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PHASE SEPARATION IN CUPRATES INDUCED BY DOPING, HYDROSTATIC PRESSURE OR ATOMIC SUBSTITUTION

E. Liarokapis
Department of Physics, National Technical University, 15780 Athens, Greece

Abstract: Results of systematic Raman studies of phase separation induced on cuprates by doping, hydrostatic pressure, and atomic substitutions are presented. In $YBa_2Cu_3O_x$, oxygen doping induces a separation into microphases from the ordering of the chains, at relative amounts that vary with concentration. In the overdoped region, a similar coexistence of phases appears, which is due to the modification of the CuO_2 buckling. The excess doping of $YBa_2Cu_3O_{7-\delta}$ by Ca creates domains of pure Y123 and others where the Ca atoms are surrounded by yttrium as first neighbours. Hydrostatic pressure induces non-linear effects in almost all A_g–symmetry phonons of $YBa_2Cu_3O_x$, $YBa_2Cu_4O_8$, and the $Bi_2Sr_2CaCu_2O_8$ superconductors. A coexistence of phases seems to appear at a critical pressure where changes in the superconducting transition temperature have been observed.

1. INTRODUCTION

Structural and electronic inhomogeneities are characteristic intrinsic properties of the cuprate superconductors related with the unconventional character of these compounds. The $YBa_2Cu_3O_x$ (Y123x) compound is a prototype of cuprates with two CuO_2, planes been extensively investigated over the $0 \leq x \leq 7.0$ range of oxygen concentration [1]. The properties and the crystal structure of this material are closely related to x, with superconductivity appearing for $x \geq 6.4$. Ordering of the chains results in the formation of various phases, such as the ortho-II phase having a transition temperature of 60K, and the optimally doped phase with T_c=92K for x=6.92. On the other hand, oxygen concentrations above nominal optimal amounts (x=7) are not easily attained, and overdoping of Y1237 is usually achieved by Ca substitution for Y. This substitution was originally considered to follow the generally accepted scheme of the increase of carriers [2]. Raman spectroscopy is suitable for investigating the local structural order, due to its discrimination limit of a few unit cells. Results on Raman scattering of Ca doped Y1237 will be examined in order to investigate the role of the additional carriers for the reduction of the T_c.

In Y123x a systematic Raman study has discovered an anomalous softening of the (A_g symmetry) in-phase vibrations along the c-axis of the oxygen atoms O_{pl} of the CuO_2 planes at the optimal to overdoped oxygen concentrations [3]. This decrease in energy with the addition of carriers beyond x~6.92 doping is accompanied with a reduction in T_c [4]. Actually a gap has been observed for x>6.95 in the distribution of the energy of this phonon, pointing out to the coexistence of phases in the overdoped region (x>6.975) and to a 1^{st} order phase transition [3]. This behaviour was found to be independent of the temperature [5]. Magnetic measurements have shown that there are two transition temperatures above optimal doping pointing again to a coexistence of phases [6]. Finally, EXAFS measurements have shown that there is a local structural modification at the optimal to overdoped region, which originates from a sudden change of the buckling of the CuO_2 planes [7].

A more clear way than chemical doping to investigate the effects of the local structural modifications and the phase separation to the transition temperature is the application of a hydrostatic pressure. The effect of the hydrostatic pressure in most of the cuprates has been studied extensively [8,9]. Usually, the dependence of the superconducting transition temperature on hydrostatic pressure (dT_c/dP) varies in a large range of values, indicating in some cases the tendency of the material to reach higher T_c values. Single crystals of $YBa_2Cu_3O_x$ (with x=6.5 and 7), $YBa_2Cu_4O_8$, and $Bi_2Sr_2CaCu_2O_8$ have been studied under hydrostatic pressure by Raman spectroscopy [10-13]. In all cases the results show a clear correlation between the spectral modifications and the transition temperature. Whenever structural data at high pressures are available, they also indicate local structural modifications at the characteristic pressures where T_c is modified.

2. EXPERIMENTAL

Raman scattering results were obtained from several polycrystalline compounds of $YBa_2Cu_3O_x$ (Y123:x, with 6<x<7) and $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (Y-Ca123) and from single crystals of $Bi_2Sr_2CaCu_2O_8$ (Bi2212) and $YBa_2Cu_4O_8$ (Y124). All measurements have been carried out at room and low temperatures and at high hydrostatic pressures using a T64000 Jobin-Yvon triple spectrometer. A liquid nitrogen cooled charge coupled device (CCD) was the detector and the spectrometer was equipped with a microscope of magnification ×100 (×40 for the hydrostatic pressure measurements). For the high-pressure measurements (up to 7.5 GPa) a Merrill-Bassett type diamond anvil cell (DAC) was used, which has allowed the Raman studies to be carried out in a back scattering geometry. The pressure-transmitting medium was a mixture of methanol-ethanol. For monitoring the pressure a small "standard" silicon crystal was used inside the gasket. The beam from several lines of an Ar^+ laser was focused on the sample at a spot of diameter 1-2 μm (100) or 3-5 μm (40), while the power level was kept below 0.20 mW (or 0.40 mW for the high pressure measurements). Typical accumulation times were 1-2 hours (room temperature) or 2-6 hours (high pressure) depending on the scattering polarization. Always freshly cut samples were used for the study of the various scattering geometries.

3. RESULTS AND DISCUSSION

3.1 Doping induced phase separation

The formation of phases in $YBa_2Cu_3O_x$ is mostly related with the chain ordering [1]. In the Raman spectra, characteristic changes are observed in the phonons due to the apical oxygen O_{ap} and the in-phase vibrations of the plane oxygen atoms O_p related with the formation of the ortho-II, ortho-III, and the tetragonal phases [1,4,5]. With increasing amount of oxygen, the peak position of the apical oxygen atom shifts to higher energies roughly as the T_c changes with doping (Fig.1). Its width is a non-linear function of doping with minima at $x \geq 6.94$, $x \cong 6.45$-6.47, and $x \leq 6.15$ (Fig.1). Both the energy and the width of the in-phase phonon remain constant in the insulating range (Fig.2). The mode energy decreases and the width increases with oxygen doping for x>6.3. These changes can be attributed to the formation of phases [1,4,5] from the ordering of the chain oxygen atoms.

In Fig.2 one can see another spectral modification of the in-phase phonon, which for $x \geq x_{opt}$ softens by ~7 cm^{-1}.

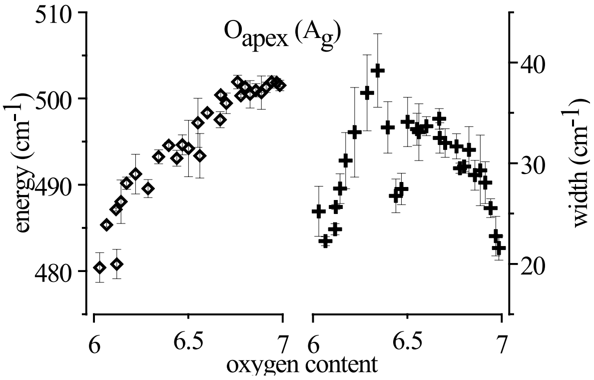

Figure III:2:1. The energy (left) and width (right) of the A_g-symmetry apical oxygen atom.

The amount of softening is independent of temperature (the same above or below T_c) [5]. Magnetic measurements have shown that there are two transition temperatures, one related with the optimal doping at 92K and another of the overdoped phase with a reduced transition temperature of 88K [6]. At the optimal doping an anomaly on the c-axis has been discovered by neutron scattering and XRD (for samples prepared with certain methodology), both related with a sudden increase of the Cu_{pl}-O_{pl} distances [1]. The use of EXAFS as a local probe at the neighbor of the Y atom has shown that in all samples there is a sudden increase of the buckling at the phase transition from the optimal to overdoping [7].

Besides, in the Raman spectra one could detect in different microcrystallites either the high energy value of the in-phase phonon, which corresponds to the optimal doping or to the lower by ~7 cm^{-1}, apparently linked to the overdoped phase with the reduced transition temperature and the increased buckling angle [1]. All these results from various methodologies point to a spatial inhomogeneity driven by doping with coexisting phases like a 1st order phase transition.

The softening of the in-phase phonon in the overdoped region can be attributed to a double well potential and a strong anharmonicity of this phonon. Systematic Raman measurements of the oxygen anharmonicity of $YBa_2Cu_3O_x$ have been carried out in the whole range of doping [14]. The results have shown that the B_{1g} phonon of the O_{pl} does not show any anharmonicity in the whole range of doping [14]. For the apex mode there is a slight deviation in the oxygen concentration region $6.4<x<7.0$, which diminishes towards x~6.4 and x~6.9 and this can be attributed to the coexistence of phases from the chain ordering [14].

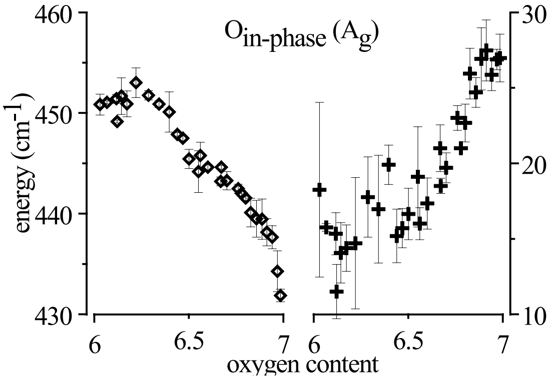

Figure III:2:2. Energy and width of in-phase phonon

In Fig.3 the energy of the in-phase mode is normalized to the B_{1g} phonon energy in order to cancel uncertainties in the amount of ^{16}O substituted by ^{18}O. It is clear that the in-phase phonon shows a decreasing amount of anharmonicity for x>6.5 and the anharmonicity disappears completely at optimal doping. On the other hand, there is anharmonicity at lower oxygen concentrations, which may originate from the coexistence of chain-ordering phases

The buckling of the CuO_2 is mostly induced by the unequal charge of the Ba and the Y atoms in connection with the carriers in the planes [15]. The vibrations of the plane oxygen atoms are expected to be sensitive to the carriers in the planes. The sudden increase of the width of the in-phase phonon, as well as the changes in its energy for x>6.3 are consistent with the introduction of carriers in the CuO_2 planes and a strong electron-phonon interaction for this mode. The coexistence of the high and low energy values for the in-phase phonon in the overdoped region and the sensitivity of the phonon to the buckling of the CuO_2 planes [1,14], indicates that there is an heterogeneous distribution of the two phases above optimum doping. It is unclear whether the carriers have the tendency to distribute inhomogeneously or other effects like strains induce the phase separation. Since lattice is strongly coupled to the carriers, the structural change will affect also the transition temperature.

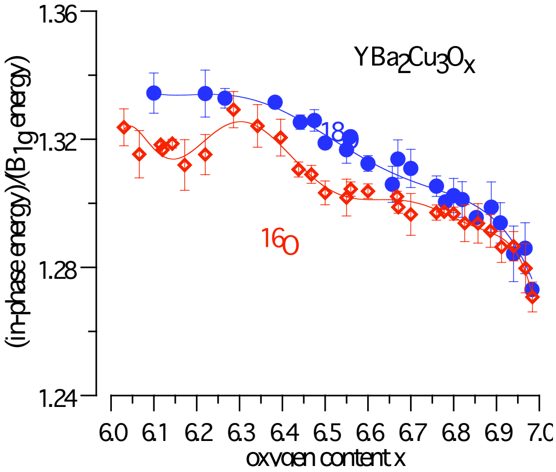

Figure III:2:3. The in-phase phonon energy normalized to the B_{1g}.

The effect of the excess carriers induced by Ca substitution for Y up to the solubility limit of 20% has been investigated by Raman spectroscopy. In the xx scattering geometry of the Y-Ca123 compounds the phonon due to the out-of-phase vibrations of O_{pl} of B_{1g} symmetry, contains in addition to the well-known mode at 340 cm^{-1} another at ~322 cm^{-1} (Fig.4).

This mode becomes very strong in high Ca concentrations while a much weaker mode appears at ~296 cm^{-1} (Fig.4). The energy of the mode at 322 cm^{-1} remains independent of the amount of Ca and it has exactly the B_{1g}-like (Fig.4:Left). The other peak at ~340 cm^{-1} corresponds in energy to a pure undistorted Y123:x=opt compound [16,17].

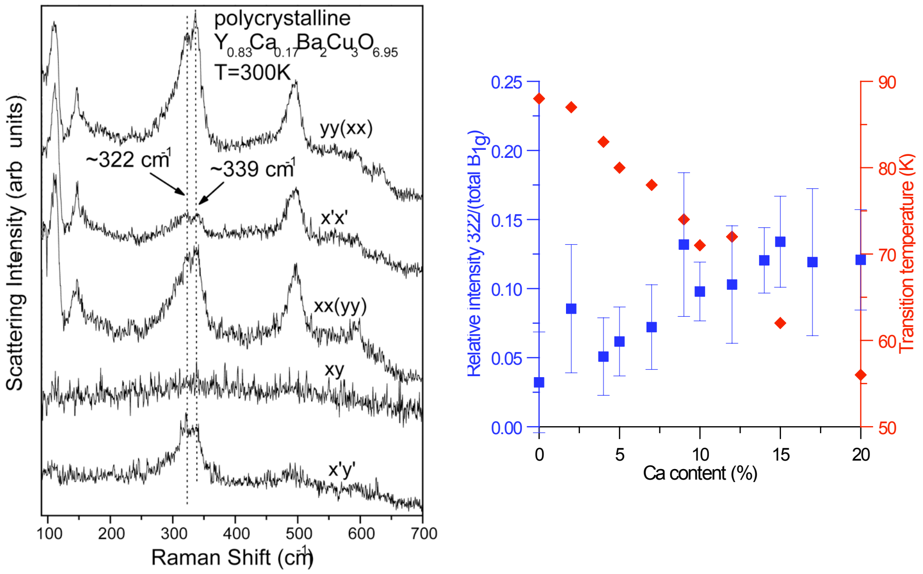

Figure III:2:4. Left: selection rules for the mode at 322 cm^{-1}, which prove its pure B_{1g} character for Ca concentration 17%. *Right*: The Ca dependence of the relative intensity of the 322 cm^{-1} mode to the total of the band, in connection with the transition temperature

In mixed compounds where Y has been substituted by a rare earth or a mixture of them ($R1_{1-y}R2_yBa_2Cu_3O_{7-\delta}$), there is a tendency for a separation into three phases; two of them correspond to the pure end compounds ($R1Ba_2Cu_3O_{7-\delta}$ and $R2Ba_2Cu_3O_{7-\delta}$) and another to an intermediate phase ($R1_{1-y}R2_yBa_2Cu_3O_{7-\delta}$), where y may not coincide with the nominal value [18-20]. The separation into phases is mainly driven by the internal strains from the difference in the ionic size of Y and the rare earths [18-20]. A similar effect should happen with the substitution of the larger Ca ion for the smaller Y. In Fig.4 (Left) the modes at ~340 cm^{-1} and ~322 cm^{-1} remain constant in energy independently of the amount of Ca [17]. The high-energy mode at ~340 cm^{-1} apparently corresponds to the pure Y123:x=opt phase and the other one at ~322 cm^{-1} should be the intermediate phase. The constant value of the intermediate mode energy would imply a constant ratio Y, Ca in this mixed phase not depending on the nominal value of Ca concentration. Based on the dependence of the B_{1g} phonon energy on the rare earth ion size [18-20], we can calculate that the energy of the ~322 cm^{-1} mode should correspond to a mixed $Y_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ phase with approximately equal amounts of Ca and Y atoms. EXAFS measurements on the same samples have suggested that there are no Ca-Ca clusters and each Ca is surrounded by four Y atoms [1,21]. If the two results (local probe and collective) are combined, one concludes that there must be a separation into phases one of pure Y123:x=opt and another mixed one of equal amounts of Y and Ca. This separation should be independent of the amount of Ca. The absence of any sign of two chemical phases in XRD or neutron scattering measurements indicates that the intermediate phase should be in small clusters of a size of a few unit cells, enough to be observed by Raman spectroscopy, but indiscriminate by XRD or neutron scattering. In Fig.4 right it is seen that the amount of the intermediate phases correlates with the reduction of the T_c. This implies that the spatial heterogeneity modifies the local carrier concentration as well and the two phases have a different T_c. Such a phase separation makes doubtful the generally accepted picture presented in Ref.[22] about the Ca overdoping of Y123.

3.2 Hydrostatic pressure effects

The above-discussed cases of doping-induced phase separation indicate that the compounds examined are close to a structural instability at the optimal doping. The attempt to overdope either by oxygen or Ca induces a separation into phases with different T_c. In general, atomic substitutions may induce disorder and its effect cannot be estimated easily. An alternative way of altering the properties of the compound is by applying hydrostatic pressure. Although Raman measurements under hydrostatic pressure for such compounds with low scattering efficiency are rather difficult, a series of superconductors have been investigated [10-13]. In all cases studied (Y123:x~6.5, Y123:x~7, Y124, and Bi2212), a clear deviation from linear dependence on pressure has been observed for several modes and this deviation, though it was measured at room temperature (RT), correlates with changes in T_c with pressure.

Figures 5-6 show characteristic spectra at RT and the pressure dependence of the energy of the A_g-symmetry phonons for Y123:x~6.5 and x~7. The pressure dependence of the energy of the B_{1g}-like mode is almost linear for the yttrium-based compounds we have studied. As seen in Fig.6, the A_g phonons due to Ba, in-phase, and apex show a deviation from linearity for pressures ~2.0 GPa. The deviation from linearity for the mode due to Cu(2) is smaller and harder to discriminate. At about the same pressures the width of the phonons changes abruptly [12]. Especially the phonon of the in-phase vibrations of the O_{pl} appears as a double peak above the same pressures (Fig.5).

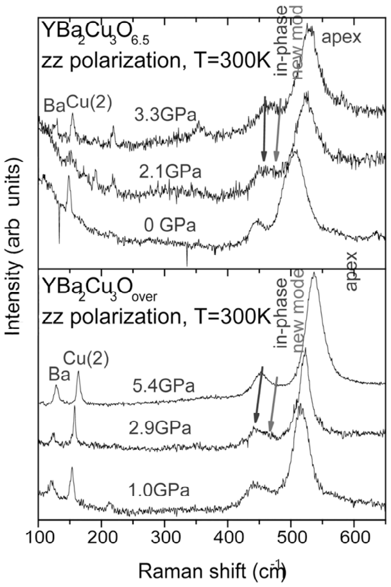

Figure III:2:5. Typical Raman spectra of the Y123:x~6.5 (top) and Y123:x~7 (bottom) compounds at various hydrostatic pressures in the xx/yy scattering geometry.

The behaviour of the phonons can be related to pressure induced structural modifications. Unfortunately, for the Y123 compounds, the variation of the bond lengths as a function of pressure has been studied only for low pressures, up to 0.56 GPa [23] and there are no data available for an independent verification of the predictions of local structural modifications. The structural hydrostatic pressure measurements have found a similar pressure dependence of the a- and c-axes for the underdoped and overdoped Y123, while, for the b axis, the underdoped exhibits a larger compression (~20%) than the overdoped sample [23]. The Raman data for low pressures

(<2GPa) indicate the same rate of phonon energy increase with pressure for the two concentrations (Fig.6) in agreement with the XRD data.

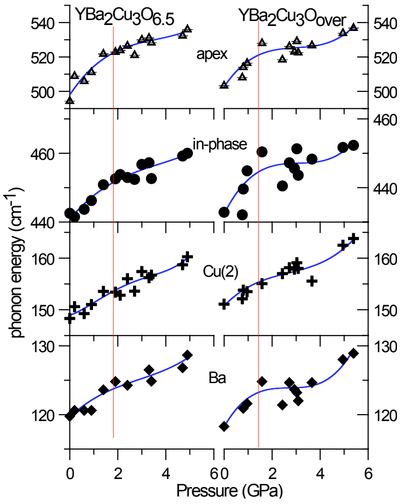

Figure III:2:6. The hydrostatic pressure dependence of the energy for the A_g Raman modes of the Y123x compounds. The lines are 3rd order polynomial best fits to the data

Ambient pressure studies have shown that the energy of the B_{1g}-like mode is independent of the oxygen concentration and the Cu_{pl}-O_{pl} bonds [4], but it is significantly affected by a rare earth substitution for Y showing a phase separation [19]. All available data indicate that the B_{1g} mode depends mainly on the Y-O_{pl} bonds [4,18-20]. Our Raman data show no anomaly for the pressure dependence of the B_{1g}-like mode energy for both Y123:x~6.5 and Y123:x~7 compounds [11-12], indicating that the Y-O(2,3) bonds do not undergo abnormal modifications with pressure in Y123 independently of the amount of doping.

According to lattice dynamical calculations, the in-phase phonon energy depends mainly on the plain Cu_{pl}-O_{pl} bonds [24] and this agrees with the ambient pressure studies of Y123x, where with increasing x the length of the Cu_{pl}-O_{pl} bonds increases almost linearly [1], while the in-phase mode energy decreases [4]. Therefore, the appearance of another mode with hydrostatic pressure is a sign that the Cu_{pl}-O_{pl} bonds of the planes undergo some modifications at a critical pressure, inducing a separation into phases.

The Y124 has double chains along the *b* axis giving stronger O_{ch}-Cu_{ch} bonds and diminishing the oxygen defects. Although the structure and T_c of Y124 is similar to Y123:x~7, the dT_c/dP is quite different from 5.5K/GPa for Y124 [25-27] to ~(1 to –2.5) K/GPa for Y123x [28]. Fig.7 presents typical Raman spectra of Y124 at high pressures and again considerable spectral modifications can be observed. For the pressure dependence of the energy of the modes, a deviation from linearity begins at ~3.8 GPa for several modes (Fig.8). At higher pressures (>5.5 GPa) the energy of the modes stops increasing (Fig.8). The modifications at ~3.8 GPa are accompanied by an increase of the width for the A_g-symmetry modes, while the $B_{2g,3g}$ phonons remain unaffected (Fig.7). In the case of the in-phase phonon the increase of the width is clearly due to the appearance of another mode at higher by ~20 cm^{-1} energy to the in-phase phonon (Fig.7).

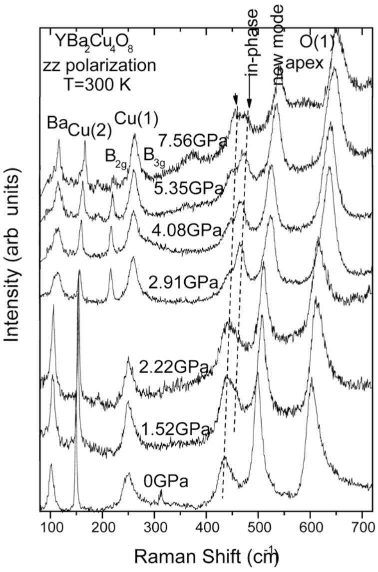

Figure III:2:7. Typical Raman spectra of the $YBa_2Cu_4O_8$ compound at selected hydrostatic pressures in the zz scattering geometry

The relative intensity of the in-phase to the new mode changes by rotating the crystal by a few degrees and keeping the same (zz) polarization for the incident and scattered light. It has been observed that the relative intensity of this new mode increases simultaneously with the intensity of the

B_{2g} phonon attributed to the vibrations of the O_{ch} atoms along the a-axis. It seems that the intensity variations and the appearance of the new mode are related with local distortions close to the CuO_2 planes and possibly a titling of the axis, which drives a phase separation in Y124 [11,12].

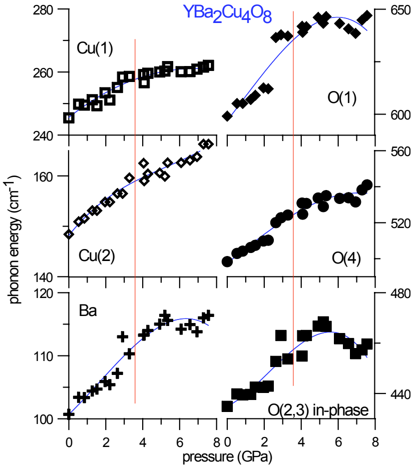

Figure III:2:8. Hydrostatic pressure dependence of the energy for the A_g-symmetry Raman modes of $YBa_2Cu_4O_8$. The lines are 3rd order polynomial best fits to the data.

Structural data under hydrostatic pressure from XRD measurements of Y124 exist up to ~5 GPa [29]. They have shown, as expected, that the lattice parameters and all bond lengths decrease with increasing pressure, but the rate of change deviates from linearity above ~3.8 GPa [29]. At hydrostatic pressures ~5.5 GPa the dTc/dp changes rapidly and gradually the transition temperature saturates [26]. This behaviour is correlated with the changes observed in several phonons for the same pressure (Fig.8). Unfortunately, there are no structural data available above 5 GPa to investigate any anomaly on the interatomic bonds. One should remark once more that the presented Raman measurements are at RT and correlate with changes in T_c.

In Bi2212 there are many modes that are Raman active. Under hydrostatic pressures only the strong modes could be investigated [13]. At ambient pressure these are located at ~60 cm^{-1} (Bi), ~118 cm^{-1} (Sr), ~290 cm^{-1} (out of phase vibrations of O_{pl}, the B_{1g} mode), ~330 cm^{-1}, ~458 cm^{-1} and ~465 cm^{-1} (a doublet), and at ~630 cm^{-1}, (O_{Bi}). The assignment for certain modes is still controversial, but there is a general agreement for the low energy phonons at 60 cm^{-1} and 118 cm^{-1}, and the B_{1g} phonon [30-33]. The two strong modes at ~458 cm^{-1} and ~465 cm^{-1} appear with varying relative intensities with pressure. Both modes have shown a characteristic independence on pressure and they show an abnormal behaviour with temperature with a maximum energy around 150 K [13].

In Figure 9 we observe that the pressure dependence of the phonons due to Bi, Sr, the B_{1g}, and mainly the double mode at 458-465 cm^{-1} shows a strong modification at ~1.8 GPa.

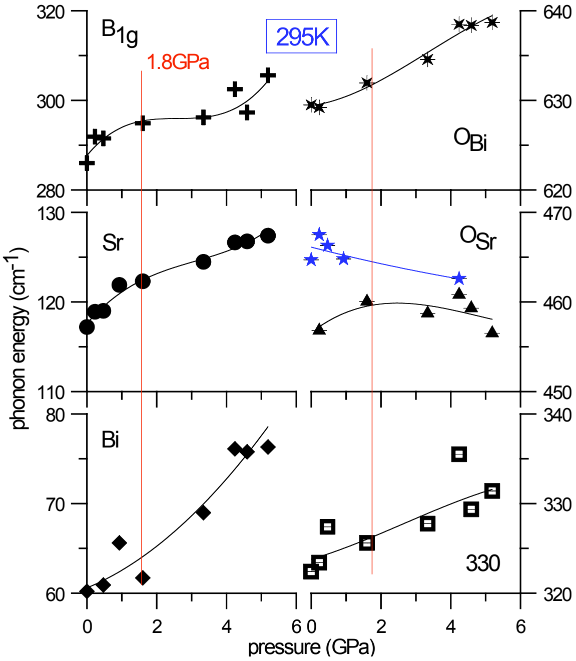

Figure III:2:9. The pressure dependence of the Raman active modes of Bi2212.

At exactly the same hydrostatic pressure an anomaly has been measured for the transition temperature and it has been attributed to a deformation of the CuO_5 pyramids [31]. This structural modification affects several phonons but mainly the double peak at ~458-465 cm^{-1}. The splitting of this mode must again be related with a phase separation mechanism, similar to the ones discussed above for the other cuprates.

In Bi2212 there is an uncertainty about the assignment of the high-energy modes. The mode at 630 cm^{-1} appears also in the Bi2201 compound [34] and it cannot be associated with the in-phase phonon. Since it does not show any anomaly at 1.8 GPa pressure (Fig.9) when there is a structural distortion at the pyramids, it is improbable to be related with the apical oxygen. It is therefore reasonable to assign it to the oxygen atoms in the BiO planes [13]. The peak at ~330 cm^{-1} could be the in-phase mode since it shows a similar behaviour with the B_{1g} mode of the plane oxygen atoms [13]. This agrees with the association of the changes with an anomaly in the CuO_5 pyramids [31]. The doublet cannot be related with the O_{Bi} atom [30.31], since it should not be sensitive to the change in the pyramids. So, it has to be assigned to the vibrations either of the apical oxygen [13] or the in-phase phonon [33]. In either case, it is affected by the structural distortions of the CuO_5 pyramids and the double peak pointing to a phase separation scenario.

4. CONCLUSIONS

The presented Raman measurements, performed at RT, clearly show for certain phonons considerable deviations from the linear dependence on pressure. These modifications seem to originate from small structural changes induced by pressure. A similar small local structural modification that affects a certain phonon (in-phase) has been observed in Y123 at the boundary of the optimal to overdoped oxygen concentration, appearing as a first order phase transition [3,4]. EXAFS and neutron measurements have shown that it was due to a sudden change in the CuO_2 buckling and it was accompanied by a small change in T_c [1,3]. In another cuprate ($Bi_2Sr_2CaCu_2O_8$) a similar splitting of a mode was discovered indicating a separation into phases and correlated again with a change in the transition temperature [13]. In $La_{2-x}Sr_xCuO_4$ it was found that the T_c dependence on chemical doping follows spectroscopic changes observed also at room temperature [35]. All data obtained at ambient conditions indicate that the variation and the optimal values of T_c obtained by chemical doping or by varying an external factor like pressure, are affected by structural instabilities and phase separation.

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