Pressure-induced lattice instabilities and superconductivity in YBCO

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Combined synchrotron angle-dispersive powder diffraction and micro-Raman spectroscopy are used to investigate the pressure-induced lattice instabilities that are accompanied by $T_c$ anomalies in YBa$_2$Cu$_3$O$_8$, in comparison with the optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ and the non-superconducting PrBa$_2$Cu$_3$O$_{6.92}$. In the first two superconducting systems there is a clear anomaly in the evolution of the lattice parameters and an increase of lattice disorder with pressure, that starts at $\approx 3.7$ GPa as well as irreversibility that induces a hysteresis. On the contrary, in the Pr-compound the lattice parameters follow very well the expected equation of state (EOS) up to 7 GPa. In complete agreement with the structural data, the micro-Raman data of the superconducting compounds show that the energy and width of the $A_g$ phonons show anomalies at the same pressure range where the lattice parameters deviate from the EOS and the average Cu2-O$_{pl}$ bond length exhibits a strong contraction and correlate with the non-linear pressure dependence of $T_c$. This is not the case for the non-superconducting Pr sample, clearly indicating a connection with the charge carriers. It appears that the cuprates close to optimal doping are at the edge of lattice instability.

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INTRODUCTION

It is well accepted that structural and electronic inhomogeneities constitute intrinsic properties of cuprate superconductors [1, 2, 3]. To this context the study of any lattice distortions induced by application of either internal chemical or external hydrostatic pressure [4, 5, 6] that modify the transition temperature ($T_c$) are important for understanding the role of lattice effects in the high $T_c$ superconductivity. Lattice instabilities in hydrostatically compressed YBa$_2$Cu$_3$O$_y$ (Y123) and YBa$_2$Cu$_4$O$_8$ (Y124) cuprates where $T_c$ dependence on pressure shows saturation or non-linear behavior [1, 2, 3], manifest themselves in the Raman phonon frequencies as a deviation from an expected linear behavior at a critical pressure range 2.5-6 GPa [3, 9, 10]. In agreement with these studies, recent structural investigations, using synchrotron angle-dispersive powder diffraction and dense sampling on optimally doped Y123 superconductor have revealed a clear deviation of the lattice constants from the expected equation of state in the pressure range 3.7 GPa of applied pressure, with strong hysteresis effects and the formation of an additional new textured phase [3]. Interatomic distances in the unit cell of Y123, such as the Ba distance from the basal plane, the Cu2-O$_{pl}$ bond length, and the Cu2-Cu1 distance along the c-axis, have been found to exhibit also a non linear evolution with applied pressure that correlates with modifications of the Raman spectra of the in-phase O$_{pl}$ and the O$_{ap}$ phonon modes [3]. The correlation of the structural characteristics with the Raman frequency modifications [3] and corresponding changes of $T_c$ [3] imply that the trigger of the lattice instabilities lies among the CuO$_2$ and BaO planes. Redistribution of the carriers among the planes, that has been found to occur in the case of application of chemical pressure [11], which affects also the $T_c$, must certainly play a role in the observed effects.

The main questions that arise is whether similar effects are present in other cuprates and how they are related to the amount of charge carriers and superconductivity. The isostructural to Y123 compound PrBa$_2$Cu$_3$O$_7$ (Pr123) is a good example to study, having apparently no free carriers [3]. Structural and Raman studies under hydrostatic pressure in this compound are absent. The Y124 superconductor is another good case to study, since it can be considered as a model compound for the underdoped region of the YBCO system. Structural studies under hydrostatic pressure up to 5 GPa (using a laboratory source) gave only some marginal evidence of a non-linear pressure dependence above 4 GPa [12]. We present here high quality synchrotron angle-dispersive powder diffraction data and micro-Raman spectra under hydrostatic pressure for Pr123 ($T_c=0K$) and Y124 ($T_c=80K$) in comparison with those of Y123 ($T_c=92K$) [3]. The pressure region up to 13 GPa has been investigated with a pressure step of $\approx 0.5$ GPa. Our combined structural and spectroscopic results provide strong evidence that the presence of charge carriers and the pressure-induced lattice instabilities in the superconducting cuprates are strongly related affecting the $dT_c/dp$ dependence.

Experimental details

We have studied a powder PrBa$_2$Cu$_3$O$_{6.92}$ sample with an oxygen content comparable to the previously investigated optimally doped Y123 [3] and the YBa$_2$Cu$_4$O$_8$ compounds. Synchrotron angle-dispersive powder diffraction experiments at high pressures have been carried out at the Swiss-Norvegian beamline BM01A of ESRF (Grenoble), using a diamond anvil cell (DAC) and a 4:1 methanol-ethanol mixture as pressure
medium, which is known to remain hydrostatic and do not cause peak broadening in powder samples at least up to $\sim 10$ GPa [13]. Ruby crystals were used for measuring the pressure. Diffraction patterns have been collected with a wavelength $\lambda=0.71174 \AA$ and a MAR345 image plate detector. The pressure cell was left to relax for approx. 20-30 min at each pressure. The 2D raw images have been converted to 20 patterns, after correcting for distortions and refining the detector-sample distance using a LaB$_6$ standard by the program FIT-2D [14].

The Raman spectra were obtained at room temperature and high hydrostatic pressures with a T64000 JobinYvon triple spectrometer equipped with a liquid nitrogen cooled charge coupled device (CCD) and a microscope lens of magnification x 40. A Merrill Bassett type diamond anvil cell (DAC) was used for the high-pressure measurements (up to 6.8 GPa), 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, with analogy (4:1). Silicon single crystals distributed around the sample were used for calibration of the pressure and for monitoring the hydrostatic conditions. The 514.5 nm line from an Ar$^+$ laser was used for excitation, which produced the lowest luminescence from the diamonds. The laser beam was focused on the sample at a spot of diameter 4 $\mu$m while the power level was kept below 0.20 mW. Typical accumulation times were up to 3 hours depending on the scattering polarization.

Results and Discussion

Structural data have been obtained by analyzing the intensity-vs-2θ diffraction patterns with the Rietveld method using Fullprof [15] and a pseudo-Voigt line profile function. The diffraction patterns of Pr123 have been refined with the orthorhombic Pmmn space group in the whole pressure region. Minor impurity lines belonging to BaCuO$_2$ [6] have been excluded. Lattice constants for Y124 have been refined with the Amm2m space group in the orthorhombic Pmmm space group in the whole pressure region. In the case of Pr123, at $p = 4.7$ GPa, the corresponding pattern of Y124 with the results of Le Bail refinement. The evolution of the c-axis with the applied hydrostatic pressure for Pr123 is shown in Fig.2a in comparison with the corresponding one of the optimally doped Y123 (Fig.2b) from ref. [6], whereas the results for Y124 are presented in Fig.2c. Fig.3 shows the pressure dependence of the $\kappa_c$ and $\kappa_a$ of the Pr123 (Fig.3a), the Y123 (Fig.3b) from ref. [6] and the Y124 (Fig.3c) compounds. Full symbols correspond to the values for increasing and open symbols to those for releasing the pressure. In the case of Y124, we have also carried out measurements with increasing again the pressure after the pressure release (full triangles in Fig.2c,f and Fig.3c).

The lattice constants have been fitted to the empirical Murnaghan equation of state $q = q_0 [p(\kappa_q/\kappa_q') + 1]^{-\kappa_q'}$, where $p$ is the applied pressure, $q$ is the lattice constant under compression, $\kappa_q$ its compressibility and $\kappa_q'$ a parameter that expresses the pressure dependence of the compressibility. For Pr123 the solid lines are fits to the data for increasing pressure up to 7 GPa. For Y123 and Y124 the solid lines are fits to the data for increasing pressure where the pressure region $3.7 < p < 8$ GPa has been excluded as will be discussed in what follows. The values of $\kappa_a = 2.6 \times 10^{-3}$ GPa$^{-1}$, $\kappa_b = 2.1 \times 10^{-3}$ GPa$^{-1}$ and $\kappa_c = 4.1 \times 10^{-3}$ GPa$^{-1}$ obtained for Pr123 are slightly smaller but comparable to those of Y123 [6]. The Y124 compound exhibits strong anisotropy in all three lattice directions with corresponding compressibilities $\kappa_a = 3.7 \times 10^{-3}$ GPa$^{-1}$, $\kappa_b = 1.9 \times 10^{-3}$ GPa$^{-1}$ and $\kappa_c = 4.5 \times 10^{-3}$ GPa$^{-1}$.

For Pr123 the evolution of all axis follows very well the Murnaghan equation up to $\sim 7$ GPa, while upon pressure release the data follow the ones at increasing pressure. This is in contrast with the evolution of the c-axis of Y123, which exhibits a strong deviation from the expected equation of state that starts around 3.7 GPa and extends to 8-10 GPa, and there is a clear irreversibility of the effect of pressure, which results in a strong hysteresis [6]. In the same pressure region Y124 shows also a deviation from EOS but the effect is less intense than Y123. Upon decompression the c-axis of Y124 follows an equation of state with almost the same compressibility, $\kappa_c = 4.2 \times 10^{-3}$ GPa$^{-1}$ but with much bigger pressure dependence of compressibility, $\kappa_q' = 0.14$, compared to that on compression, $\kappa_q' = 0.036$ (dashed line in Fig.2c). For Pr123 no deviation is detected (Fig.3a), while for Y124 the deviation in the b- and a-axis is more pronounced than in Y123, with the b-axis showing a larger deviation than a-axis (Fig.3c). When the pressure was increased again in Y124 after the pressure release, the data for the c-axis follow well those of the pressure release (Fig.2c). In the case of the a- and b-axis the increase of pressure for a second time brings the data closer to those of pressure release for the a-axis and the original pressure increase for the b-axis. But the observed modifications in those axis are much smaller than for c-axis and the effect might be related with the anisotropy of the compound. For Pr123 and Y123 we have no data with increasing pressure for a second time in order to compare, but for Pr123 there is no deviation from the EOS and the data of pressure increase or release coincide and we could not observe any changes. Furthermore, in Y123 the deviations from the EOS for the a- and b-axis are smaller than in Y124 and any changes, even if present, might not be able to be detected.

It should be mentioned that at the pressure of $\approx 3.7$ GPa four new weak Bragg peaks appear in the diffraction patterns of Y124 and Y123 [6], which are not observed for Pr123. The new lines could not be due to the forma-
tion of a superstructure, as the systematic investigation of all observed lines has proved. Moreover the 2D diffraction images revealed that these new lines exhibit strong texture and strain effects unlikely to those of the main phase (Fig. 4 in ref. [6]). We therefore assume that they are due to the formation of an additional textured and distorted phase at this critical pressure in both Y123 and Y124 compounds. Interestingly, the new lines completely disappear upon pressure release below roughly the same pressure ($\approx$ 3 GPa), to appear again with the increase of pressure once more in Y124. In the diffraction pattern of Y124, we have also observed at 10.3 GPa the appearance of two additional lines at $\theta \approx$ 15.5 and 28 degrees, with texture effects, which disappear again for $p < 9$ GPa on decompression. At the same pressure the b-axis deviates from the expected equation of state. The formation of the new phases happens at the pressure where there is a deviation from the EOS, and whenever this does not occur, as in Pr123, the new lines do not appear. Apparently, they are related with a phase separation, which is triggered by the hydrostatic pressure and cause deviations from the EOS. Besides, at those critical pressures (e.g. 3.7 GPa and 10.3 GPa) there are modification of the $T_c$ dependence on pressure in Y123 [5], which connects the lattice distortions and the phase separation with changes in the electronic system in the Y123 and the Y124 compounds.

With increasing pressure the width of the diffraction peaks is increasing. In the case of Y123, the Williamson-Hall plots have revealed that the application of pressure induces a microstrain-type diffraction peak broadening while size-type broadening is negligibly small [6]. Although it is very difficult to assess the origin of microstrains, pressure-induced disorder is most likely associated with the observed line broadening in the pressure region up to 10 GPa. In order to examine any correlation of pressure-induced disorder to the observed deviations from the expected EOS, we have estimated the upper limit of apparent microstrains-disorder in all the compounds. Since we are interested to investigate their evolution with pressure rather than absolute values, we have used the width of the single, non overlapping 113 peak. The width of the 113 reflection is not affected by intrinsic defects, such as dislocations and stacking faults, as found in the case of Pr123 [6]. The 113 peaks have been fitted with a pseudo-Voigt function and the apparent microstrain, $\varepsilon$, has been calculated as $\varepsilon = (W' - W_i)/\tan\theta$, where $W$ and $W_i$ are the full widths at half maximum of the sample and the standard LaB$_6$ respectively, which has been used to determine the instrumental resolution. The evolution of microstrains-disorder with pressure for Pr123, Y123 and Y124 is shown in Fig. 2d, 2e and 2f respectively. Full symbols correspond to the values for increasing and open symbols to those for releasing the pressure. Dotted lines are guide to the eye to emphasize the regions with different increase of disorder upon pressure. Fig. 2d shows that microstrains in Pr123 remain almost constant up to a pressure of 7 GPa and start to increase exactly at the same pressure where the c-axis deviates from the expected equation of state. No irreversibility and hysteresis effects are observed. Contrary, the microstrains of Y123 start to increase at $\approx$ 3.7 GPa where the c-axis deviates from the equation of state, for $p > 7$ GPa continue to increase with a bigger slope and for $p > 10$ GPa increase further. In addition pronounced hysteresis effects are present (Fig. 2e). Analogous results have been obtained for Y124 (Fig. 2f). It is clear in Fig. 2 that the increase of microstrains occurs in all cases exactly at the same pressure where there is an anomaly in the expected lattice constants behavior on pressure. With the reduction of pressure to ambient conditions, the Pr123 compound practically returns to the original state of microstrains indicating that they are not permanent lattice distortions. On the contrary, the Y123 and Y124 compounds show strong hysteresis in the whole pressure range. It should be noted that, the 2D patterns obtained with the 

\[ \text{peak function of the FIT2D [14] software do not bear any sign of a non-hydrostatic pressure on the diffraction lines of Pr123, Y123 (Fig. 4 in ref. [6]) and Y124. This is in agreement with all measurements performed up to now that do not provide any evidence for a non-hydrostatic environment in the methanol-ethanol mixture for pressures up to 10 GPa.}

The evolution of microstrains-disorder in Pr123 indicates two regions of almost linear pressure dependence for the compound; namely for pressures up to 7 GPa and above it. The deviation of the c-axis decrease from the expected EOS and the increase of disorder for $7 < p \leq 10$ GPa would imply that the system undergoes a phase transition likely related to a distorted orthorhombic phase. In the case of Y123 and Y124 there is an intermediate pressure region (3.7-7 GPa), where microstrains exhibit again an almost linear increase on pressure but with a different slope (Fig. 2e and 2f). Interestingly, in the two pressure regions, e.g. $p < 3.7$ GPa and $7 < p \leq 10$ GPa microstrains increase with same pressure slopes in the Y123, Y124, and Pr123 compounds. Since Pr123 and Y123 have comparable compressibilities, the different evolution of microstrains-disorder in the Y123 cuprate for the intermediate (3.7-7 GPa) pressure region implies that pressure-induced disorder in that region is an intrinsic effect of Y123 and Y124, which appears together with the hysteresis, the anomaly in the lattice constants evolution and the new lines reminiscent of the development of a new phase. To this context the different microstrain regions marked by dotted straight lines with a different pressure slope in Figures 2e and 2f may indicate the formation of different distorted orthorhombic micro-phases in Y123 and Y124. All these effects are absent in Pr123 up to a pressure of 7 GPa.

Irreversibility and hysteresis were also observed in the pressure dependence of $T_c$ for the Y124 compound by Scholtz et al [8]. In this work it was suggested that a possible transformation of the sample for pressures above 20 GPa was the reason for this unexpected hysteresis. However, our data and more precisely the modification of the c-axis compressibility of Y123 and Y124 in the in-
termediate (3.7-7 GPa) pressure region, which correlates with the increase of microstrains, the appearance of extra Bragg peaks and the modifications in Tc implies that most probably the origin of these phenomena must be an intrinsic instability of the superconducting cuprates, which results in the development of another phase that appears together with the hysteresis. Such effects and a new phase are absent in the non-superconducting Pr123 at least up to 7 GPa.

Typical Raman spectra of the hydrostatically compressed Pr123 compound are shown in Fig.4. All five $A_g$ symmetry phonons with eigenvectors along the c-axis were studied in the two scattering polarizations, xx (Fig.4a) and zz (Fig.4b) corresponding to incident and scattered light polarization parallel or perpendicular to the CuO$_2$ planes. Those are at $\sim128$ cm$^{-1}$ (Ba-atom), $\sim150$ cm$^{-1}$ (Cu$_{pl}$-atom), $\sim300$ cm$^{-1}$ (out of phase (B$_{1g}$-like) vibrations of the O$_{pl}$ atoms), $\sim435$ cm$^{-1}$ (in phase vibrations of the O$_{ap}$ atoms) and $\sim523$ cm$^{-1}$ (vibrations of the O$_{ap}$ atoms). Fig.5 shows that the energy of the four $A_g$ symmetry phonons in Pr123 increases almost linearly with pressure. For comparison, the pressure dependence of the ortho-I and ortho-II phases of Y123, corresponding to oxygen content $\approx7$ (Y123) and $\approx6.5$ (Y1236.5), are also shown, where it is clear that in the region 2.5-4 GPa there is no increase in the phonon energy despite the increase in pressure. This softening of the four $A_g$ phonons is in contrast to their almost linear behavior for Pr123. For the B$_{1g}$-like mode the phonon energy has been found to increase almost linearly with increasing pressure, as expected, without showing any anomaly, for all compounds. Figure 6 presents the variation of the corresponding phonon width of the four $A_g$ symmetry phonons for the sets of compounds, which again indicates that both Y123 and Y1236.5 have an unusual behavior with pressure compared with Pr123. Especially the apical phonon mode shows a considerable increase in width for p=2 GPa and then a decrease to almost the original value for p=$\approx3.7$ GPa and an afterwards increase. This unconventional variation of the width with pressure is not a result of error in the fitting procedure, but it is quite clear from the spectra (Fig.1 of ref. [3]). The initial increase in width and frequency of the mode up to $\approx2$GPa is a typical increase of the modes with pressure. Afterwards, both the width and the frequency show abnormal behavior, which indicates that another mechanism is active. This could be a pressure induced lattice instability that results in phase separation, mode frequency softening, and decrease in the width, which finally relaxes the internal strains.

For the in-phase mode the high-pressure Raman results for the Y123 compound have indicated modifications, which appear as a double peak at about 2 GPa [9], i.e. at the pressure where the bond distance Cu2-O$_{pl}$ and the position of the Ba atom show a non-linear dependence on pressure [10]. Similar modifications from linearity with increasing pressure were also detected for the apical oxygen frequency [10], which correlates (as expected) with the pressure dependence of the Cu2-Cu1 bond lengths [6]. The same Raman results have also been obtained for the Y124 compound [12]. However, the non superconducting Pr123 compound does not show such anomalies. In complete agreement with the corresponding Raman results, the average Cu2-O$_{pl}$ bond length obtained from the Rietveld refinement for Pr123 (shown in Fig.7a) exhibits only a very small, if any, modification at the characteristic pressure of $\approx3.7$ GPa contrary to the Y123 compound (Fig.7b). The abrupt contraction of the Cu2-O$_{pl}$ bond in Y123 at $\approx3.7$ GPa may be related to a pressure-induced redistribution of the carriers.

The combined XRD and Raman results show for Y123 and Y124 in the pressure region 3.7<p<8 GPa; a clear deviation from the expected EOS of the c-axis (Figs.2b, 2e), the modifications of disorder (Figs.2e, 2f), which correlate with a softening of the four $A_g$ phonons (Fig.5) and the anomaly in their width (Fig.6). Furthermore, there is also a strong irreversibility and hysteresis together with the appearance of a new phase. In the corresponding data of the isostructural Pr123 no similar phenomena are observed. One could assume that for 3.7<p<8 GPa a new phase is created with pressure in these cuprates, which is accompanied with modifications in the lattice along the Cu2-O$_{pl}$ and Cu2-O$_{ap}$ bonds, directly affecting the carrier distribution and the transition temperature in Y123 and Y124, while having no appreciable difference in Pr123, which does not have carriers. The main effects are observed for the $A_g$ symmetry phonons with eigenvectors along the c-axis while the B$_{1g}$ phonons are not affected. The pressure data in the cuprates studied point to a lattice instability close to optimal doping, which once exceeded by pressure (present work) or doping [12], induces local lattice distortions mostly in the CuO$_2$ planes that modify the transition temperature.

Conclusions

The data show a correlation of the deviations from the normal EOS and hysteresis in the lattice constants with the lattice microstrain-disorder, and the existence of carriers for yttrium family of the cuprates. The Raman data and the Tc-dependence on pressure show anomalies at the same pressures with the synchrotron diffraction data. The results from all sets of measurements for the studied cuprates indicate a strong tendency of those compounds towards lattice instability, which apparently is related to the amount of carriers and superconductivity. This seems to be an intrinsic property of the cuprates, at least for the ones studied. Although we cannot anticipate the behavior of the other cuprates, our up-to-now data reveal a systematic behavior in the studied compounds, which provides a hint about the role of the lattice in the high Tc superconductivity.
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FIGURE CAPTIONS

Figure 1. (Color online) Rietveld refinement of synchrotron powder diffraction patterns for Pr123 at $p=4.7$ GPa (a) and LeBail refinement for Y124 at $p=4.7$ GPa (b). Experimental (circles), calculated (continuous line) intensities, their difference (bottom line) and corresponding positions of Bragg peaks (bars). The part of the pattern near $2\theta=20^\circ$, where the lines from the gasket appear, has been excluded. (*) shows the peaks of impurity BaCuO$_2$ in Pr123 and (♦) the weak peaks appearing for $p \geq 3.7$ GPa in Y124.

Figure 2. (Color online) Pressure dependence of the c-axis for the Pr123 (a), Y123 (from ref. [6]) (b) and Y124 (c) compounds. Evolution of apparent disorder $\varepsilon$ with applied pressure for the Pr123 (d), Y123 (e) and Y124 (f) compounds. Full symbols correspond to increasing pressure and open symbols to pressure release. Full triangles correspond to the increase of pressure for second time. Solid lines (and dashed line in 2c) are fits to the Murnaghan EOS as described in the text. Dotted lines in 2d-f are guide to the eye to emphasize the regions with different increase of disorder upon pressure.

Figure 3. (Color online) Pressure dependence of the a-, b-axis for the Pr123 (a), Y123 (ref. [6]) (b) and Y124 (c) compounds. Full symbols correspond to increasing pressure and open symbols to pressure release. Full triangles correspond to the increase of pressure for second time. Solid lines are fits to the Murnaghan EOS.

Figure 4. Typical Raman spectra of the Pr123 compound at selected pressures in the xx (a) and zz (b) scattering configuration.

Figure 5. (Color online) The variation of the energy of the Cu$_{pl}$ (a), O$_{ap}$ (b), Ba (c) and O$_{pl}$ (d) phonon upon pressure for different cuprates; YBa$_2$Cu$_3$O$_{6.5}$ (Y1236.5), YBa$_2$Cu$_3$O$_7$ (Y123) and Pr123.

Figure 6. (Color online) The variation of the width of the (Cu$_{pl}$ (a), O$_{ap}$ (b), Ba (c) and O$_{pl}$ (d) phonon upon pressure for the cuprates of Fig.5.

Figure 7. The pressure dependence of the Cu2-O$_{pl}$ bond length for the Pr123 (a) in comparison to that of Y123 (ref. [6])(b). Dashed lines are guide to the eye.
Figure 1

(a) Pr123, p=4.7 GPa

(b) Y124, p=4.7 GPa

Intensity (arb. units)

2θ (degrees)
Figure 2a_d
Figure 2b_e
Figure 2c_f
Figure 3
Pr123 powder
xx polarization
295K

6.80GPa
5.52GPa
4.90GPa
3.8GPa
2.54GPa
1.24GPa
0.74GPa
1atm

Raman Shift (cm\(^{-1}\))

Intensity (arb. units)

Figure 4a
Figure 4b
Figure 5

Ag symmetry phonons (zz polarization), 295K

(a) Cupl

(b) Opap

(c) Ba

(d) Oppl in-phase

Phonon energy (cm$^{-1}$) vs. Pressure (GPa)
Figure 6

Ag symmetry phonons (zz polarization), 295K

(a) (b)

Phonon width (cm\(^{-1}\))

Pressure (GPa)

(c) (d)

Phonon width (cm\(^{-1}\))

Pressure (GPa)

Pr\(_{123}\) Y\(_{1236.5}\) Y\(_{123}\)

Ba

O\(_{ap}\)

Cu\(_{pl}\)
Figure 7