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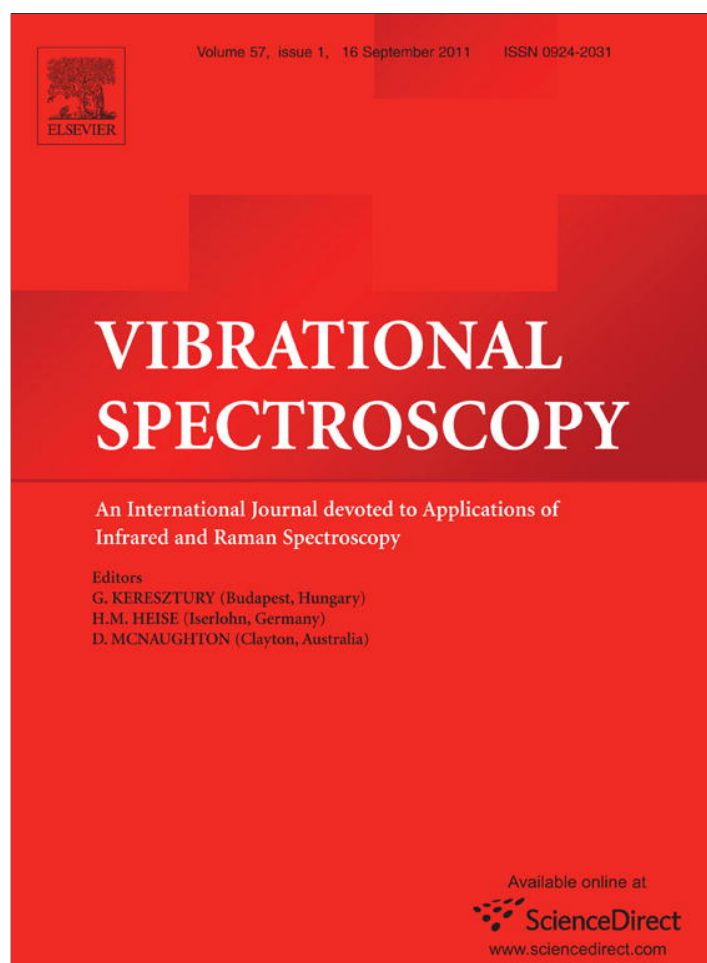


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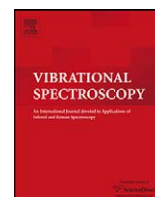
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## High-pressure Raman spectra of L-histidine hydrochloride monohydrate crystal

G.P. De Sousa, P.T.C. Freire\*, J.A. Lima Jr., J. Mendes Filho, F.E.A. Melo

Departamento de Física, Universidade Federal do Ceará, C. P. 6030, CEP 60455-760 Fortaleza, CE, Brazil

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## ABSTRACT

Single-crystals of L-histidine hydrochloride monohydrate,  $C_6H_9N_3O_2 \cdot HCl \cdot H_2O$ , were studied by Raman spectroscopy as a function of pressure in a diamond anvil cell up to 7.5 GPa at room temperature over the spectral range  $3450\text{--}30\text{ cm}^{-1}$ . The effect of changing pressure on the vibrational spectrum is discussed. From the analysis of results we inferred that the crystal undergoes a reversible structural phase transition between 2.7 and 3.1 GPa. This transition is characterized by the splitting of a band related to torsion of  $CO_2^-$ , the disappearance and appearance of modes related with stretching of  $OH^-$  and deformation of  $CO_2^-$ , as well as with bands of low wavenumber which are assigned as lattice modes, and by the discontinuities of the curves of wavenumber versus pressure. Pressure coefficients for all modes observed in this work are also given.

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## 1. Introduction

Amino acids are small molecules with general formula  $HCCO_2^-NH_3^+R$ , where R is a lateral chain characteristic of each molecule, which form the protein structure of all living beings. Because both hydrogen bonding (HB) interactions play a pivotal role on the secondary structure of proteins and the amino acids in crystal structure present complex networks of HB, they have been studied extensively in the last years [1–25]. These studies can be seen as important background to understand static structure and dynamics properties of proteins such as denaturation, renaturation, folding itself, changes of folds, among others [1]. In particular, the amino acid crystals have been submitted to high pressure conditions, because in this manner hydrogen bonding interactions can be altered significantly and their influence on the crystal structure can be studied. The simplest protein amino acid is  $\alpha$ -glycine, which was investigated by Raman spectroscopy under high pressure conditions, being discovered that up to 23 GPa the crystal structure does not undergo any phase transition, although modifications in the Raman spectra indicate changes in the intra-layer HB interactions [2]. On the other hand, the  $\beta$ -glycine crystal undergoes a reversible first order transition at low pressure, 0.76 GPa, accompanied by jump-wise changes in the vibrational frequencies of the Raman spectrum [4,5]. The other form of glycine, the  $\gamma$ -glycine, has a very complex behavior under high pressure conditions, undergoing a phase transition to a  $\delta$ -form at 2.74 GPa (maintaining partially the  $\gamma$ -form) and going to a  $\zeta$ -form under decompression [6–8],

although the  $\delta$ -form is also preserved down to the atmospheric pressure.

The simplest chiral amino acid, L-alanine, seems to present a structural phase transition at  $\sim 2.3$  GPa [10,11], although recent works reinterpreted X-ray diffraction measurements as conformational changes of the ammonia group [12,13], with two cell parameters becoming accidentally equal to each other at 2 GPa, but the crystal remaining with the original orthorhombic ( $D_2^4$ ) symmetry. In the case of L-leucine, another aliphatic protein amino acid, studies through Raman spectroscopy revealed that the crystal presents at least three anomalies between 0 and 6 GPa, which could be associated to conformational changes of the molecules into the unit cell with small changes of HB network [14].

Other studies tried to follow the behavior of HB and the stability of the crystal structures of L-cysteine [17,18], L-isoleucine [19], L-methionine [20], L-serine [22–25], among others. In all these investigations, the occurrence of phase transitions involving change in the dimension of the several HB in the unit cell seems to be the role. Although from a biological point of view the pressure range relevant is up to 1 GPa, the studies performed on these several amino acid crystals are important because they give informations about chemical and physical aspects related to polymorphism and chemical bonds – mainly hydrogen bonds – in substances related to life.

This work provides results for the high pressure Raman scattering for L-histidine hydrochloride monohydrate crystal (LHICLM), and establishes the occurrence of a new polymorph for pressures higher than 3.1 GPa. Besides, the results obtained with a diamond anvil cell give insights about the modifications verified with vibrational modes related to hydrogen bonds when the crystal is submitted to pressures as high as 7.5 GPa.

\* Corresponding author. Tel.: +55 85 3366 9906; fax: +55 85 3366 9450.  
E-mail address: [tarso@fisica.ufc.br](mailto:tarso@fisica.ufc.br) (P.T.C. Freire).

## 2. Experimental

Crystals of L-histidine hydrochloride monohydrate were grown from aqueous solution by the slow evaporation method at controlled temperature (294 K). The crystal structure of the samples obtained was confirmed through powder X-ray diffraction. Raman experiments were performed in the backscattering geometry employing a Jobin Yvon Triplemate 64000 micro-Raman system equipped with a N<sub>2</sub>-cooled charge-coupled device (CCD) detection system. The slits were set for a 2 cm<sup>-1</sup> spectral resolution. Raman spectra were excited with the 514.5 nm line of an argon ion laser. High-pressure experiments at room temperature were performed on a small piece of sample compressed using a diamond anvil cell (model NBS—National Bureau of Standards). As hydrostatic pressure medium it was used a mineral oil. An Olympus microscope lens with a focal distance  $f = 20.5$  mm and a numerical aperture 0.35 was used to focus the laser beam on the sample surface, which was located in the pressure cell. The pressure in the cell was monitored using the standard shifts of the Cr<sup>3+</sup>:Al<sub>2</sub>O<sub>3</sub> emission lines.

## 3. Results and discussion

LHICLM crystallizes in an orthorhombic structure belonging to the  $P2_12_12_1$  ( $D_2^4$ ) space group with four molecules of C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>·HCl·H<sub>2</sub>O per unit cell with lattice parameters  $a = 15.36$ ,  $b = 8.92$  and  $c = 6.88$  Å [26]. The molecule is found in the zwitterion form and the two nitrogen atoms of the imidazole ring form hydrogen bonds with two different neighboring molecules. The strong bond between N–H of the imidazole ring and the carboxyl group of a neighboring molecule is the fundamental intermolecular link, resulting in a spiral arrangement along the  $c$ -axis [27]. Such an intermolecular link is common to most amino acid crystals, such as L-threonine [28,29], monohydrated L-asparagine [30] and L-alanine [10]. The coupling of the four zwitterions in the unit cell leads to 297 optical normal modes decomposed into irreducible representations of the factor group  $D_2$  as  $\Gamma_{\text{op}} = 75A + 74(B_1 + B_2 + B_3)$  and the acoustic modes can be expressed as  $\Gamma_{\text{ac}} = B_1 + B_2 + B_3$ . Phonons with A symmetry are Raman active but infrared inactive; phonons with B<sub>1</sub>, B<sub>2</sub> and B<sub>3</sub> symmetries are both Raman and infrared active.

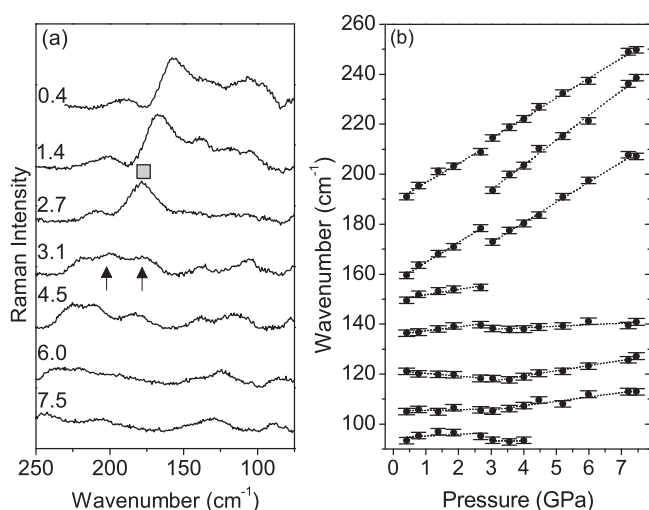
Fig. 1(a) shows the Raman spectra of LHICLM for selected pressure values on compression in the spectral range 250–80 cm<sup>-1</sup>. The peak wavenumbers were obtained by fitting the lineshapes with Lorentzian functions. In this region we expected to observe the

bands associated with lattice vibrations and internal modes with low wavenumber, for example, the torsional vibration of CO<sub>2</sub><sup>-</sup> unit,  $\tau(\text{CO}_2^-)$ , which is observed at 188 cm<sup>-1</sup> at ambient pressure. This region is known to be very sensitive to changes of the crystal symmetry when an external parameter is modified, even when almost no change in the high-wavenumber region is observed [4,31]. In fact, low-temperature experiments in the same crystal showed that it undergoes a structural phase transition between 140 and 110 K where only changes in the low-wavenumber region were observed [32].

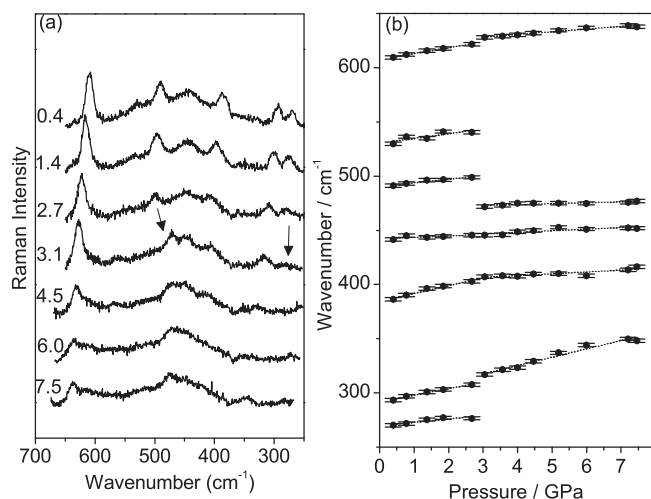
In Fig. 1(a), an important change occurs for pressure between 2.7 and 3.1 GPa. With increasing pressure, the mode marked by a square in the spectrum of 2.7 GPa is divided into two new bands, marked by up arrows, in the spectrum of 3.1 GPa. The splitting of  $\sim 16$  cm<sup>-1</sup> of this band is too large to be neglected and indicates a pressure-induced anomaly in the vibrational properties of the LHICLM crystal. After splitting of the band it continues as a double band up to the highest pressure obtained in our experiments. A similar splitting of a band associated with external mode was previously observed in the L-asparagine monohydrate crystal when subjected to high pressure hydrostatic conditions [33] or at low temperature conditions [34]. A quantitative analysis of the evolution of the Raman spectrum of LHICLM with pressure was performed by fitting all bands and the dependence of wavenumber versus pressure for this spectral region is shown in Fig. 1(b). In this plot the splitting of the mode with wavenumber of 188 cm<sup>-1</sup> is clear (error bars are shown for the experimental points). The strong pressure dependence of wavenumber of the  $\tau(\text{CO}_2^-)$  bands, as shown in Fig. 1(b), can be associated with the reduction of the intermolecular hydrogen bonds N–H...O, where N belongs to the imidazole ring or to the NH<sub>3</sub><sup>+</sup> group. One very interesting aspect we could observe in the same figure is the discontinuities of the wavenumber curves of all peaks. In the wavenumber versus pressure plots of Fig. 1(b), some discontinuities occur for pressure values higher than 3.1 GPa, with a mode changing from positive to negative and another from negative to positive slopes.

The set of changes in the low-wavenumber region of the Raman spectra when pressure is applied in the crystal [e.g. the discontinuity of the wavenumber curves and the splitting of the mode relative to a unit involved directly in hydrogen bonds] can be an indication that some change in structure is occurring for pressure values between 2.7 and 3.1 GPa. This assumption is reinforced by the results of Raman spectroscopy in the region of internal modes, presented below. In taurine crystal similar changes were observed when the crystal was subjected to high hydrostatic pressure (about 0.7 GPa). Some discontinuities of the wavenumber curve bands and the appearance of a phonon in the external mode region of the spectrum were associated with a phase transition undergone by the taurine crystal at about 0.7 GPa [35].

Raman spectra of LHICLM for several pressures in the 650–270 cm<sup>-1</sup> spectral region are shown in Fig. 2(a). In this region, many internal vibrations of the histidine molecule are found, among them vibrations of the skeletal structure (442 and 490 cm<sup>-1</sup>), torsion of NH<sub>3</sub><sup>+</sup> (385 cm<sup>-1</sup>) and rocking of CO<sub>2</sub><sup>-</sup> (530 cm<sup>-1</sup>) [32]. Some modifications in this region are observed in the range 2.7–3.1 GPa: (i) the disappearance of the bands at 276 and 500 cm<sup>-1</sup> and (ii) the appearance of a new band at 473 cm<sup>-1</sup> in the spectrum taken at 3.1 GPa. The disappearance of the band at 490 cm<sup>-1</sup> can be related to a change in the conformation of the L-histidine molecule in the crystal. It is interesting to note that the intensity of the band associated to torsion of NH<sub>3</sub><sup>+</sup> decreases with increasing pressure, also indicating that there may be a conformational change of histidine molecule, what can be understood as consequence of the change of the intermolecular hydrogen bond length. A similar phenomenon was observed in the L-threonine single crystal at high pressure [36], where bands between 300 and



**Fig. 1.** (a) Raman spectra of the LHICLM crystal for selected pressures (in GPa) in the spectral region 250–80 cm<sup>-1</sup>; (b) wavenumber versus pressure of Raman modes of LHICLM in the spectral region 250–80 cm<sup>-1</sup>.

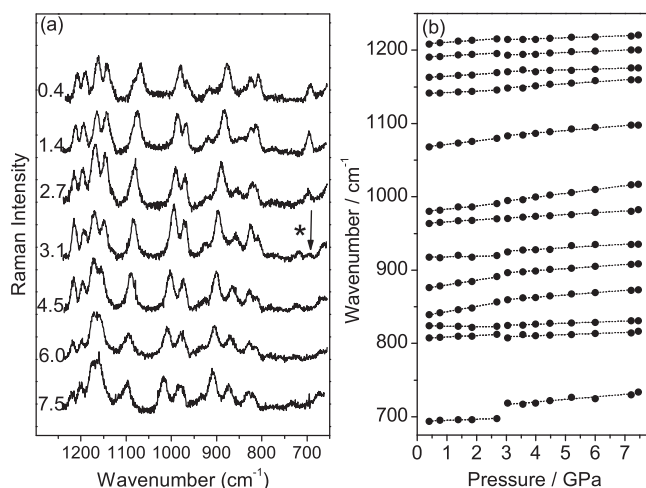


**Fig. 2.** (a) Raman spectra of the LHICLM crystal for selected pressures (in GPa) in the spectral region 650–270  $\text{cm}^{-1}$ ; (b) wavenumber versus pressure of Raman modes of LHICLM in the spectral region 650–270  $\text{cm}^{-1}$ .

500  $\text{cm}^{-1}$  show a decrease in intensity with increase in pressure. It is possible that the band of LHICLM observed at 530  $\text{cm}^{-1}$ , in the spectrum taken at 0.4 GPa, is present for pressure values greater than 2.7 GPa, but it is not visible due to its low intensity.

Fig. 2(b) presents the pressure evolution of the wavenumber of modes appearing in Fig. 2(a); error bars are shown for all experimental points. From this figure, a clear discontinuity of the wavenumber curve of bands at 318 and 629  $\text{cm}^{-1}$  is observed for pressures between 2.7 and 3.1 GPa. With increasing pressure, the band initially at 385  $\text{cm}^{-1}$ , which is associated with a torsion vibration of the  $\text{NH}_3^+$  unit, shifts linearly toward higher wavenumbers thereby showing a behavior in some ways similar to that of taurine [35] and L-threonine [36]. Based on this comparison, we can say that the pressure decreases the length of the hydrogen bonds, increasing the wavenumber of the band associated to torsional vibration of  $\text{NH}_3^+$  unit. It is important to mention that the modifications observed in this region occur at pressures that agree well enough with those observed in the spectral region 80–250  $\text{cm}^{-1}$ . One interesting aspect is that the wavenumber of the bands associated with vibrations of the skeletal structure (442 and 490  $\text{cm}^{-1}$ ) are less sensitive to pressure changes. This is expected because these bands are not directly related to hydrogen bonds.

Fig. 3(a) shows the Raman spectra of LHICLM crystal in the spectral range 1250–670  $\text{cm}^{-1}$  for selected pressure values. In this region, one expects to observe vibrations assigned to the deformation of  $\text{CO}_2^-$ , stretching of C–C and C–N, wagging of  $\text{H}_2\text{O}$  and rocking of  $\text{NH}_3^+$ , among others [32]. The band observed at  $\sim 694 \text{ cm}^{-1}$  is associated to a deformation vibration of  $\text{CO}_2^-$ ,  $\delta(\text{CO}_2)$ , while the out-of-plane vibration of  $\text{CO}_2^-$ ,  $\gamma(\text{CO}_2)$ , is observed at  $\sim 822 \text{ cm}^{-1}$ . The band at 807  $\text{cm}^{-1}$  is associated with a wagging vibration of the water molecule,  $w(\text{H}_2\text{O})$  [32]. Bands at 1191 and 1210  $\text{cm}^{-1}$  can be assigned as the rocking of  $\text{NH}_3^+$  unit,  $r(\text{NH}_3^+)$  [31,37]. In this spectral region, some changes are observed in the range 2.7–3.1 GPa: (i) the disappearance of the band at 694  $\text{cm}^{-1}$  (marked by a down arrow in the Fig. 3(a)); (ii) the appearance of a new weak band at 717  $\text{cm}^{-1}$  (marked by a star in the same figure); (iii) the inversion of intensity of the two bands located at 807 and 822  $\text{cm}^{-1}$  which are related to units directly involved in the hydrogen bonds and (iv) the inversion of intensity of the two bands associated to a rocking of  $\text{NH}_3^+$  unit,  $r(\text{NH}_3^+)$ , located at 1191 and 1210  $\text{cm}^{-1}$ . The dependence of the wavenumber versus pressure plot for this spectral region is presented in Fig. 3(b); in this figure the error bars are enclosed into the dot symbols. From the Fig. 3(b) we see that many

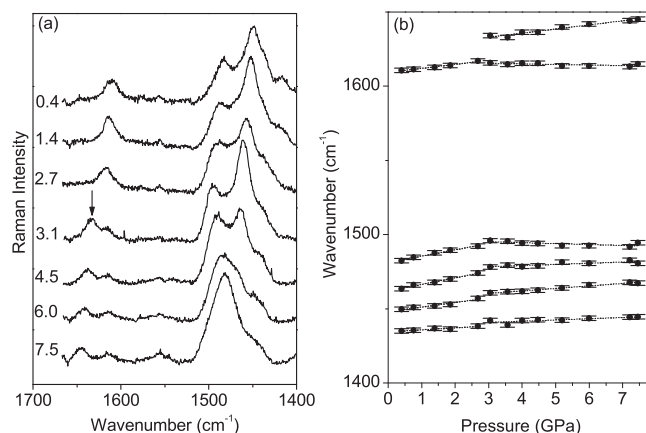


**Fig. 3.** (a) Raman spectra of the LHICLM crystal for selected pressures (in GPa) in the spectral region 1250–670  $\text{cm}^{-1}$ ; (b) wavenumber versus pressure of Raman modes of LHICLM in the spectral region 1250–670  $\text{cm}^{-1}$ .

of the observed Raman modes show a small discontinuous change in the slope in the pressure-induced variation of its wavenumber in range 2.7–3.1 GPa.

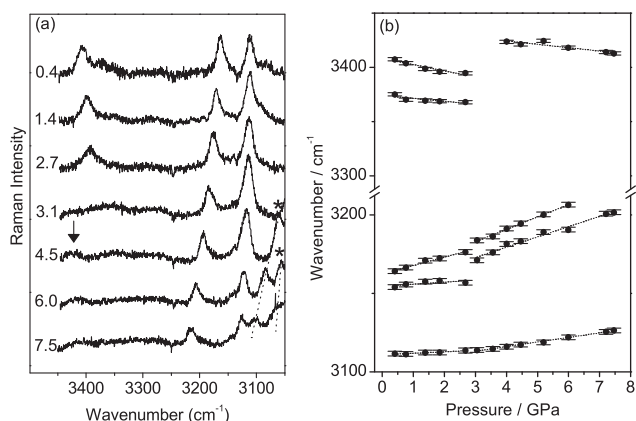
Fig. 4(a) shows the Raman spectra of the LHICLM crystal in the spectral range 1670–1400  $\text{cm}^{-1}$  for selected pressure values, and in Fig. 4(b) the respective wavenumber versus pressure plots are given, with error bars for the experimental points. In this region, one expects to observe vibrations assigned to a deformations of the imidazole ring of the histidine molecule, asymmetric stretching of the  $\text{CO}_2^-$  units, stretching of C=O, among others [32]. In Fig. 4(a) two modifications are observed in the range 2.7–3.1 GPa: (i) the decreasing of the relative intensity of the band originally at 1433  $\text{cm}^{-1}$  and (ii) the appearance of a band at 1642  $\text{cm}^{-1}$  (marked with an arrow). In the wavenumber versus pressure plot of Fig. 4(b), a subtle discontinuity occurs in the range 2.7–3.1 GPa, with appreciable differences in slopes, where two modes change from positive to negative slopes.

The Raman spectra of LHICLM crystal in the range 3450–3070  $\text{cm}^{-1}$  are shown in Fig. 5(a) and in Fig. 5(b) the respective wavenumber versus pressure plots are given. In this region, we expected to observe stretching vibrations of several units of the amino acids and of the water molecule ( $\text{CH}$ ,  $\text{NH}_3^+$  and  $\text{OH}^-$ ) [32]. It is important to note that for wavenumbers lower than 3000  $\text{cm}^{-1}$  there are some modes related to the mineral oil



**Fig. 4.** (a) Raman spectra of the LHICLM crystal for selected pressures (in GPa) in the spectral region 1670–1400  $\text{cm}^{-1}$ ; (b) wavenumber versus pressure of Raman modes of LHICLM in the spectral region 1670–1400  $\text{cm}^{-1}$ .

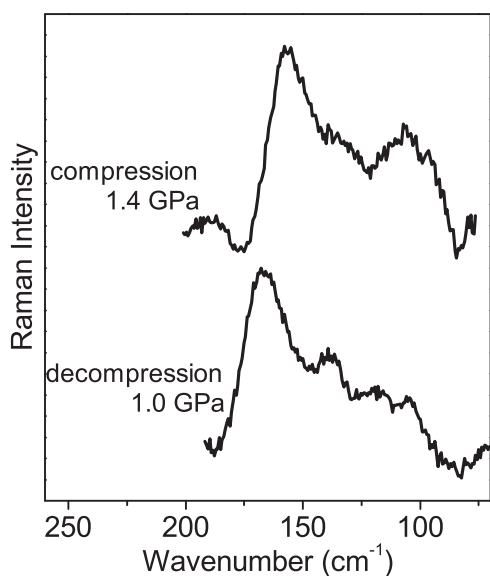




**Fig. 5.** (a) Raman spectra of the LHICLM crystal for selected pressures (in GPa) in the spectral region 3450–3050  $\text{cm}^{-1}$ ; (b) wavenumber versus pressure of Raman modes of LHICLM in the spectral region 3450–3050  $\text{cm}^{-1}$ . The band appearing in the spectrum taken at 4.5 GPa (marked by an asterisk) and that splits at 6.0 GPa is originated from the mineral oil compression media.

used as compression media; the peaks marked by asterisks in the spectra at high pressures are originated from mineral oil. In detail, the band at 3111  $\text{cm}^{-1}$  can be associated to a stretching vibration of  $\text{NH}_3^+$  unit,  $\nu(\text{NH}_3^+)$ , while the bands observed at 3155 and 3163  $\text{cm}^{-1}$  are associated to a CH stretching vibration of imidazole ring. The bands observed at 3374 and 3408  $\text{cm}^{-1}$  is related to the  $\text{OH}^-$  stretching of the water molecules. In this spectral region, for the range 2.7–3.1 GPa, the main changes are the following: (i) the disappearance of the bands related to a  $\text{OH}^-$  stretching vibration (initially located at 3367 and 3393  $\text{cm}^{-1}$ ); (ii) the appearance of a band of weak intensity at 3424  $\text{cm}^{-1}$  (marked with an arrow) and (iii) the discontinuity of the wavenumber curve of bands at 3155 and 3163  $\text{cm}^{-1}$ , which are associated with a CH stretching vibration.

In Fig. 6 we show, in order to investigate the reversibility of the phase transition, the spectra obtained in the compression (at 1.4 GPa) and after decompression (at 1.0 GPa). When the pressure is released back to 1.0 GPa, the spectrum observed (top panel of Fig. 6) is qualitatively the same obtained at 1.4 GPa (bottom panel of Fig. 6), showing that the pressure-induced anomalies are reversible.



**Fig. 6.** Raman spectra obtained in the compression (at 1.4 GPa) and after decompression (at 1.0 GPa).

A quantitative analysis of the evolution of the Raman spectra of LHICLM crystal with pressure was performed by fitting all bands to a linear expression:  $\omega = \omega_0 + \alpha \cdot P$ . The pressure coefficients,  $\omega_0$  and  $\alpha$ , are listed in Table 1. In this table, the first column ( $\omega_{\text{obs}}$ ) represents the wavenumber of the Raman bands as observed at room pressure, the second and third columns correspond to adjustment of data for pressure values between 0 and 2.7 GPa and the two last columns correspond to adjustment of the high-pressure phase (pressure values between 3.1 and 7.5 GPa).

Pronounced changes in the Raman spectra of the LHICLM crystal were observed in all spectral regions. The modifications include wavenumber shifts with discontinuities, changes in the relative intensities of the vibrational bands, splitting of the band in the low-wavenumber lattice range (188  $\text{cm}^{-1}$  at ambient pressure) and change in the number of bands associated to internal modes (Figs. 2–5). Some changes were observed for the deformation vibrations of the  $\text{OH}^-$  (water molecule),  $\text{NH}_3^+$  and  $\text{CO}_2^-$  groups, as well as for the skeletal vibrations, indicating large conformational changes of the molecules in the unit cell, as observed for DL-serine crystal under high pressure conditions [38].

In the crystal structure of LHICLM five atoms per histidine molecule are available for the formation of hydrogen bonds. Such bonds are the main responsible for the constitution of the crystalline three-dimensional network [39]. The effect of high pressure on the hydrogen bonds can be understood by the observation of bands associated to the hydrogen bonds. It is worth to note that, as discussed with the results presented in Fig. 1, the dependence of wavenumber of  $\tau(\text{CO}_2^-)$  bands could be associated with the reduction of  $\text{N-H} \cdots \text{O}$  hydrogen bond. The behavior of the torsion of  $\text{NH}_3^+$ , as pointed out in the discussion of Fig. 2, indicated a conformational change of histidine molecule that has as consequence, change of the intermolecular hydrogen bond length. It was also very interesting to note that the wavenumber of bands associated with vibrations of the skeletal structure were less sensitive to compression because they were not directly related to hydrogen bonds. Additionally, from the discussion of Fig. 3 we noted an inversion of bands associated to wagging of  $\text{H}_2\text{O}$  and out-of-plane vibration of  $\text{CO}_2^-$ , which were related to units involved in the hydrogen bonds.

In LHICLM, beyond the hydrogen bonds originated from the histidine molecule, there are two hydrogen bonds from the water molecule [39]. In Fig. 5(b) we observe that the wavenumber of  $\text{OH}^-$  stretching,  $\nu(\text{OH}^-)$ , decreases with increasing pressure. Because the  $\text{OH}^-$  units participate of hydrogen bonds, one to a carboxyl oxygen e another to the chloride ion, this means that between 0.0 and 3.1 GPa the hydrogen bond strength increases (the wavenumber of  $\nu(\text{OH}^-)$  decreases in this pressure range). Also, after the phase transition, the wavenumber of  $\nu(\text{OH}^-)$  suffers a jump and continues to decrease up to the highest pressure obtained in our experiments: this points again to a further increase of the hydrogen bonds formed by the water molecules.

Remember that each set of histidine, HCl and water molecule can form seven hydrogen bonds. Because the modifications observed in the Raman spectra are related to bands associated to units involved in the hydrogen bonds, certainly, as occur with other amino acid crystals, these bonds are playing an important role in the mechanism of the transition (and must be investigated by others techniques). It is interesting to note that similar changes in the low-wavenumber region were also observed for the same crystal, when subjected to low temperatures. However, in the transition undergone by the crystal at low temperatures, the Raman spectra for the region of internal modes do not present large changes [32]. Similar behavior was observed in L-asparagine monohydrate, which presents the splitting of a mode (in the low-wavenumber region) when subjected to high hydrostatic pressure (the first transition undergone with the variation of this thermodynamic parameter) or at low temperatures [33,34]. Summarizing, it is clear that LHICLM

**Table 1**  
Atmospheric pressure wavenumber values of the bands appearing in Figs. 1–5 ( $\omega_{\text{obs}}$ ) and adjustment data by linear fitting ( $\omega = \omega_0 + \alpha \cdot P$ ) for the two phases observed.

$\omega_{\text{obs}}$ (cm <sup>-1</sup> )	Phase 1 ( $0 \leq P \leq 2.7$ GPa)		Phase 2 ( $3.1 \leq P \leq 7.5$ GPa)	
	$\omega_0$ (cm <sup>-1</sup> )	$\alpha$ (cm <sup>-1</sup> )/(GPa) <sup>-1</sup>	$\omega_0$ (cm <sup>-1</sup> )	$\alpha$ (cm <sup>-1</sup> )/(GPa) <sup>-1</sup>
94	94.5	0.669	93.7	-0.103
105	105.2	0.276	100.2	1.771
121	121.4	-1.087	110.9	2.092
136	135.7	1.616	136.0	0.623
149	149.7	2.128	–	–
159	156.8	8.033	148.3	8.105
–	–	–	163.9	9.960
188	189.1	7.661	190.2	8.059
270	269.7	3.093	–	–
293	291.9	6.118	294.5	7.683
385	384.6	7.236	401.5	1.675
442	442.3	1.223	442.3	1.461
–	–	–	470.7	0.785
491	490.5	3.319	–	–
530	530.4	4.335	–	–
609	607.8	5.312	620.8	2.463
693	693.5	1.529	–	–
–	–	–	706.4	3.449
807	806.7	2.042	804.7	1.467
824	824.0	-0.498	820.4	1.442
838	836.1	7.335	850.4	3.124
875	873.4	6.438	888.1	2.777
917	917.3	0.810	918.7	2.356
963	963.0	2.757	963.6	2.411
980	978.7	4.489	978.7	5.206
1068	1066.7	4.790	1073.2	3.418
1141	1140.3	1.890	1140.3	2.744
1162	1161.9	2.611	1167.4	1.120
1190	1190.0	2.277	1188.5	1.637
1208	1207.9	2.859	1210.1	1.341
1434	1434.5	1.316	1438.2	0.846
1448	1448.1	3.059	1455.4	1.677
1463	1462.1	4.415	1476.0	0.778
1481	1481.3	4.238	1497.0	-0.619
1609	1609.3	2.739	1616.6	-0.374
–	–	–	1624.9	2.736
3111	3111.0	0.919	3104.5	2.914
3154	3154.6	1.287	3153.2	6.564
3164	3162.6	5.305	3159.3	7.905
3375	3373.9	-2.638	–	–
3407	3408.1	-5.745	–	–
–	–	–	3437.1	-3.169

crystal displays a phase transition induced by pressure, although the nature of the high-pressure phase requires further structural studies, e.g. by diffraction techniques.

#### 4. Conclusions

A study of the Raman spectra as a function of hydrostatic pressure was performed in the crystal of LHICLM. The experiments were performed in the spectral range between 3450 cm<sup>-1</sup> and 30 cm<sup>-1</sup> at pressures up to 7.5 GPa. The changes observed in Raman bands in different regions of the spectrum, show a transition undergone by the crystal of LHICLM between 2.7 GPa and 3.1 GPa. The results obtained after decompression indicates that the phase transition is reversible. The pressure coefficients for all modes observed in this work were given.

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