with the applied pressure, which apparently is not the case. At low temperatures a larger deviation from hydrostatic environment should be expected, but temperature does not affect the splitting of the in-phase mode, which remains constant at all temperatures and pressures (Figs. 1 and 3). The splitting has not been observed in previous Raman studies probably because of the mixed polarization spectra that have been obtained at high pressures.^{16,17} Nevertheless, anomalous pressure dependence for the energy of the in-phase phonon and a substantial increase in the width had been

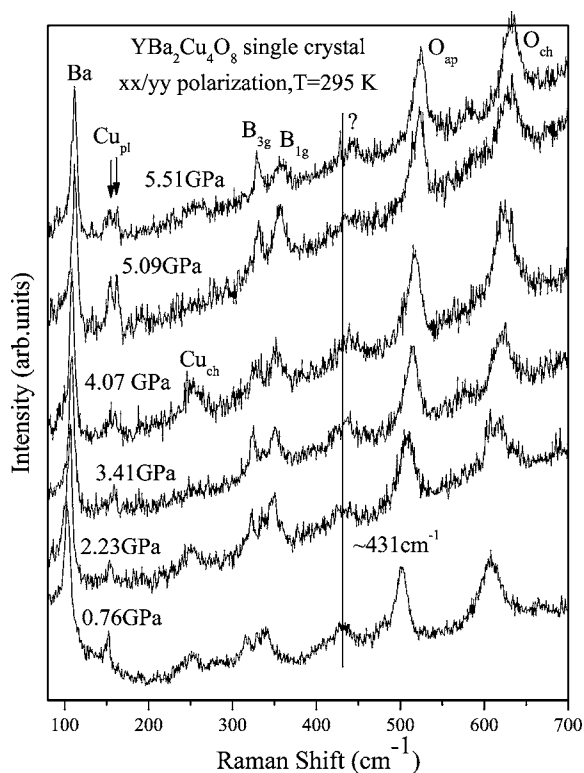


FIG. 4. Typical room temperature Raman spectra of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ compound for selected hydrostatic pressures. The almost complete absence of the in-phase A_g -symmetry mode of the O_{pl} atoms and the reduced intensity of the Cu_{pl} atoms A_g mode denote the nearly pure xx/yy scattering configuration (Ref. 12). However, the splitting of the latter can be clearly seen in the low energy part of the spectra, as well as the appearance of an unknown mode at $\sim 431 \text{ cm}^{-1}$, which does not seem to be affected by the application of hydrostatic pressure.

observed,¹⁶ which can be attributed to the averaging of all polarizations for the split mode. It is plausible to assume that the splitting can only be observed on properly oriented samples.

In the spectra from the other polarization (xx/yy) the intensity of all A_g phonons decreases (Fig. 4) as expected.^{12,30,31} In this polarization the B_{1g} -like phonon attributed to the out-of-phase vibrations of the O_{pl} atoms is well defined with energy $340.4 \pm 0.4 \text{ cm}^{-1}$ (at ambient pressure). Another (weak) mode is observed at $\sim 430.9 \pm 1.6 \text{ cm}^{-1}$, which has been initially attributed to the in-phase vibrations of the O_{pl} atoms.¹⁷ This assignment must be incorrect, since, as can be seen from the zz spectra, the in-phase mode appears at higher by $\sim 4 \text{ cm}^{-1}$ energies and also, as shown below, the energy of the $\sim 430.9 \text{ cm}^{-1}$ mode does not vary with increasing pressure. Above $\sim 2.5 \text{ GPa}$ a splitting is observed in the A_g Cu_{pl} mode, which appears to be related with the splitting of the in-phase mode in the zz polarization spectra since the relative intensity of the two Cu_{pl} components changes with a slight rotation of the polarization, just like the two in-phase components. The splitting of the Cu_{pl} phonon can be also observed in the low-temperature spectra of Fig. 3 and this must be the reason for the broadening of Cu_{pl} mode that has been observed in the room temperature zz spectra of Fig. 1.

Finally, in both zz and xx/yy polarization spectra two more weak phonons have been observed at ambient pressure with energies 209.3 ± 1.0 and $313.8 \pm 1.0 \text{ cm}^{-1}$. As mentioned before, the symmetry of these phonons is B_{2g} and B_{3g} and they have been attributed to the motion of the O_{ch} and Cu_{ch} atoms along the x and y axis, respectively.¹²

The energy variation of the A_g phonons as a function of pressure at RT is presented in Fig. 5(a) for the zz spectra for all crystallites studied (from the same sample). The modes have been fitted with one Lorentzian or an asymmetric Fano shaped band, except in the case of the in-phase mode, which was fitted by two Lorentzians when the splitting in two modes was obvious (i.e., above $\sim 2.5 \text{ GPa}$). At low ($< 2.5 \text{ GPa}$) and high ($> 6 \text{ GPa}$) pressures the mode energies increase with pressure as expected. For intermediate pressures (~ 2.5 – 6 GPa) two different values exist for the same pressure depending on the crystal orientation of the microcrystallite studied [Fig. 5(a)] as coexisting phases in a first-order phase transition. Systematically at some pressure $\geq 2.5 \text{ GPa}$ the in-phase mode was observed to split and certain other phonons would show an abrupt upward shift or increase in the width. In the cases and crystal orientations where no splitting of the in-phase mode was observed, all other phonons did not show any abnormal shift in energy [Fig. 5(a)]. In previous works the only abnormal behavior observed was the nonlinearity of the Cu_{pl} and the in-phase O_{pl} modes.^{16,17} Figure 5(b) presents the variation of the linewidth of the A_g phonons as a function of pressure at room temperature. The linewidth of all phonons shows similar abnormalities with the energies in the same pressure range, which must reflect the coexistence of two phases with different mode energies. Figure 6(a) presents the pressure dependence of the energy of the B_{1g} -like O_{pl} mode, where only the fitting results of the xx/yy polarization spectra have been taken into account. Contrary to the zz polarization results, no significant differences have been found between the different crystallites. In particular, the energy of this mode increases almost linearly with increasing pressure, as expected, without showing any anomaly. The width of this mode does not increase with pressure, although an accurate determination of its behavior is very difficult because of the existence of the B_{3g} Cu_{ch} mode at the low-energy side of the band (see Fig. 4).

In Fig. 6(b) the energy of the weak mode at $\sim 431 \text{ cm}^{-1}$ observed in the xx/yy spectra is shown, which remains constant with pressure. Therefore, it is an independent mode from the in-phase one, which increases with pressure [Fig. 5(a)]. The mode does not appear in the crossed polarizations and must have A_g symmetry. Its energy indicates that it should involve oxygen atoms, though it is not possible to determine which ones.

Normal behavior with pressure has also been observed for the energy of the B_{3g} mode of the Cu_{ch} atoms, as seen in Fig. 6(c). On the other hand, the energy of the B_{2g} mode of the O_{ch} atoms as a function of pressure seems to deviate from linearity and the increment rate decreases for pressures above $\sim 2.5 \text{ GPa}$ [Fig. 6(d)]. It should be noticed that the graphs of Figs. 6(b)–6(d) include the fitting results of both zz and xx/yy spectra, since these modes appear in the parallel polarization Raman spectra of Figs. 1 and 4 as escapes from the

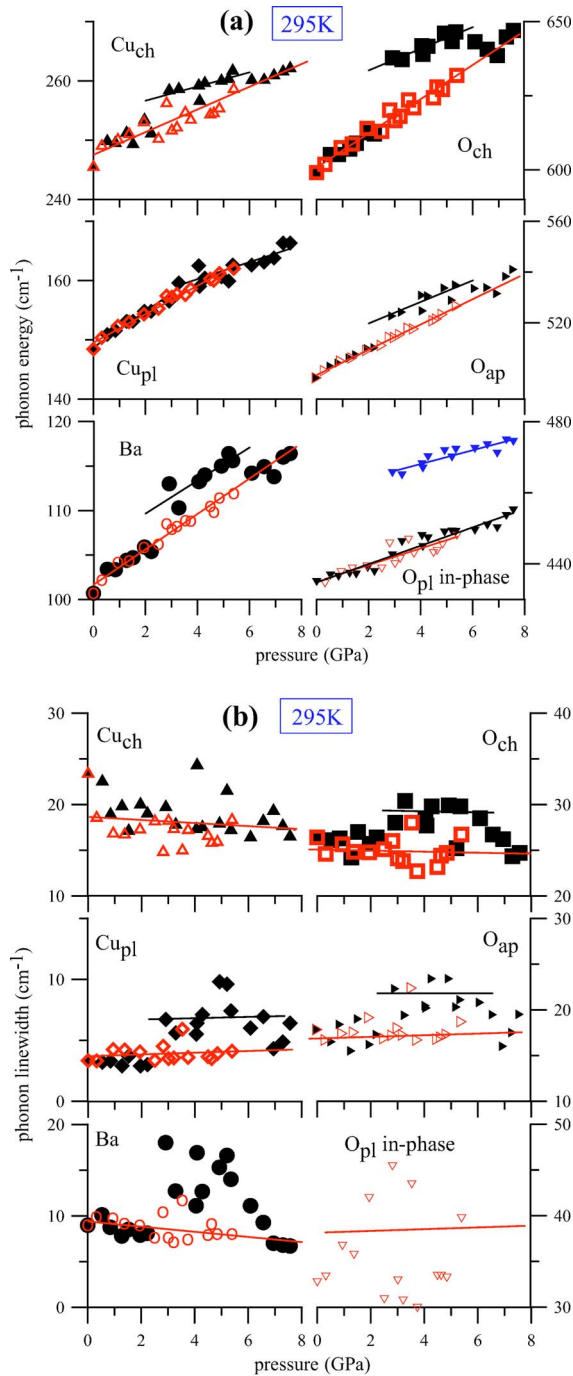


FIG. 5. (Color online) Hydrostatic pressure dependence of the (a) energies and (b) widths for the A_g Raman modes appearing in the zz polarization spectra of the $YBa_2Cu_4O_8$ compound, at RT. The open symbols represent the measurements and the crystal orientations where, due to the crystal orientation inside the DAC, no splitting of the in-phase mode has been observed, while the filled symbols represent the measurements where the splitting of this phonon was obvious. For the width of the in-phase mode, only the data where no splitting was apparent were plotted.

crossed polarization configurations. The pressure derivatives of the energies for the observed modes in this work are listed in Table I. The results are in good agreement with previous publications.^{16,17} It should be noticed that, for the A_g modes,

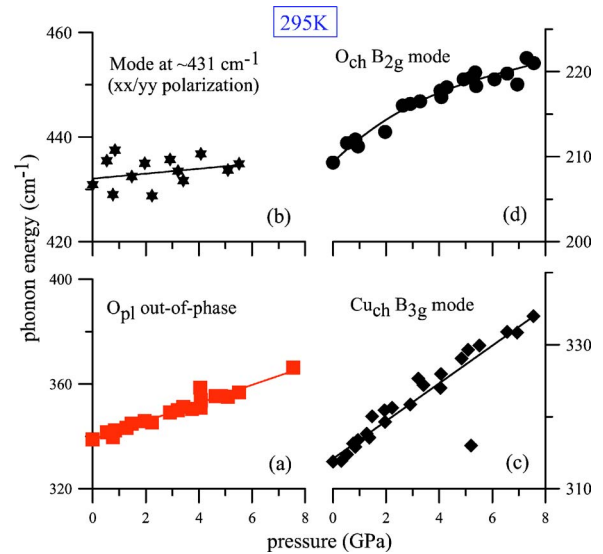


FIG. 6. (Color online) Hydrostatic pressure dependence of the energy for the B_{1g} -like Raman mode of the O_{pl} atoms appearing in the xx polarization spectra (a), the mode at ~ 431 cm^{-1} (b), the B_{3g} mode of the Cu_{ch} atoms, appearing in the parallel polarization spectra (c), and the B_{2g} mode of the O_{ch} atoms (d).

Table I contains only the data where no splitting of the in-phase mode has been observed due to the crystal orientation [open symbols in Fig. 5(a)]. The whole pressure range data have also been taken into account for the energy pressure derivatives of the B_{1g} , B_{2g} , and B_{3g} modes, as well as for the abnormal mode at ~ 431 cm^{-1} (see Fig. 6).

DISCUSSION

The modes presented in Fig. 5 show an abnormal behavior in the pressure range ~ 2.5 – 6 GPa, while at even higher pressures the phonon mode energies appear to follow again the trend at low pressures. It has been observed (Fig. 2) that the orientation of the sample is very critical for enhancing the second component of the in-phase phonon. In order to delineate the origin of this effect, the doping and pressure dependencies of the structural parameters and bond lengths of Y124 and Y123 are compared.

In Y123 the length of the Cu_{pl} - O_{ap} bond is very sensitive to the charge distribution between the planes and the chains.^{32,33} Ambient pressure studies of $YBa_2Cu_3O_x$ over a wide range of oxygen concentrations x have shown that the O_{ap} mode of A_g symmetry depends mainly on the Cu_{pl} - O_{ap} bond.^{20,34} With increasing x the length of the Cu_{pl} - O_{ap} bond decreases almost linearly up to the optimal doping and, then, in the overdoped region remains practically constant.³⁴ In a similar way, the apex mode energy increases almost linearly with increasing x up to the optimally doped region and, then, in the overdoped region remains constant.^{18–20} In the homologous system Y124 the energy of the apex phonon increases linearly with pressure, with the exception of a sudden change in the range ~ 2.5 – 5 GPa, which was always accompanied by the appearance of the second peak in the in-phase phonon [Fig. 5(a)]. The Cu_{pl} - O_{ap} bond length has shown a

TABLE I. The measured pressure derivatives for the modes of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ compound. For the A_g modes only the data where no splitting of the in-phase mode has been observed are included [see open symbols in Fig. 5(a)]. The results of Refs. 16 and 17 are also given for comparison.

Symmetry	Assignment	Pressure derivatives $d\omega/dp$ ($\text{cm}^{-1}/\text{GPa}$)		
		From Ref. 16	From Ref. 17	This work
A_g	Ba	...	1.57 ± 0.08	2.0 ± 1.0
A_g	Cu_{pl}	2.2 ± 0.2	3.12 ± 0.29	2.4 ± 1.0
B_{2g}	O_{ch}	1.4 ± 0.9
A_g	Cu_{ch}	2.5 ± 0.2	2.22 ± 0.18	1.7 ± 0.7
B_{3g}	Cu_{ch}	3.3 ± 0.2	2.96 ± 0.35	2.6 ± 0.9
A_g	O_{pl} out-of-phase	3.5 ± 0.3	3.24 ± 0.14	3.5 ± 0.9
?	Abnormal mode	0.5 ± 0.1
A_g	O_{pl} in-phase	Nonlinear	...	2.3 ± 0.7
A_g	O_{ap}	4.5 ± 0.2	3.83 ± 0.16	5.0 ± 1.0
A_g	O_{ch}	5.0 ± 0.2	4.87 ± 0.37	5.8 ± 1.0

similar dependence on pressure³⁵ with the Raman results [Fig. 5(a)].

According to lattice dynamical calculations, the in-phase O_{pl} phonon energy of the Y123 compound depends mainly on the plane $\text{Cu}_{pl}-\text{O}_{pl}$ bonds.³⁰ This prediction is supported from ambient pressure studies of $\text{YBa}_2\text{Cu}_3\text{O}_x$, since with increasing x the length of the $\text{Cu}_{pl}-\text{O}_{pl}$ bonds increases almost linearly up to the optimally doped region³⁴ and the in-phase mode energy decreases.^{18–20} Indirectly the energy of this mode is affected by the buckling of the CuO_2 planes, since the softening of this mode and the phase separation in the overdoped region^{18–20} is correlated with the increase of the CuO_2 buckling and the relaxation of the $\text{Cu}_{pl}-\text{O}_{pl}$ bonds.²¹ In the case of the Y124 compound, the variation with pressure of the $\text{Cu}_{pl}-\text{O}_{pl}$ bonds is relatively small and it is very difficult to discriminate changes above ~ 3 GPa.³⁵ According to Ref. 35, the changes in the $\text{Cu}_{pl}-\text{O}_{pl}$ lengths (as well as in the intrachain $\text{Cu}_{ch}-\text{O}_{ch}$ bonds) are determined almost entirely by the cell dimensions. They have found that, while the a axis decreases almost linearly with pressure, the rate of change of the b axis clearly reduces above ~ 3 GPa.³⁵ The splitting of the in-phase mode and the apparent separation into two phases if not correlated with changes in the $\text{Cu}_{pl}-\text{O}_{pl}$ bond length is most probably related with modifications in the buckling of the CuO_2 planes as was the case in optimally to overdoped structural and in-phase O_{pl} phonon changes in Y123.²¹

The energy of the A_g symmetry Cu_{pl} mode depends on the $\text{Cu}_{pl}-\text{O}_{ap}$ bond and the buckling of the $\text{Cu}_{pl}-\text{O}_{pl}-\text{Cu}_{pl}$ bonds.³⁰ Therefore, this mode is expected to show similarities with the pressure dependence of the apex, but also with those of the in-phase mode (splitting in two peaks), which is sensitive to the CuO_2 buckling, as it is really observed in Fig. 3.

Concerning the energy of the A_g -symmetry mode of O_{ch} , it is expected to depend strongly on the bonds with the neighboring atoms Cu_{ch} , O_{ap} , and the other chain oxygen O'_{ch} .¹² Nelmes *et al.* have found that the $\text{Cu}_{ch}-\text{O}_{ch}$ and $\text{Cu}_{ch}-\text{O}'_{ch}$ (and consequently the $\text{O}_{ch}-\text{O}'_{ch}$) bonds decrease

with increasing pressure. Although these bonds vary linearly with pressure, the changes in the intra chain $\text{Cu}_{ch}-\text{O}_{ch}$ bond lengths are determined almost entirely by the cell dimensions, where there is a clear deviation from linearity for the b axis above ~ 3 GPa. This can explain the abnormal behavior of the O_{ch} phonon energy above ~ 2.5 GPa (Fig. 5). In a similar way, the A_g -symmetry phonon due to the Cu_{ch} chain atoms must be related with the coupling with the neighboring atoms O_{ch} , O_{ap} , and the other copper Cu_{ch} atom of the chains.¹² Therefore, the modifications observed above ~ 2.5 GPa for this mode can be also anticipated from the structural changes.

The A_g mode attributed to vibrations of the Ba atoms does not depend on the bonds of the Ba atom with the copper and oxygen atoms of the CuO_2 layers and chains, which are quite far away but, instead, on the Ba- O_{ap} bond, which is very short. This bond also shows a clear deviation from linearity for pressures above ~ 3 GPa,³⁵ which explains the behavior of the Ba phonon energy (Fig. 5).

In $\text{YBa}_2\text{Cu}_3\text{O}_x$ the mode energy attributed to the out-of-phase vibrations of the O_{pl} atoms of B_{1g} -like symmetry remains practically constant with the variation of the oxygen concentration and the induced changes in the $\text{Cu}_{pl}-\text{O}_{pl}$ bonds.^{18–20} Instead, this mode is significantly affected by the size of the rare earth element substituting for Y.³⁶ At ambient conditions the Y- O_{pl} bond length does not vary with x (Ref. 34) and the energy of the B_{1g} -like phonon is also independent of the Y- O_{pl} bond lengths.³⁷ In the case of Y124, the mean distance of the plane O_{pl} oxygen atoms from the Y site initially increases linearly with pressure, but then for pressures above ~ 3 GPa decreases.³⁵ This deviation from linearity above ~ 3 GPa is not related with the energy of the B_{1g} -like phonon [Fig. 6(a)] since this energy is independent of the Y- O_{pl} bond lengths.

As explained above the B_{2g} and B_{3g} symmetry modes were observed as escapes in the parallel polarization Raman spectra. The energy of the B_{3g} -symmetry vibrations of Cu_{ch} along the y axis appears to increase almost linearly with pressure without showing any anomaly like that observed for

the A_g -symmetry Cu_{ch} mode [Fig. 5(a)]. Instead, the B_{2g} symmetry vibrations of O_{ch} along the x axis, which are just a chain-bending mode, like in the Y123 case,¹² slightly deviate from linearity for pressures above ~ 3 GPa. Nevertheless, it should be noticed that reliable results concerning the behavior of these two phonons with pressure can only be obtained by crossed polarization spectra that have not been studied due to the very low scattering efficiency from inside the diamond anvils.

The main question to be addressed is the origin of the in-phase mode splitting for pressures ~ 2.5 GPa, which is accompanied by spectroscopic changes of other zz polarization phonons and small structural modifications. As mentioned in the Introduction, the critical temperature of Y124 shows an almost linear increase with pressure up to ~ 3 GPa; afterwards the rate of increase is gradually reduced and above ~ 6 GPa there is another reduction in dT_c/dP .⁶⁻¹¹ From the previous discussion one could induce a correlation between the pressure dependence of T_c and spectral modifications of the phonons, obviously connected with the appearance of local lattice distortions. It should be noticed that, although the T_c of the samples used in this work has not been measured as a function of pressure, their characterization at ambient pressure by structural, magnetization,²⁹ and Raman (this work) measurements have shown high-quality Y124 single crystals. Therefore, their $T_c(P)$ dependence is expected to be similar to the common one reported in Refs. 6-11, where different types of samples and pressure transmitting media have been used.

The most pronounced changes were observed for the in-phase vibrations of the O_{pl} atoms, which split in two (Fig. 1). Other phonons show a sudden increase in energy and width at about the same characteristic pressure ~ 2.5 GPa (Fig. 5). A sudden decrease in energy for the in-phase mode energy of the Y123 compound has been detected at the optimal to overdoped oxygen concentration¹⁸⁻²⁰ and associated with changes in the buckling of the CuO_2 planes at ambient pressure.²¹ A coexistence of phases differing in the amount of buckling was induced from the spectral modifications of the in-phase mode.²¹ Interestingly, the situation in Y124 seems quite similar with the pronounced changes observed in the in-phase mode again. The variation of the relative intensity of the two components of the in-phase with the slight rotation of the scattered light polarization indicates that there are two structures, which must differ by the orientation of the c axis or more accurately the tilting of the CuO_6 octahedra. This tilting is expected to affect the in-phase and the Cu_{pl} A_g -symmetry phonons.^{21,30} The structural modifications can induce a separation into different coexisting phases with either normal or tilted octahedra. Alternatively a superlattice phase of tilted and normal octahedra may appear in the same crystallite. The fact that the splitting of the in-phase mode does not change with pressure implies that in either case a new lattice distorted phase has been created, which is not modified by pressure. It seems that in Y123 the excess oxygen doping drives the small lattice distortions and a phase separation, while in Y124 this happens from the hydrostatic pressure.

A well-investigated compound where lattice distortions of the octahedra are present is $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO). Even in

optimally doped LSCO local lattice distortions were reported and associated with lattice modulations.²⁵ In particular, the $\mathbf{E}\parallel\mathbf{ab}$ EXAFS data have shown the existence of two different Cu-O (planar) distances, an anomalous long and a short one. The appearance of the anomalous in-plane long distance was assigned to the tilting of the CuO_4 square plane where two oxygen atoms per CuO_4 square plane get displaced along the c axis. The instability of the Cu site was also indicated by the $\mathbf{E}\parallel\mathbf{c}$ EXAFS data, which have shown the presence of two Cu-O (apical) distances, an anomalous short and a long one. The above results suggested that, apart from the normal (undistorted) octahedra CuO_6 , there is also a percentage of distorted octahedra CuO_6 , which are associated with the anomalous short Cu-O (apical) and long Cu-O (planar) bond lengths. It is worth mentioning that analogous distortions have been observed in oxygen doped $\text{La}_2\text{CuO}_{4+\delta}$ (Ref. 38) and in Bi2212 compounds.³⁹

In the Y124 compound the Raman study has shown characteristic changes of the phonons correlated with modifications in the lattice parameters around ~ 2.5 GPa.³⁵ We suggest that the high-energy peak of the in-phase mode (and probably the low-energy component of the Cu_{pl} phonon) corresponds to sites with distorted octahedra, while the low-energy peak of the in-phase mode (and the high-energy component of the Cu_{pl} phonon) corresponds to the undistorted ones. XRD measurements may have not detected these slight lattice distortions since they probe average atomic distances. Furthermore, the existence of two phases with different T_c can explain the correlation between pressure-induced changes in the phonon energies and dT_c/dP .

In the cuprate superconductors there is a correlation between T_c and the density of the charge (hole) carriers in the two CuO_2 planes.²⁶⁻²⁸ The displacement of the O_{ap} ion towards the CuO_2 layers with pressure has been taken as a signature of a charge transfer from the chains to the CuO_2 planes.³⁵ This assumption is supported by neutron powder diffraction studies,^{40,41} Hall effect measurements,^{42,43} and NMR and NQR studies.⁴⁴ It was proposed that the large dT_c/dP derivative originates from the large increase of the charge concentration in the CuO_2 planes through the charge transfer from the pressure. The charge redistribution to the CuO_2 planes is expected to affect the intensity of the Raman phonons because of the increased screening with charge transfer and the modifications in the electronic states.

Figure 7 presents the variation with pressure at room temperature of the intensities of several phonons, which bring some information on the charge distribution at the relative sites (O_{pl} , Cu_{pl} , O_{ap} , O_{ch} , and Cu_{ch}). It can be seen that the relative intensity of the in-phase phonon of the O_{pl} increases with pressure up to 2.5 GPa and then suddenly decreases [Fig. 7(a)]. Above this pressure the relative intensity does not change at least for pressures up to ~ 6 GPa. The relative intensity of the Cu_{pl} mode shows a modification above ~ 5 GPa [Figs. 7(d) and 7(e)]. In certain cases the data are separated in two groups, an effect which is more pronounced for the relative intensity of the Cu_{pl} mode [Figs. 7(d)-7(f)], but it can be also seen for the O_{ch} , Cu_{ch} modes [Fig. 7(b)]. This effect occurs above ~ 2.5 GPa and therefore it must be connected with the phase separation. It should be noted that, for these results, the intensity of the in-phase mode has been

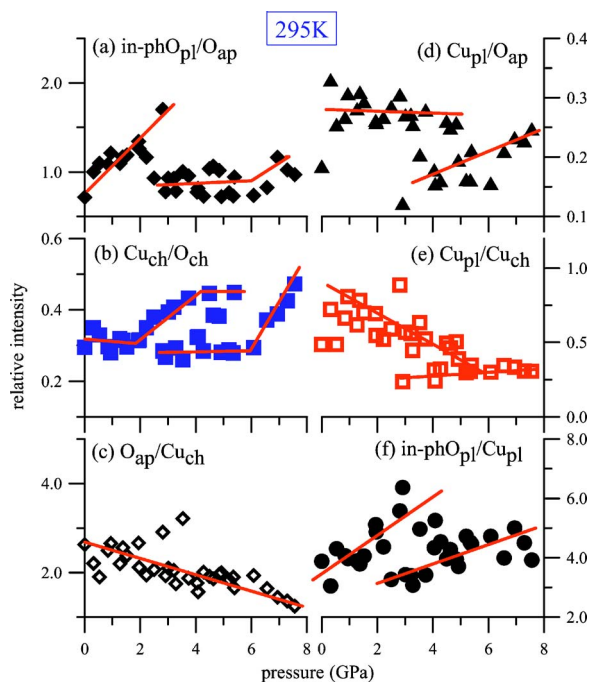


FIG. 7. (Color online) The variation of the intensities of the in-phase vibrations of the O_{pl} and Cu_{pl} A_g modes over the intensities of the O_{ap} , O_{ch} , and Cu_{ch} phonons as a function of hydrostatic pressure at RT (a)–(e). (f) The relative intensity of the O_{pl} to Cu_{pl} modes. Total intensity of the bands has been taken into account.

calculated as a sum of the intensities of the two in-phase components.

The above results are connected with the proposed charge transfer from the Cu-O chains to the CuO_2 planes followed by a charge redistribution between the two plane ions. In particular, from the intensity variations shown in Fig. 7, one can induce that there is a charge transfer to the Cu_{pl} and O_{ap} sites (reduction of their relative intensities), while carriers seem to be removed from the O_{pl} and Cu_{ch} ions [Figs. 7(c)–7(f)]. Besides, there is a clear separation in groups, which involves several phonons and it is probably related with the redistribution of the carriers and/or a chain reordering. Also, it should be noticed that a previous study of the

application of an internal pressure by partial Sr substitution for Ba has shown similar results (i.e., redistribution of the charge carriers from O_{pl} to Cu_{pl} and from Cu_{ch} to O_{pl}), indicating a similarity of the effect of external hydrostatic pressure to the internal one.²⁹ However, although T_c increases in both cases, the amount is significant only in the first case.^{6–11,29} This probably originates from the differences in the variation of the structural parameters under pressure and Sr doping.^{29,35} Therefore, a further high-pressure study of the Y124 compounds with partial Sr substitution for Ba is necessary in order to delineate this difference.

CONCLUSIONS

Systematic deviations of the characteristics of the A_g -symmetry phonons from their previously observed almost linear dependence on hydrostatic pressure have been discovered for the $YBa_2Cu_4O_8$ compound. In particular, modifications in the spectra are observed at pressures ~ 2.5 and ~ 6 GPa. In the first case, the in-phase vibrations of the O_{pl} atoms and all other A_g modes show a sudden change in energy and increase of width. For the in-phase mode a second peak clearly appears with intensity varying with the slight change of the polarization of the incoming and scattered light, indicating that it originates from a phase with slightly tilted CuO_6 octahedra. Similar modifications in the relative intensity of various phonons support the hypothesis that the spectral changes are related with a charge transfer from the chains to planes, its redistribution between the Cu-O plane ions, and the separation into phases. The changes in the Raman spectra correlate with the hydrostatic pressure dependence of the superconducting transition temperature, which can be anticipated from the suspected carrier transfer towards the CuO_2 planes and among the ions in the planes.

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