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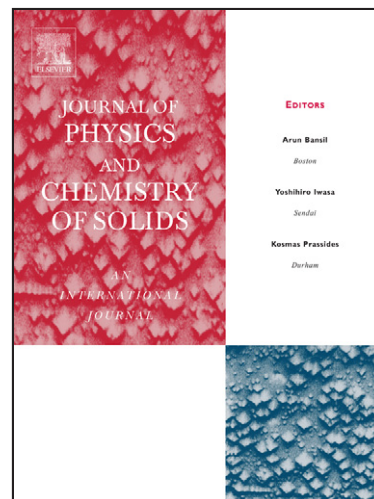
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Pressure-induced phase transformations in L-alanine crystals

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Abstract

Raman scattering and synchrotron X-ray diffraction have been used to investigate the high-pressure behavior of L-alanine. This study has confirmed a structural phase transition observed by Raman scattering at 2.3 GPa and identified it as a change from orthorhombic to tetragonal structure. Another phase transformation from tetragonal to monoclinic structure has been observed at about 9 GPa. From the equation of state, the zero-pressure bulk modulus and its pressure derivative have been determined as (31.5 ± 1.4) GPa and 4.4 ± 0.4 , respectively.

Key words:

- A. Organic compounds.
- C. High pressure.
- C. Raman spectroscopy.
- C. X-ray diffraction.
- D. Phase transitions.

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Introduction

Amino acids are among the most important molecules of the living organisms not only because they are the basic blocks of the protein molecules, but also because they have a relatively simple structure compared with other bio-molecules. Consequently, they are used as model systems for a large number of important processes in biochemistry. Moreover, studies of amino acid crystals can give information about the long-range interaction between molecules in the zwitterion form [1], shed light on the nature of hydrogen bonds in biologically important substances [2], and assist in designing supramolecular devices [3].

L-alanine [$\text{C}_2\text{H}_4(\text{NH}_2)\text{COOH}$] is the smallest naturally occurring chiral amino acid and, as a consequence, many of its physical and chemical properties have been studied. For example, the structure of L-alanine at ambient conditions has been determined by X-ray diffraction (XRD) [4], and its vibrational spectra have been investigated [1, 5–8]. These studies have unveiled interesting and, to some extent, surprising results. Among them we may mention an unusual temperature dependence of the energy of the infrared band related to the torsion of NH_3^+ group [1, 7], the negative thermal expansion along the *c*-axis [9], the non-linear temperature dependence of the intensities of Raman modes located at about 42 and 49 cm^{-1} , which are associated with a dynamic localization of vibrational energy [10], the unusual thermal conductivity [11], the unusual low-temperature symmetry breaking observed by birefringence [12] as well as NMR experiments [13], but not yet confirmed by XRD [9].

While some of these questions are yet open, others can be understood if one considers two points. The first one is the existence of a strong dynamic Jahn-Teller effect due to the NH_3^+ charge-lattice coupling [14]. The second point is the fact that the L-alanine crystal has a complex structure formed by molecules joined together by means of intermolecular hydrogen bonds. Such bonds are relatively easy to be changed when the external conditions (temperature or pressure) are modified. As a consequence, it is possible, for example, to correlate the strength of hydrogen bonds in the structure with the anisotropy of thermal expansion [15]. Also, high-pressure conditions can induce several polymorphs like those observed in monohydrated L-asparagine [16], L-serine [17] and glycine [18]. In particular, previous high-pressure, Raman-scattering experiments on L-alanine have indicated a structural phase transformation at about 2.3 GPa [19].

The goal of the present work is to investigate the equation of state and possible pressure-induced phase transitions in L-alanine crystals using synchrotron X-ray diffraction (XRD). As the results will show, the XRD study confirms the structural phase transition at 2.3 GPa, mentioned above, and identifies it as a transition from an orthorhombic to a tetragonal structure. Moreover, the present results will shed light on the high-pressure structural behavior of L-alanine up to 12 GPa, including another transformation to a monoclinic phase at about 9 GPa.

Experimental procedures

L-alanine crystals were grown from an aqueous solution maintained at controlled temperature as reported previously [19]. Room temperature, high-pressure synchrotron XRD spectra were recorded at HASYLAB-DESY in Hamburg, Germany. The diffractometer, working in the energy-dispersive mode, has been described elsewhere [20]. High pressures were obtained in a Syassen-Holzapfel type diamond-anvil cell [21]. A powdered sample and a ruby chip as a pressure marker were placed in a hole with diameter 200 μm in an Inconel gasket, pre-indented to a thickness of 60 μm . A 16:3:1 methanol: ethanol: water mixture was used as the pressure-transmitting medium. The pressure was determined by the ruby luminescence method, applying the non-linear pressure scale of Mao et al. [22]. The Bragg angle of each run was calculated from a zero-pressure spectrum of sodium chloride (NaCl) replacing the sample in the diamond-anvil cell.

XRD spectra were recorded at pressures up to 12 GPa. At each pressure, values for the lattice parameter and the unit-cell volume were derived and refined using standard crystallographic techniques and the PURUM code [23]. The compression curve could then be described by the Birch-Murnaghan equation of state [24, 25]:

$$P = \frac{3}{2} B_0 (x^{-7/3} - x^{-5/3}) \left[1 - \frac{3}{4} (4 - B_0') (x^{-2/3} - 1) \right], \quad (1)$$

where $x = V/V_0$, V is the volume at pressure P , and V_0 is the volume at zero pressure; B_0 is the bulk modulus and B_0' its pressure derivative, both parameters evaluated at zero pressure. Values for B_0 and B_0' were obtained from a non-linear least-squares fit of Equation (1) to the experimental pressure-volume data points.

Results and discussion

Raman scattering

Before discussing the XRD results, we will summarize the previous high-pressure Raman scattering data for L-alanine crystals [19]. The four zwitterionic molecules of L-alanine in the unit cell give rise to 153 optical modes distributed among the irreducible representations of the point group as follows: $39 A + 38 B_1 + 38 B_2 + 38 B_3$. From these modes, 21 are associated with lattice vibrational modes (expected to be observed below 180 cm^{-1}), while 132 modes are associated with internal vibrational modes [1]. Therefore, the six Raman bands (labeled A to F) are assigned as lattice modes, being peaks A and D associated with N-H...O vibrations.

Fig. 1 shows the frequency vs. pressure plot for the low-frequency Raman modes in L-alanine crystals. The insert presents the Raman spectrum of L-alanine at 2.84 GPa in the spectral region $40\text{--}180 \text{ cm}^{-1}$. The peaks A and B are associated with the normal modes with lowest energy for L-alanine (42 and 49 cm^{-1} at atmospheric pressure). These bands are those that presented the interesting effect of dynamic localization of vibrational energy: the sum of the intensities obeys Maxwell-Boltzmann statistics in the $20\text{--}340 \text{ K}$ temperature range, while the individual intensities do not [10]. Their intensities also change with increasing pressure, but neither splitting nor any jump in frequency was observed. The peak C is a band of low intensity barely observed in some scattering geometries; its frequency changes slightly with pressure in the $0\text{--}3 \text{ GPa}$ interval.

The peaks D and E have a small splitting in frequency at ambient conditions. When pressure is increased, the frequency dependence of these two bands is very diverse as can be seen in Fig. 1. In particular, it is clearly observed that the pressure derivative of the frequency, $d\nu/dP$ is larger for peak E than for peak D. The band observed at atmospheric pressure at 140 cm^{-1} , among those of low frequency, presents the largest $d\nu/dP$ value in the studied pressure range. It is also important to state that although this band has a large linewidth and, in principle, could be identified as being a second-order vibrational mode (such as combination mode), it is associated with a lattice vibrational mode as established in Ref. [1].

Visual inspection of the Fig. 1 allows us to discriminate the most important aspect of the pressure dependent Raman measurements in L-alanine: the splitting of band E for pressures higher than 2.2 GPa. The new peak, (labeled as G), is marked by an arrow in the insert. The splitting of a low-frequency band can be associated with a change in the symmetry of the unit cell, i.e. a change in translational symmetry. In other words, the Raman-scattering data indicate that the sample undergoes a structural phase transformation at about 2.3 GPa.

X-ray diffraction

At ambient conditions, L-alanine crystallizes in an orthorhombic structure with space group $P2_12_12_1$ (#19) and four molecules per unit cell. The unit-cell parameters are $a_0 = 6.032(1)$, $b_0 = 12.343(1)$, and $c_0 = 5.784(1)$ Å [4]. Figures 2a–c are examples of x-ray diffraction spectra of L-alanine at ambient conditions, at 2.8 GPa and at 10.4 GPa, respectively. It is satisfying to notice that it has been possible to obtain a diffraction spectra of reasonable quality in spite of the weak X-ray scattering power of a low- Z compound such as L-alanine. The large background and the low resolution of the energy-dispersive method have been compensated by background subtraction, escape-peak correction and deconvolution using the maximum-entropy method [26].

At high pressure, the 110/011 and 120/021 doublets of the orthorhombic structure are merging into single peaks. Although barely visible in the raw data (Fig. 2a), the doublets are clearly resolved in peak-profile analysis. The merging of the doublets is suggesting that the sample undergoes a structural phase transformation from orthorhombic to tetragonal symmetry. At still higher pressure, new diffraction lines appear, indicating another structural change to lower symmetry. The phase transformations are more clearly seen when plotting the evolution of the lattice plane spacing as a function of pressure (Fig. 3). It is seen that the merging of the 110/011 and 120/021 doublets of the orthorhombic structure is completed at about 2.3 GPa. Above this pressure, the structure of L-alanine is tetragonal. The results for the orthorhombic to tetragonal transition are summarized in figure 4 showing the lattice parameters as function of pressure. The c/a ratio for the tetragonal unit cell is found to be practically independent on pressure, $c/a = 2.11(2)$.

It follows from above that the structural phase transformation indicated by Raman scattering at about 2.3 GPa has been confirmed by X-ray diffraction and identified as a change from orthorhombic to tetragonal symmetry. Upon further compression, it is found that new diffraction peaks are appearing at about 9 GPa (Fig. 3), indicating another phase transformation to a lower symmetry. Using the PowdMult code [27], the diffraction peaks of the high-pressure phase above 9 GPa could be indexed, assuming a monoclinic unit cell. Table 1 shows the observed and calculated d values for the monoclinic phase at 10.4 GPa. At this pressure, the lattice parameters are $a = 10.159(18)$, $b = 4.757(12)$, $c = 7.282(13)$ Å, and $\beta = 100.67(15)^\circ$. The uncertainties in parentheses are the standard errors of the fit, in units of the last decimal place. The goodness of the fit can be expressed as

$$\frac{\sum |d_{\text{obs}} - d_{\text{calc}}|}{\sum d_{\text{obs}}} = 2.1 \times 10^{-3}. \quad (2)$$

This value is quite satisfying, considering the difficult diffraction conditions mentioned above.

The resolution of the energy-dispersive method, used in the present work, generally does not allow any determination of the atomic positions and hence the space group of the observed high-pressure phases. However, it can be concluded that the unit cells of the high-pressure phases are tetragonal and monoclinic distortions of the original orthorhombic unit cell. Thus, both the tetragonal and the monoclinic unit cells contain four molecules like the original orthorhombic unit cell.

Figure 5 shows the unit-cell volume as a function of pressure up to 12 GPa, i.e. the compression curve of L-alanine. It is seen that there is practically no volume change at the orthorhombic-to-tetragonal phase transition. The compression curve for these two phases can therefore be described by a single equation of state. A least-squares fit of the Birch-Murnaghan equation (1) to the experimental pressure-volume data points gives the zero-pressure bulk modulus $B_0 = 31.5 \pm 1.4$ GPa, and its pressure derivative $B_0' = 4.4 \pm 0.4$. For the monoclinic phase there are too few experimental data points to determine the

equation of state. Upon decompression the sample reverts to the original state, but more work is needed to clarify the chemical stability of the high-pressure phases.

To our best knowledge there is no published value of the bulk modulus for L-alanine to compare the present result with. However, it may be mentioned that the bulk modulus for L-serine is about 37 GPa [17], which is about the same value as we report for L-alanine in the present work. It is interesting to notice that L-serine II has the same space group $P2_12_12_1$ as orthorhombic L-alanine, and there is no volume change at the transition from L-serine II to L-serine III [17].

Conclusion

Synchrotron XRD has confirmed the structural phase transition in L-alanine, observed by high-pressure Raman scattering at about 2.3 GPa, and identified it as a transition from orthorhombic to tetragonal symmetry. Moreover, XRD has shown that there is another phase transformation of tetragonal-to-monoclinic nature at about 9 GPa. There is no volume discontinuity at the orthorhombic-to-tetragonal transitions. The high-pressure behavior of the orthorhombic and tetragonal phases can therefore be described by a single equation of state. The bulk modulus of L-alanine is 31.5 ± 1.4 GPa, and its pressure derivative is 4.4 ± 0.4 . The present work has provided new knowledge about structural parameters of L-alanine crystals that will be useful for feeding back into theoretical models for describing the properties of amino acid crystals.

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Table 1. Observed and calculated d spacing for monoclinic L-alanine at 10.3 GPa. The Miller indices are denoted h , k and l . The lattice parameters are $a = 10.159(18)$, $b = 4.757(12)$, $c = 7.282(13)$ Å, and $\beta = 100.67(15)^\circ$.

$h k l$	d_{obs} (Å)	d_{calc} (Å)
2 0 0	4.9938	4.9916
1 1 0	4.3079	4.2946
0 1 1	3.9558	3.9616
2 0 1	3.7960	3.7787
$\bar{1}$ 0 2	3.5926	3.5855
1 0 2	3.1714	3.1859
2 1 1	2.9579	2.9589
3 1 0	2.7187	2.7268
$\bar{3}$ 0 2	2.6895	2.6986
$\bar{4}$ 0 1	2.5074	2.5053
3 1 1	2.4269	2.4284
3 0 2	2.2342	2.2387
$\bar{2}$ 1 3	2.0951	2.0898
$\bar{3}$ 1 3	1.9475	1.9477

Figure Captions

Fig 1. Pressure dependence of the low frequency Raman modes for L-alanine. The dotted vertical line at 2.3 GPa indicates approximately the transition pressure. The insert shows a typical Raman spectrum of L-alanine at 2.84 GPa. The features A–G are discussed in the text.

Fig. 2. Energy dispersive X-ray diffractogram of L-alanine. The Bragg angle is $\theta = 4.43^\circ$.

a) At ambient pressure. The main peaks are indexed. The vertical bars below the spectrum are showing the calculated peak positions assuming an orthorhombic unit cell with space group $P2_12_12_1$.

b) At pressure 2.8 GPa showing the tetragonal phase. The dip at 24 keV is an artifact of the detector.

c) At pressure 10.4 GPa showing the monoclinic phase.

Fig. 3. Evolution of the observed lattice plane spacing, d , as function of pressure. The horizontal bars at the left-hand side are showing the calculated d -values assuming an orthorhombic unit cell with space group $P2_12_12_1$. Note the merging of the 110/011 and 120/012 doublets of the orthorhombic structure.

Fig. 4. Unit-cell parameters of orthorhombic and tetragonal L-alanine as function of pressure.

Fig. 5. Compression of L-alanine. Experimental data points for the orthorhombic, tetragonal and monoclinic phases are indicated by solid squares, triangles and circles, respectively.

The full curve shows the fit of the Birch-Murnaghan equation to the experimental points for the orthorhombic and tetragonal phases.

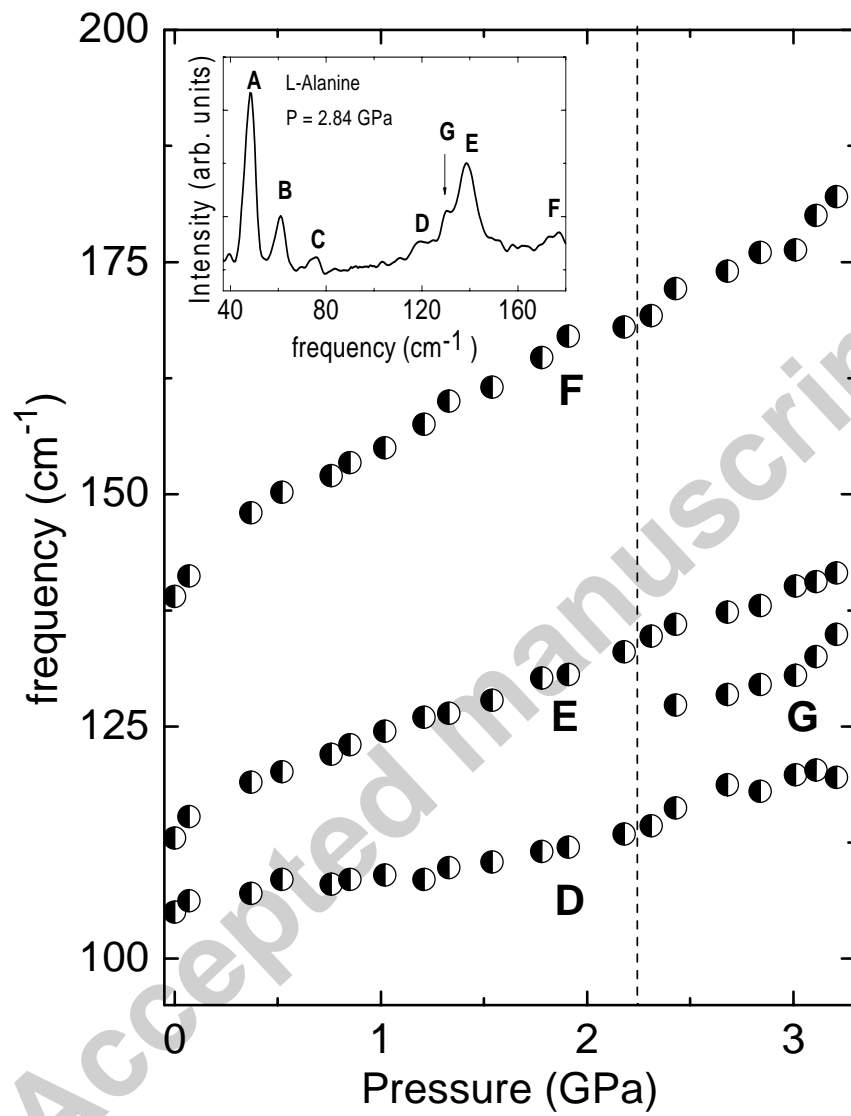


Fig 1.

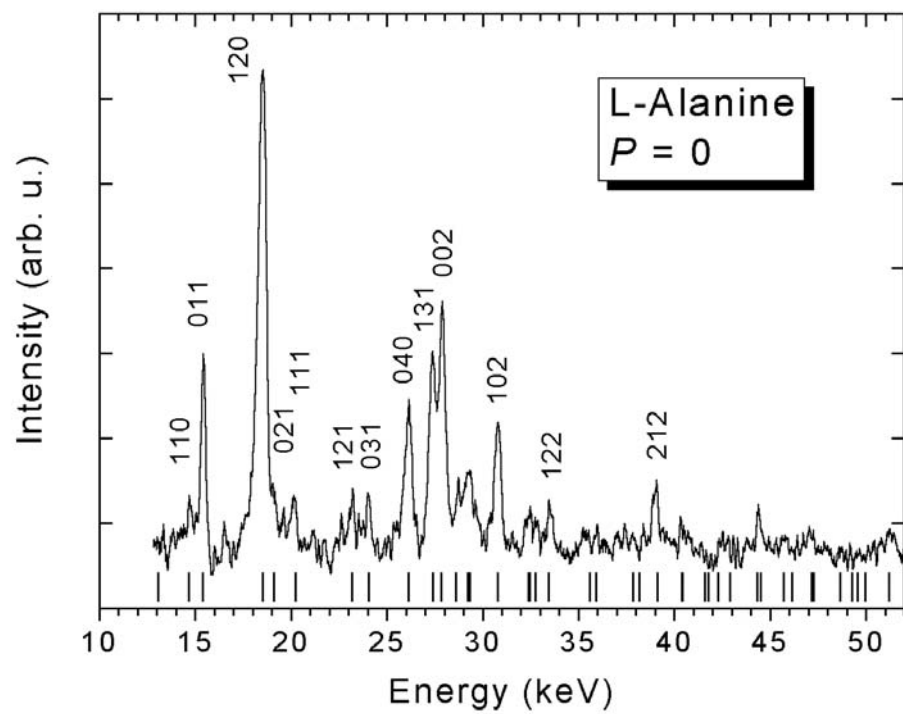


Fig. 2a.

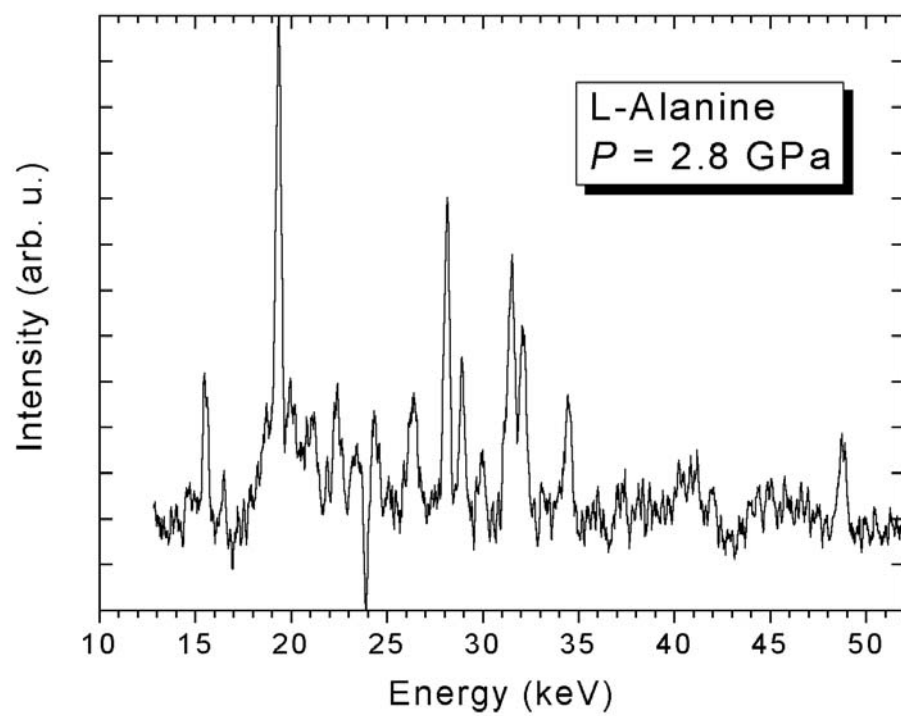


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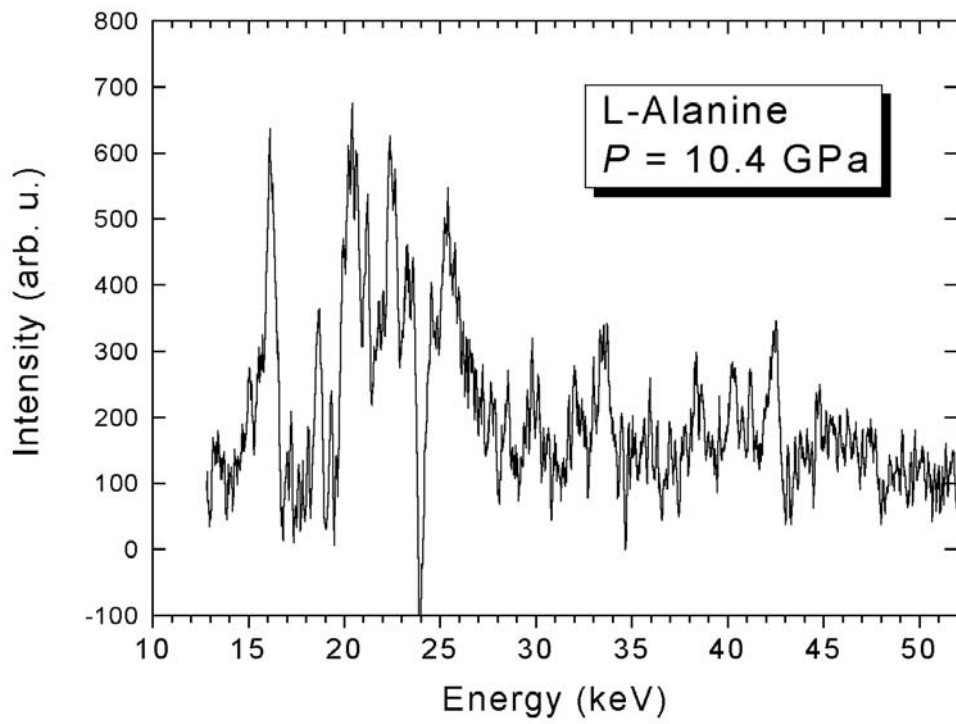


Fig. 2c.

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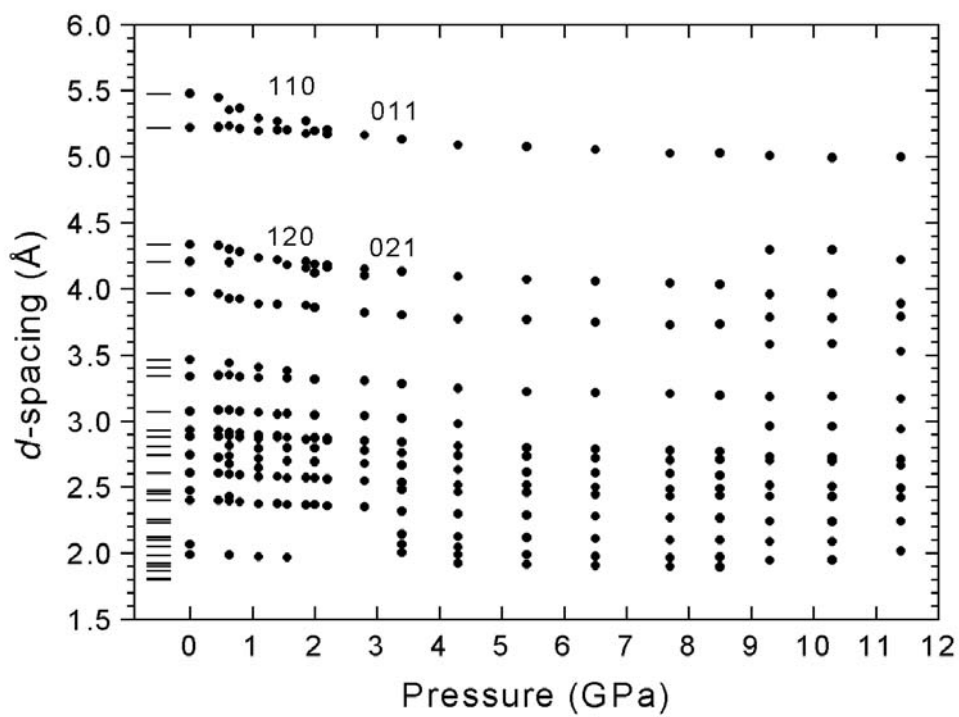


Fig. 3.

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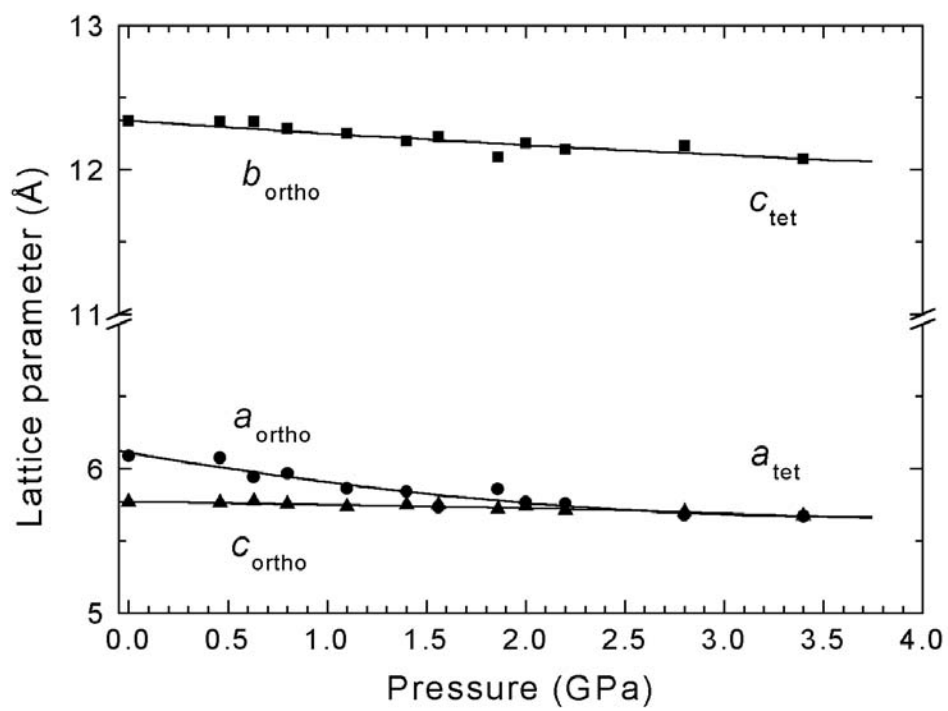


Fig. 4.

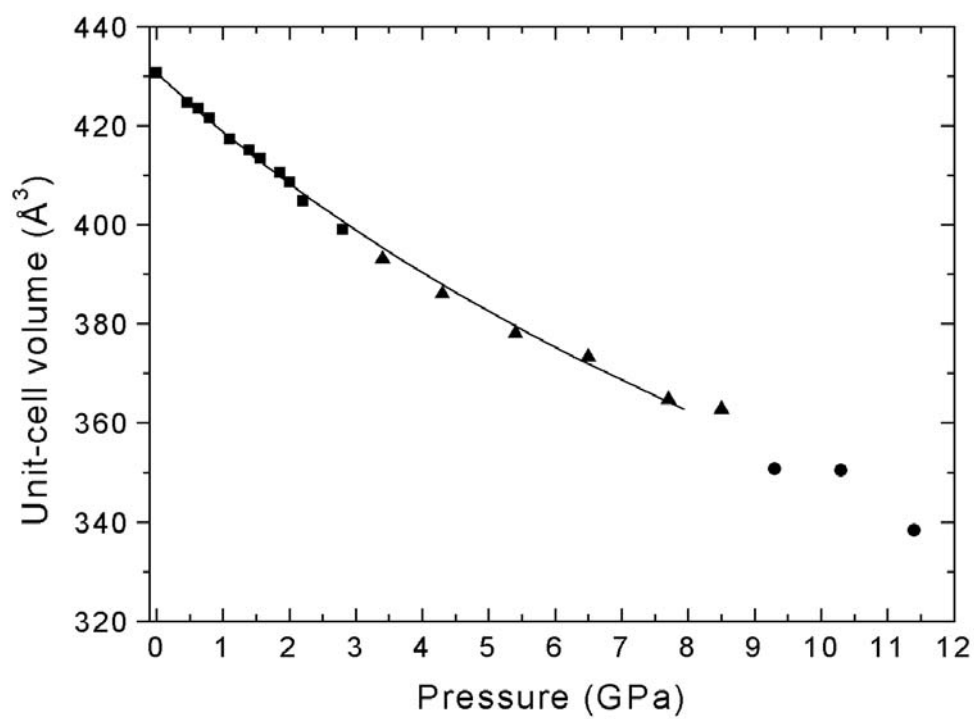


Fig. 5.

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