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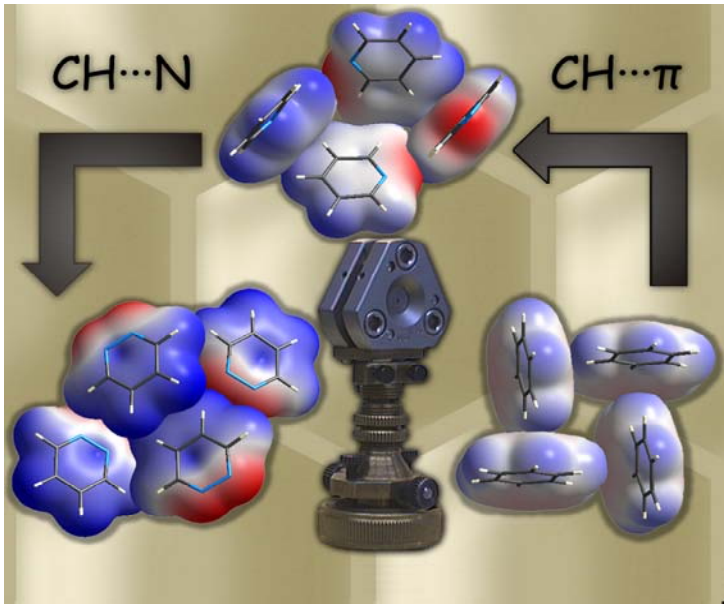

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Low temperature/high pressure polymorphism in DL-cysteine†

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We compare the response of the crystalline DL-cysteine to cooling and to increasing pressure. The structure undergoes a low-temperature phase transition into an isosymmetric polymorph, DL-cysteine-II, with the conformation of zwitterion changing from *gauche*− to *gauche*+. The first pressure-induced transition at 0.1 GPa (the lowest pressure reported for a phase transition in a crystalline amino acid thus far) gives the same polymorph. Further compression of DL-cysteine-II proceeds differently on cooling and with increasing hydrostatic pressure. DL-cysteine-II is preserved down to 3 K, but undergoes phase transitions on compression at about 1.55 GPa, and 6.20 GPa. The changes in the hydrogen bond network preceding the phase transition in DL-cysteine-II in the range 0.25–0.85 GPa differ from those observed on cooling the same structure, but resemble those preceding pressure-induced phase transitions in β- and γ-glycine.

Introduction

Importance of the problem

Variations in temperature and pressure are the two efficient tools in "crystal engineering", which are used for producing new polymorphs of compounds. Both temperature and pressure are scalars, and according to Neumann's principle the symmetry of the crystal structure response to changing temperature, or to hydrostatic compression, should depend solely on the symmetry of the crystal structure.[1,2] This does not necessarily mean that the anisotropy of structural strain on cooling and on hydrostatic compression must be similar, since there are many different ways to compress a low-symmetry structure not violating the Neumann's principle. For example, in a monoclinic structure, the only restriction imposed by the symmetry is that one of the principal axes of strain ellipsoid must coincide with the direction of the two-fold axis or be normal to the only mirror or glide plane.[1,2] At the same time, the structure may be the most compressible, or the most robust in this direction. There is even more "freedom" in all the other directions: any orientations of the remaining two principal axes of the strain ellipsoid are allowed, provided they remain orthogonal to each other and to the first principal axis.

The anisotropy of strain of a crystal is a structure-sensitive property. In the case of molecular crystals it is determined by the conformational flexibility of molecules and the interplay between the different types of multiple intermolecular interactions, some of which are specific and directional, whereas the other not. The studies of the anisotropy of strain can, therefore, serve as a tool of understanding the intermolecular interactions and structure-properties relations in molecular crystals.[3–6]

For cubic crystals the compression either on cooling, or at hydrostatic pressure is isotropic and can be characterized by a single parameter. The relation between the coefficients of thermal expansion and isothermal compressibility is given by Grüneisen equation.[2] For the crystals with lower symmetry, however, the bulk compressibility is no longer sufficient to characterize the structure compression. The bulk compression can be negligible, but at the cost of a considerable linear structure expansion in some directions, and structure compression in the other. The two crystal structures may have similar bulk compressibility but differ in the strain anisotropy. Numerous examples have been reviewed in ref. 3–5, 7.

The phases, which grow from the liquid phase (or crystallize from solution) on cooling or at high hydrostatic pressure are also often different (see ref. 8 for a recent review and numerous references therein). Understanding the reasons, why low-temperature and high-pressure phases are not the same, provides additional insight into the factors determining the crystal structures in general. The same holds for the phases formed as a result of solid-state low-temperature/high-pressure phase transitions from the same starting crystalline form.

The choice of the system

The effect of low temperatures/high pressures on the crystalline amino acids attracts a special interest since about a decade, and an overview of results achieved in this field has been given recently by several authors.[9–13] Various aspects of this research are related to comparing (i) the anisotropy of strain on cooling with that on hydrostatic compression and (ii) the stability of the same structure with respect to phase transitions on cooling and on hydrostatic compression.

The L-amino acids are studied much more extensively than their racemic DL-counterparts. L-/DL-serine seem to be the only exception. For this couple the anisotropy of strain and the phase transitions have been studied on cooling and with increasing

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pressure. Whereas two phase transitions on increasing pressure[14–18] and a continuous phase transition on cooling[19,20] were reported for L-serine, the DL-serine was shown to be stable with respect to phase transitions on variations of temperature and pressure.[19–21] The polymorphism of L-serine is related to the change in the intermolecular hydrogen bonding of the $–CH_2OH$ side chains—they can form O–H···O bonds either to the $–CH_2OH$ groups, or to the carboxylate $–COO^-$ groups of the neighbouring molecules in the structure. Cysteine can be considered as a structural analogue of serine, in which the oxygen atom in the side chain is substituted for the sulfur atom ($–CH_2SH$ replaces the $-CH_2OH$ side chain groups). This substitution results in a considerable change in the dynamics of the side chain. The intermolecular hydrogen bonds S–H···O and S–H···S are much weaker than the O–H···O bonds. As a consequence, the side chains in the crystals of cysteine are much more labile than those in the crystals of serine, and this has an effect on the stability of structures with respect to variations in temperature and pressure: the phase transitions are more numerous and the local energy minima are less pronounced. The monoclinic and the orthorhombic polymorphs of L-cysteine both undergo a sequence of phase transitions with increasing pressure.[22–24] Interestingly enough, although the monoclinic polymorph transforms into the orthorhombic form on grinding, the hydrostatic pressure does not induce any transformations between the monoclinic and the orthorhombic polymorphs, but each polymorph undergoes its own sequence of phase transitions at different pressures into different polymorphs. At the same time, the orthorhombic and to even a larger extent, the monoclinic polymorphs of L-cysteine are quite stable with respect to the phase transitions on cooling. An extended phase transition related to the partial re-orientation of the side $–CH_2SH$ chains in favour of the S–H···S hydrogen bonds at low temperatures has been reported for the orthorhombic polymorph of L-cysteine,[25–27] and a very subtle dynamic change on cooling has been observed in the monoclinic polymorph of L-cysteine.[28] None of the several high-pressure phases of L-cysteine coincides with the low-temperature states of either orthorhombic, or monoclinic L-cysteine.

In contrast to L-/DL-serine, not only the two polymorphs of L-cysteine, but also the DL-cysteine undergoes phase transitions on cooling[29] and with increasing pressure.[23] The Raman spectroscopy study[23] has suggested that the structure of the first high-pressure polymorph of DL-cysteine formed at about 0.1 GPa is similar (if not identical) to the low-temperature polymorph DL-cysteine-II.[29] The aim of the present work was to test this hypothesis by the X-ray diffraction, *i.e.* to compare the low-temperature and the high-pressure polymorphs of DL-cysteine. We aimed to understand, what makes the structure of DL-cysteine-I unstable with respect to variations in temperature/pressure, and for this purpose have compared in details the molecular conformations, H-bonds and molecular packing in DL-cysteine-I and DL-cysteine-II. We have also compared the response of the structure of DL-cysteine-II to further compression either on cooling or on increasing pressure.

Experimental

The powder sample of DL-cysteine was obtained from Fluka (assay 99.5%) and finely ground by hand in a mortar with a pistil.

High-resolution X-ray powder diffraction experiments at high pressures were carried out at BM1A at the Swiss-Norwegian Beamline (ESRF) in Grenoble using a synchrotron radiation source (λ = 0.70007 Å, a MAR345 2D-image plate detector, collimator width and height 0.1 mm). The frames were measured at pressure range from ambient to 7.90 GPa with exposing time of 1800 s on compression and on subsequent decompression. The distance between the sample and the detector (about 350 mm) and the beam center position were refined using a Si standard in a special calibration experiment. Hydrostatic pressure was created in a Boehler-Almax type diamond anvil cell equipped with 600 μm diamond culets, and a stainless steel gasket (starting thickness of 0.190 mm), pre-indented to 0.098 mm with a drilled hole diameter of 0.250 mm. A mixture of the absolute ethanol and methanol (1 : 4 volume ratio) was used as a hydrostatic pressure fluid. Pressure was estimated from the shift in the R_1-band of a ruby calibrant (±0.05 GPa).[30] The sample and a ruby ball in the DAC were arranged with respect to the beam very carefully, so that no reflections from the steel gasket or the ruby could be observed in the measured diffraction patterns. For more reliability of phase transitions registration, Raman spectra at each pressure were recorded before and after the X-ray diffraction data collection using a Renishaw Raman spectrometer equipped with a doubled frequency type laser with wave length of 532 nm.

Fit2D program[31] was used for processing diffraction data measured with the synchrotron source (calibration, masking, integration). The unit cell dimensions were determined with the indexing program DICVOL04[32] and Win XPOW software[33] using the first 20 peak positions. A preliminary structure solution was obtained using simulated annealing technique in DASH software;[34] a starting model of the cysteine zwitterion (intramolecular bond lengths, angles, and torsion angles) was based on the data obtained by single-crystal diffraction analysis of the low-temperature phase at 200 K. GSAS software[35] with a shell of

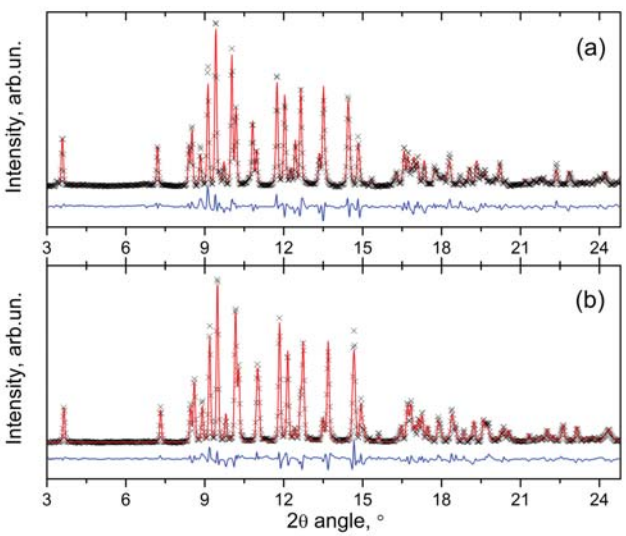

Fig. 1 Rietveld plots showing the observed and calculated profiles as well as their difference for DL-cysteine at 0.25 (a) and 0.85 GPa (b). Observed profiles are represented as crosses.

Table 1 Unit cell parameters, volume, X-ray density and selected torsion angles for DL-cysteine-II at 200 K[29] and DL-cysteine at 0.25 and 0.85 GPa

Parameter	DL-cysteine II at 200 K	DL-cysteine at 0.25 GPa	DL-cysteine at 0.85 GPa
a/Å	9.690(3)	9.712(5)	9.6352(4)
b/Å	4.9736(11)	4.976(2)	4.9435(2)
c/Å	13.124(4)	13.107(6)	12.8853(5)
β/°	121.75(2)	121.85(2)	121.808(2)
V/Å^3	537.9(3)	538.0(4)	521.57(4)
D_{calcd}/g cm^{-3}	1.496	1.496	1.543
NCCS	74.7(4)	80.3(5)	77.2(5)
CCCS	−49.9(4)	−44.5(5)	−46.6(5)

the EXPGUI[36] was used for further Rietveld refinement. Bond lengths and angles were constrained using data from the structure model at 200 K and ambient pressure. An r.m.s. deviation for bond lengths and angles was estimated as 0.01 Å and 0.5°, correspondingly with a common isotropic displacement parameter U_{iso} equal to 0.025 Å^2 for non-hydrogen atoms and 0.03 Å^2 for hydrogen atoms. Typical Rietveld plots demonstrating the observed, calculated and difference profiles for DL-cysteine-II at 0.25 and 0.85 GPa are shown in Fig. 1. Parameters characterizing the quality of structure refinement are summarized in the ESI, Table S1.†

Mercury,[37] CrystalExplorer[38,39] and PLATON[40] were used for visualization and analysis of the crystal structures.

Results and discussion

DL-cysteine-I

At ambient conditions DL-cysteine (DL-cysteine-I) crystallizes in a monoclinic space symmetry group $P2_1/a$ with one molecule in the asymmetric unit. The side chain –CH_2SH in cysteine is very labile, and as a result the cysteine can adopt multiple conformations, which are usually characterized by the value of the torsion angle NCCS: if this value is equal to *ca.* +60°, the conformation is termed *gauche*+, and if it is *ca.* −60°, then it is termed *gauche*−. The two conformations (*gauche*− or *gauche*+) are typical for the crystals of pure cysteine and its salts.[41–45] In the orthorhombic polymorph of L-cysteine[27,46,47] cysteine has *gauche*+ conformation with the value of the torsion NCCS angle equal to 65.32(15)°; in the monoclinic polymorph[48,49] one molecule in the asymmetric unit has *gauche*+ conformation (the value of the NCCS torsion angle is equal to 74.39(10)°), and another—*trans* conformation, with the NCCS torsion angle equal to 170.15(7)° ‡. The *gauche*− conformation of cysteine (with the NCCS torsion angle equal to −61.5(3)°) in the crystal of DL-cysteine-I[29,50] differs radically from that in the two polymorphs of L-cysteine. In L- and DL-cysteinium oxalates, the orientation of –CH_2SH group is opposite to that in the crystals of the corresponding pure L- and DL-cysteine, *gauche*− and *gauche*+, respectively.[44,45]

The L- and DL-cysteine crystal structures do not follow the Wallach's rule:[51] the crystal structures of both the monoclinic and the orthorhombic polymorphs of L-cysteine are denser than that of DL-cysteine (1.501, 1500 and 1.440 g cm^{-3}, respectively). Three different types of the N–H···O hydrogen bonds between

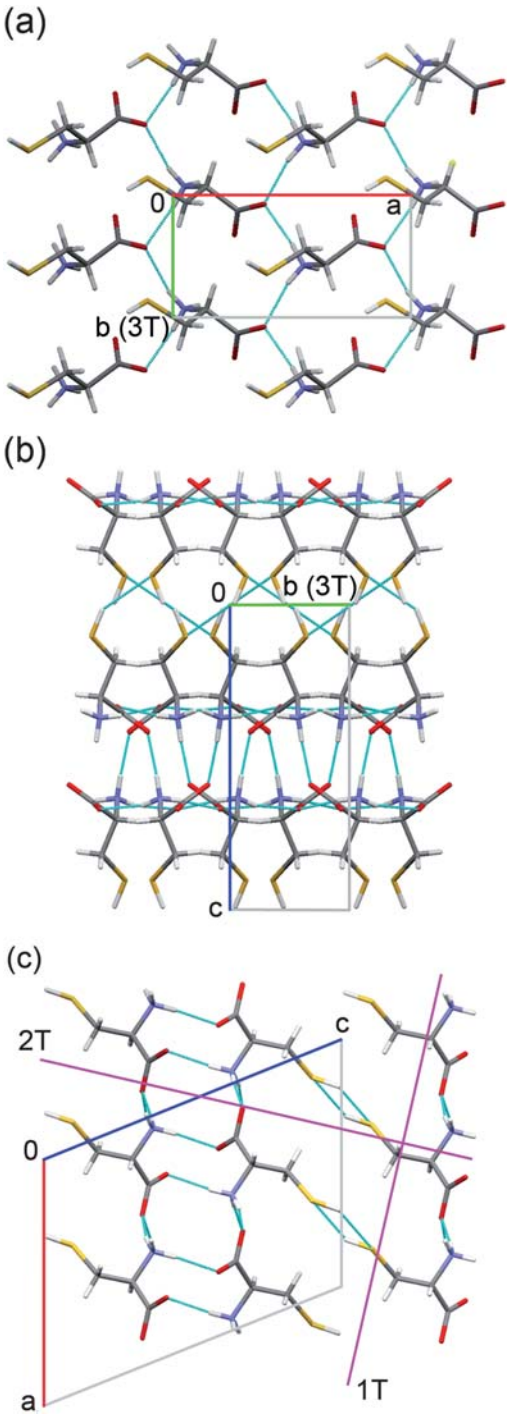

Fig. 2 The fragments of the crystal structure of DL-cysteine-I at ambient temperature and pressure [(a) parallel to *ab* plane, (b) parallel to *bc* plane, and (c) parallel to *ac* plane] with principal axes of linear strain ellipsoid on cooling from 300 K down to 200 K. The 3*T* axis (linear strain −0.33(1)%) coincides with the crystallographic axis b, the other two (1*T* and 2*T*) axes are normal to 3*T*. The 2*T* axis (linear strain −0.32(1)%) forms angles of 77(5)° and 35(5)° with *a* and *c*, respectively; the 1*T* axis (linear strain −0.19(1)%) forms angles of 13(4)° and 125(4)° with *a* and *c*, respectively. Hydrogen bonds are shown as dashed lines.

‡ The monoclinic polymorph of L-cysteine is up to now the only cysteine containing structure, in which the *trans*-conformation has been observed.

the amino and the carboxylate groups link cysteine zwitterions in the crystal structure of DL-cysteine-I into layers, whereas the weaker S–H···S hydrogen bonds between the thiol groups connect the layers into a three-dimensional network (Fig. 2). Each N–H···O hydrogen bond gives rise to an infinite head-to-tail chain $C_1^1(5)$. The hydrogen bonds N–H4···O2 link the zwitterions of the same chirality, whereas the hydrogen bonds N–H5···O1 and N–H6···O1—the zwitterions of different chirality (L-isomers and D-isomers). The hydrogen bonds between the thiol groups also form infinite S–H···S–H···S chains. Within a layer, the cycles $R_3^4(14)$ are formed by the N–H5···O1 and N–H6···O1 hydrogen bonds. The S···S distances in the S–H···S hydrogen bonds in the crystal structure of DL-cysteine-I are somewhat longer (3.8582(16) Å), than those in the orthorhombic L-cysteine (3.8494(8) Å),[27] but are much shorter than in the monoclinic L-cysteine (4.080(1) Å), which also has a layered structure.[49] The distance between the proton donor and acceptor in a hydrogen bond can be used for preliminary estimates of its strength, but only vibrational spectra (in particular, the wavenumbers of the stretching vibrations of the selected molecular groups) can provide information on the interaction energy of this fragment with its crystalline environment. The spectroscopic techniques are especially important, when a group forms many relatively weak contacts with several neighbours, as is the case in the crystal structures of cysteine and its salts. The stretching vibrations of the thiol group are in the 2500–2600 cm^{-1} range of the spectra and do not overlap with other bands, what makes their measurement very reliable. The wavenumbers of the stretching vibrations of the thiol groups involved in the formation of the S–H···S bonds in the DL-cysteine-I, orthorhombic and monoclinic L-cysteine are, respectively, 2569, 2544 and 2575 cm^{-1}, and these values suggest that the attractive interactions of the –SH groups with the neighbours in DL-cysteine-I are weaker than in the orthorhombic L-cysteine, but stronger than those in the monoclinic L-cysteine.

Structure response to cooling, the low-temperature phase DL-cysteine-II

The crystal structures of the monoclinic and the orthorhombic polymorphs of L-cysteine are stable with respect to cooling, and do not change their space-group symmetry, however some anomalies related to the changes in the dynamic properties have been observed. An extended phase transition at about 70 K manifested itself as a broad peak at the Cp(T) curve.[26] Single-crystal X-ray diffraction[25] and polarized Raman spectroscopy[27] showed that this phase transition is related to the ordering of the thiol groups in the crystal structure: at ambient temperature they are disordered, forming, alternatively, the S–H···O bonds with the neighbouring carboxylate groups, and the S–H···S bonds with the neighbouring thiol groups, whereas at 70 K the S–H···S hydrogen bonds dominate. The volume of the unit cell decreases at ~1.87% on cooling from ambient temperature down to 30 K, and the wavenumber of the SH_{str} vibrations decreases at ~31 cm^{-1}.[25,27]

The changes in the dynamic properties have been observed in the monoclinic polymorph of L-cysteine at about 150 K by inelastic neutron scattering. Some anomalies in the changes in the cell parameters not accompanied by a change in the space-group symmetry, or a discontinuity in the volume change have been registered in the temperature range 300–100 K. No thermal effects could be observed in this range by DSC measurements.[28] The volume change on cooling is larger for the monoclinic L-cysteine polymorph, than for the orthorhombic one, and is equal to 2.14%.

The response of the DL-cysteine to cooling is very different from that of the polymorphs of L-cysteine. It undergoes a pronounced first-order phase transition, with a discontinuity in the volume change, the fragmentation of the crystals, and a very large (over 100 K) hysteresis,[29] which depends on the cooling-heating rate[29] and the size of particles in the sample.[52,53]

On cooling down from ambient temperature to the phase transition point, the crystal structure is compressed anisotropically, the directions of the maximum compression (~0.32(1) %) coinciding with the directions of the N–H4···O2 hydrogen bonds and the S···S contacts (the interlayer compression), and with the crystallographic axis b (Fig. 2). The minimum compression (0.19(1) %) is observed along the head-to-tail chains (crystallographic direction a). The volume decrease is ~0.84(2) %. The distance S···S in a S–H···S hydrogen bond shortens at 0.9% and becomes equal to 3.8254(14) Å at 225 K.

On further cooling, a phase transition takes place, during which the space group symmetry is preserved, and the structure remains layered, but the unit cell volume decreases discontinuously at ~3% and the zwitterion conformation changes radically from *gauche*− to *gauche*+, twirling the side chain $–CH_2SH$ at almost 130° around the C^{α}–C^{β} bond. Interestingly, despite a decrease in the volume, the D···A distances in the N–H5···O1 and N–H6···O1 hydrogen bonds increase on cooling (2.803(3) and 2.819(3) Å at 225 K, 2.878(5) and 2.833(5) Å at 200 K, respectively), and those in the N–H4···O2 bonds do not change (2.777(5) at 225 and 200 K). However, the contacts of the $–CH_2SH$ group change noticeably as the conformation of the zwitterion changes. Thus, after the phase transition the thiol group forms S–H···O hydrogen bonds with the carboxylate group of a neighbouring zwitterion, the distance S···O being equal to 3.581(3) Å. The S···S distance between the two –SH groups increases up to 3.930(2) Å at 200 K.

The conformations of zwitterions and the Hirshfeld surfaces immediately before and after the phase transition from DL-cysteine-I to DL-cysteine-II are plotted in Fig. 3. The corresponding Hirshfeld surface fingerprints plots are shown in Fig. 4. The number of the H–H contacts decreases from 46.0% at 225 K to 28.4% at 200 K, the relative number of the O–H contacts remains practically constant (~47%), and the number of the S–H interactions increases from 14.5% to 21.8%. The short S–H contacts, which were related to the presence of the S–H···S hydrogen bonds in DL-cysteine-I disappear in the low-temperature polymorph DL-cysteine-II, and at the same time the number of medium-length contacts, which correspond to the interactions of the thiol group with the CH_2- groups, increases. As the orientation of the cysteine side chain changes in the course of the DL-cysteine-I → DL-cysteine-II phase transition making the cysteine packing denser, the energy loss due to breaking of the S–H···S bonds is compensated by the formation of stronger S–H···O bonds and multiple attractive C–H···S contacts. The phase transition takes place long before the S···S distance in a S–H···S hydrogen bond reaches its minimum possible value: much

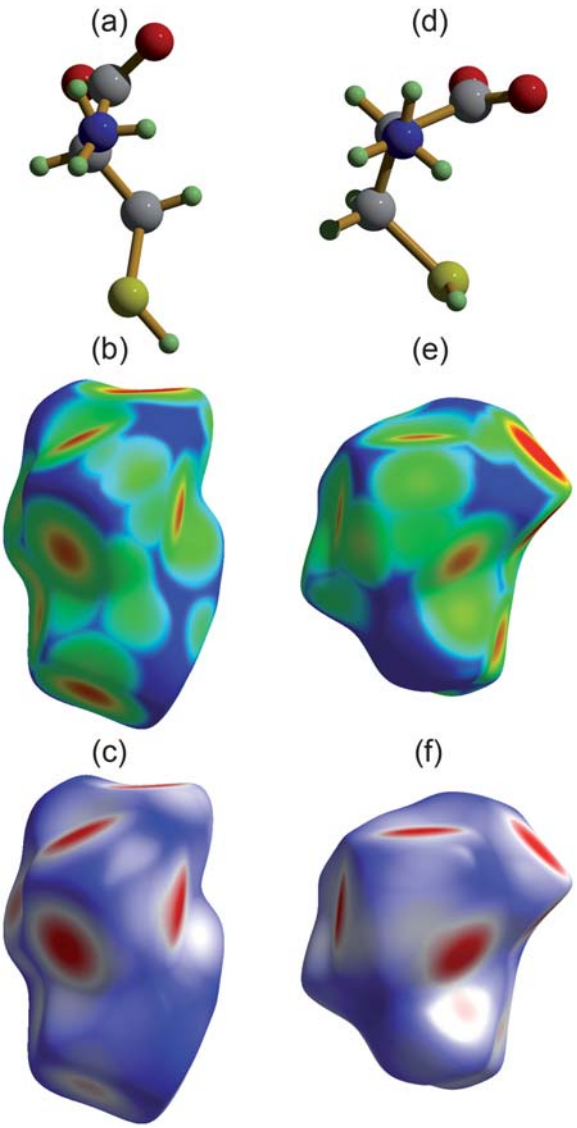

Fig. 3 Molecular conformation and Hirshfeld surfaces of DL-cysteine-I at 225 K (a, b, c) and DL-cysteine-II at 200 K (d, e, f). Each molecule is shown with the Hirshfeld surface mapped with d_e [b and e; for these series mapped between 1.0 (red) and 2.0 Å (blue)] and d_{norm} [c and f; mapped between −0.71 (red) and 1.1 Å (blue)], where d_e is the distance to the nearest atom centre exterior to the surface and d_{norm} is the normalized contact distance, which takes the van der Waals radii of the atoms into account.

shorter (3.518(1) Å) S···S contacts between the–SH groups have been described, *e.g.* in the crystal structure of DL-cysteinium oxalate.[43]

The structural changes manifest themselves in the Raman spectra (Fig. 5). The major changes are observed in the spectral ranges of the vibrations of the thiol group: the stretching CS-vibrations in the 600–700 cm^{-1} range, the stretching SH-vibrations in the 2500–2600 cm^{-1} range, the stretching CH– and CH_2– vibrations in the 2900–3000 cm^{-1} range. Thus, as the S–H···S hydrogen bonds are substituted for the S–H···O bonds, the band observed in the spectra of DL-cysteine-I at 2569 cm^{-1} disappears, and the band at 2548 cm^{-1} in the spectra of DL-cysteine-II appears.

Structure response to hydrostatic pressure

DL-cysteine undergoes a phase transition at a very low pressure of 0.1 GPa. This seems to be up to now the lowest pressure, at which a pressure-induced polymorphic transition has been observed in a crystalline amino acid. A comparison of the Raman spectrum of the high-pressure polymorph[23] with that of the low-temperature polymorph DL-cysteine-II[29] has suggested that the two forms must be very similar if not identical. The Raman spectra of DL-cysteine at ambient conditions (DL-cysteine-I), and after the phase transitions on cooling and on increasing pressure above 0.1 GPa are plotted at Fig. 5. The band at about ~2569 cm^{-1} in the Raman spectrum of DL-cysteine at 0.1 GPa can be assigned to the stretching vibrations of the –SH group of the non-transformed phase of DL-cysteine-I remaining in the samples. The X-ray powder diffraction patterns of the low-temperature phase DL-cysteine-I and the first high-pressure phase are also similar (Fig. 6). A few "extra" low-intensity reflections in the diffraction pattern collected at 0.25 GPa are a consequence of the presence in the sample of the remaining non-transformed phase of DL-cysteine-I. The incompleteness of the pressure-induced phase transition in the powder sample of DL-cysteine at 0.25 GPa is a manifestation of a pronounced kinetic effect.

The structure solution and refinement based on the X-ray powder diffraction patterns measured at 0.25 and 0.85 GPa has given a structural model practically identical with that of the low-temperature polymorph DL-cysteine-II (space group symmetry $P2_1/a$). The unit cell parameters, and the values of the torsion angles in the low-temperature and the first high-pressure polymorphs are compared in Table 1§. Thus, Raman spectroscopy and X-ray powder diffraction both show unambiguously that the low-temperature polymorph, DL-cysteine-II, is the same phase as the first high-pressure polymorph¶. It is worthy noting that the unit cell at 200 K and at 0.25 GPa is the same.

What makes DL-cysteine so unstable with respect to cooling and compression?

The stability of the crystals of such amino acids, as glycine, alanine, serine is determined by the properties of the N–H···O hydrogen bonds between the terminal amino and the carboxylate groups linking zwitterions with each other, and, in the case of serine,[54] additionally by strong O–H···O hydrogen bonds involving the side chains. The crystal structures of these amino acids are quite robust with respect to variations in temperature or pressure: no discontinuous structural changes on cooling have been observed in these systems, and, if a phase transition has been observed with increasing pressure (β-[55–57] and γ-glycine,[58–60] L-serine[14–18]), the new local minimum was deep enough, to enable the existence of the new polymorph in a rather wide pressure range.

§ The full sets of structural data are deposited as CIF in the CCDC.

¶ When the manuscript was already under review, we have succeeded to bring a single crystal of DL-cysteine intact through this first pressure-induced phase transition, and the correctness of structure solution and refinement based on powder diffraction data has been confirmed also based on single-crystal diffraction; this new material will be discussed in details elsewhere

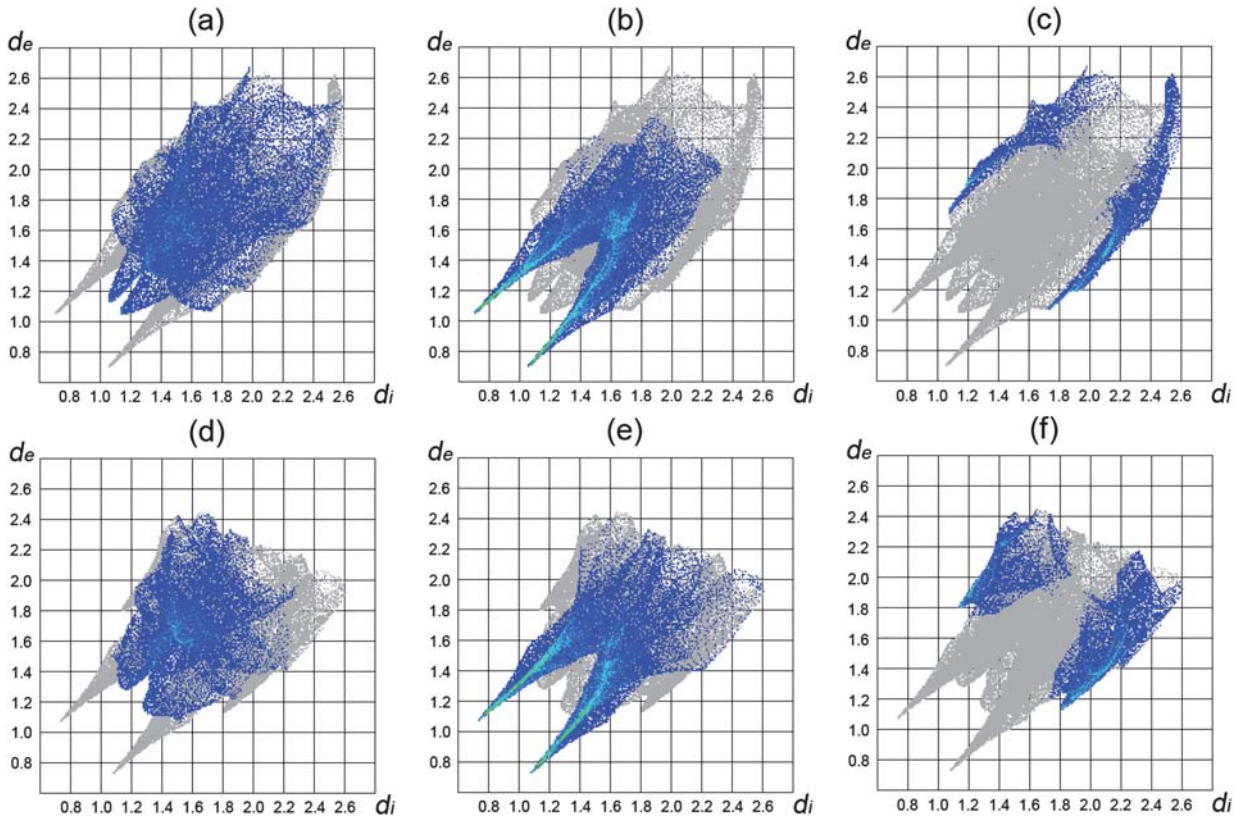

Fig. 4 Two-dimensional fingerprint plots for DL-cysteine-I at 225 K (a, b, c) and DL-cysteine-II at 200 K (d, e, f), showing the H–H contacts (a and d), the O–H contacts (b and e) and the S–H contacts (c and f) in coloured areas, but keeping the rest of the interactions present in the crystal structure in grey.

The case of cysteine differs from the examples listed in the previous paragraph. In contrast to the methyl group in L-alanine or the H-atoms in the $–CH_2$-group in glycine, the thiol side chain, $–CH_2SH$, in cysteine can form hydrogen bonds with the neighbouring atoms (S or O) in the crystal structures, but these hydrogen bonds are much weaker than the O–H···O in serine. Therefore, the side chain is very labile and can form various contacts; the multiple conformations of the zwitterion may correspond to new shallow energetic minima, thus resulting in numerous phase transitions, which can be continuous or discontinuous. Since the S–H···O and S–H···S hydrogen bonds are relatively weak, the numerous van der Waals interactions can

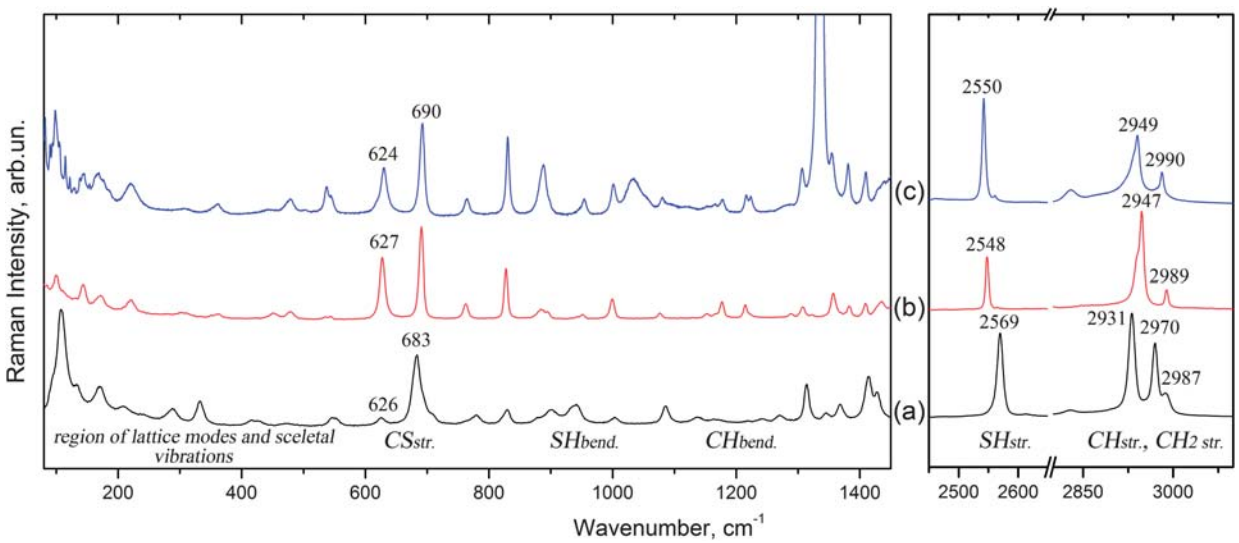

Fig. 5 Raman spectra of DL-cysteine at ambient pressure and temperature (a), DL-cysteine at 200 K (b), and DL-cysteine at 0.1 GPa (c).

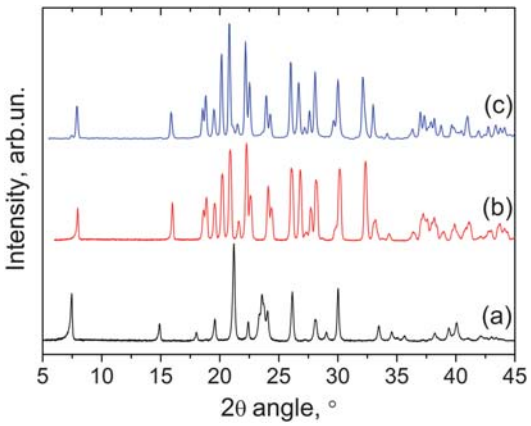

Fig. 6 Powder patterns of DL-cysteine at ambient temperature and pressure (a), at 200 K (b), and at 0.25 GPa (c).

be quite successful in competing with these hydrogen bonds for a new, more efficient molecular packing. The response to variations in temperature or pressure is to a large extent driven by the dynamics of the–CH_2SH side chains, at least, when the strain is not too large. If the rotation of the side chains preserves the main structural framework held together by stronger N–H···O hydrogen bonds and electrostatic interactions between the zwitterions with their high dipole moments, no structural phase transitions occur, or the transition is of the order-disorder type and is extended in a wide range (this is the case for the low-temperature phase transition in L-cysteine[26,27]). In other cases, breaking the S–H···S or S–H···O hydrogen bonds and rotation of the side chains results in a structural reconstruction, which is accompanied by crystal fragmentation. This is the case of the low-temperature and the first high-pressure phase transitions in DL-cysteine.

When the crystal structure of DL-cysteine-I is compressed either by decreasing temperature, or by increasing pressure, a relatively small change in the volume (a few %) is sufficient to break the weak S–H···S hydrogen bonds not because the distances between H and S atoms in these bonds (or any other intermolecular contacts) have reached the minimum possible values, so that further shortening of these contacts would result in repulsion, but because the –SH group comes close enough to other neighbouring atoms, and the attractive interactions with these neighbours compete with the S–H···S hydrogen bonds and account for a rotation of the side chain. The new conformation, which is observed in the phase of DL-cysteine-II, enables a denser packing, and corresponds to a new minimum in the free energy, but the intermolecular interactions in this new form remain rather weak, the minimum must be shallow, and one can expect that the form should not be stable on further compression. Moreover, one can expect that for a larger strain (which can be achieved at higher pressures) the structural changes in DL-cysteine will be more related to the compression of the N–H···O hydrogen bonds between the terminal groups, than to any further changes in the side chain –SH contacts, which have been already more or less optimized as a result of the first high-pressure phase transition at 0.25 GPa.

This is indeed confirmed by the experimental data. When the structure of DL-cysteine-II is cooled further down, or hydrostatically compressed to higher pressures, the main tendency in both cases is to decrease the distance between the layers in the structure (Fig. 7). At the same time, a more detailed analysis reveals a difference in the strain anisotropy on cooling and on hydrostatic compression. On cooling of DL-cysteine-II from 200 to 100 K the direction of major compression is along the crystallographic axis *c*; a twice smaller compression is observed along the crystallographic axis *b*. The linear strain along the third principal axis is almost negligible −0.05(4) %. When pressure is increased up to 0.85 GPa, the major compression (principal axis 3) is close to the crystallographic axis *c* (axis 3 forms about 14 degrees with *c*); linear strain along the two other principal axes is practically the same and is about 2.5 times less, than along the axis of the major compression.

The total volume decrease on cooling DL-cysteine-II from 200 K to 100 K is 0.72(5)%, and the maximum linear strain is −0.45(3)%. Unfortunately, we could not follow the structural changes at the temperatures below 100 K by X-ray diffraction techniques‖, but a Raman spectroscopy study has shown that the DL-cysteine-II polymorph is preserved down to 3 K. Even at this extremely low temperature the relative volume change, if the $V(T)$ based on the measured data is extrapolated (Fig. 8), would be about −1.3% only). This is much less than the strain achieved on hydrostatic compression: the change in the pressure from 0.25 to 0.85 GPa results in the total volume decrease of about 3.09(1)%, the maximum linear strain (along axis 3) is 1.75(1)%. The much larger strain on hydrostatic compression as compared to that on cooling** is related to a noticeably different distortion of the hydrogen bonds network††.

The main difference in the strain induced in DL-cysteine-II on cooling[29] and with increasing pressure is related to the changes in the D···A distances in the D–H···A hydrogen bonds in DL-cysteine-II. Thus, on cooling from 200 to 100 K, the decrease in the N···O distances in the three types of the N–H···O hydrogen bonds does not exceed 0.010(5) Å, the S···O distance continues to decrease (from 3.581(3) to 3.555(3) Å), and the S···S—to increase (from 3.942(3) to 3.967(3) Å). The effect of the increasing pressure up to 0.85 GPa on the N–H···O and S–H···O hydrogen bonds is different. The S···O distance in the hydrogen bond S–H···O slowly increases from 3.57(1) to 3.60(1) Å, whereas the S···S distance shortens from 3.843(8) to 3.811(8) Å. The N–H···O hydrogen bonds, in which atom O1 acts as an acceptor, *i.e.* N–H5···O1 and N–H6···O1 shorten (the N···O distance decreases from 2.99(1) and 2.83(1) Å at 0.25 GPa to 2.91(1) and 2.75(1) Å at 0.85 GPa, respectively). At the same time, the N–H4···O2 hydrogen bond expands (the N···O distance increases from 2.673(8) to 2.741(8) Å), whereas the N···O distance in the

‖ A single crystal is no longer preserved after the transition into the DL-cysteine-II polymorph, and we have no technical facilities to measure powder diffraction patterns at temperatures below 100 K.

** In order to achieve the volume decrease equivalent to that at 0.85 GPa, one would need to cool the sample down to about −600 K, if the same $V(T)/V(P)$ curves were followed (Fig. 8).

†† The similarity of the structures of the low-temperature and the first high-pressure phases of DL-cysteine, DL-cysteine-II can be explained by a relatively small volume decrease, which is sufficient to trigger the phase transitions. At the same time, examples are known, when the anisotropy of strain was very different, even though the volume change on cooling and on hydrostatic compression was small and practically the same.[61,62]

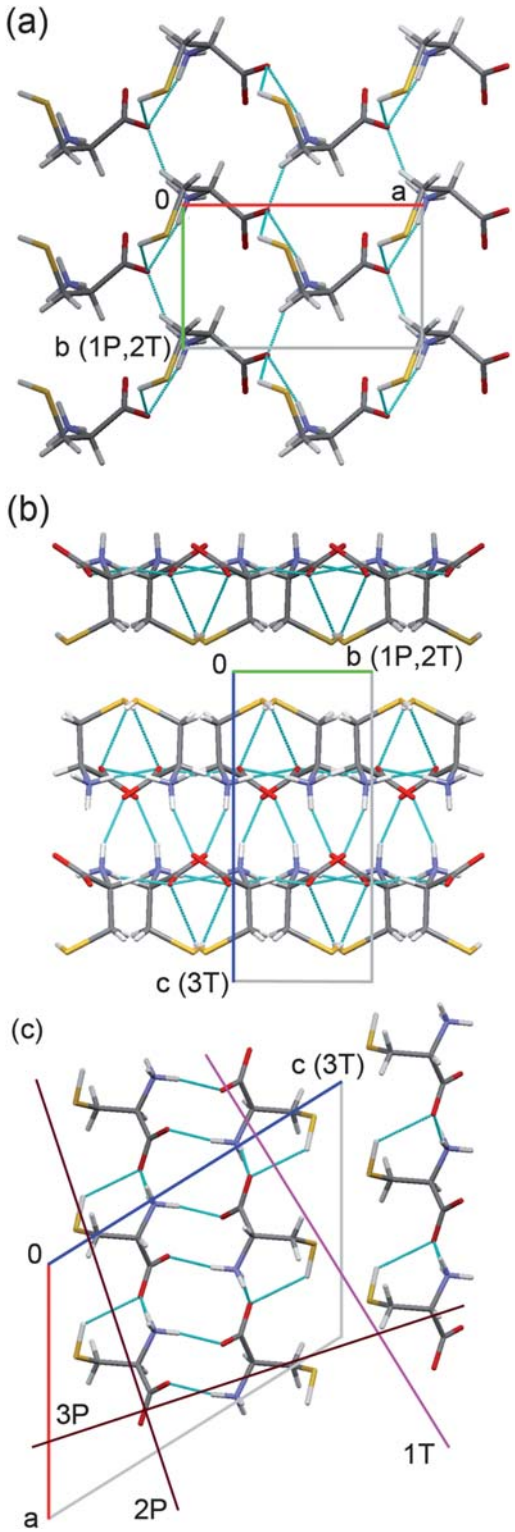

Fig. 7 The fragments of the crystal structure of DL-cysteine-II at 200 K [(a) parallel to ab plane, (b) parallel to *bc* plane, and (c) parallel to the *ac* plane] with principal axes of linear strain ellipsoid on cooling from 200 to 100 K (pink line) and on increasing pressure from 0.25 to 0.85 GPa (brown lines). The axes 1*P* (linear strain −0.65(1)%), and 2*T* (linear strain −0.22(2)%) coincide with the crystallographic axis *b*; the most compressible direction on cooling, 3*T* (linear strain −0.45(3)%), coincides with axis *c*; the 1*T* axis (linear strain −0.05(4)%) forms angles of 23(3) and 98(3)° with *a* and *c*, respectively; the 2*P* axis (linear strain −0.69(1)%) forms angles of 18(1) and 104(1)° with *a* and *c*; the 3*P* axis (linear strain −1.75(1)%) forms angles of 108(1) and 14(1)° with *a* and *c*, respectively. Hydrogen bonds are shown as dashed lines.

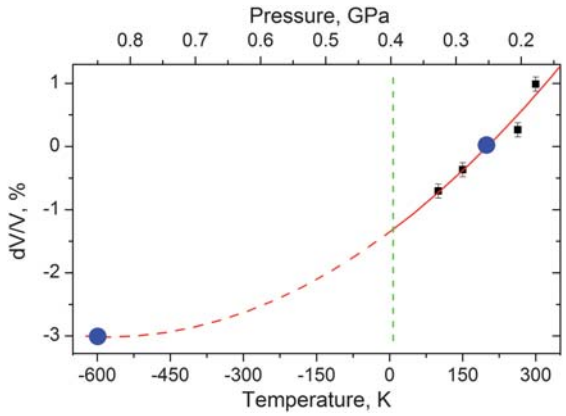

Fig. 8 Relative decrease of the volume of DL-cysteine on cooling and on increasing pressure. The green dashed line at 3 K corresponds to the lowest temperature of the Raman study,[29] blue circles show the values of the volume at 0.25 and 0.85 GPa. Extrapolated red line shows, at which hypothetical temperature the volume change on increasing pressure would be equal to that on cooling.

N–H5···O2 contact decreases from 3.19(1) to 3.13(1) Å, so that it approaches the limits which would be considered as a "hydrogen bond". One can consider this process, as if a bifurcation hydrogen bond were formed instead of a single shorter bond. A similar process has been observed previously in the β- and γ-polymorph of glycine, in which a phase-transition into a high-pressure β′- and δ-polymorph occurred at the pressure, when a single hydrogen bond was substituted for a bifurcation one.[11] In L-serine such a bifurcated bond is already present even at ambient conditions and nevertheless there are two phase transitions at about 5 and 8 GPa[14–18] and a dynamic phase transition on cooling at 140 K.[19] But in the case of L-serine phase transitions are related mainly to the re-orientation of the side chain $-CH_2OH$, changing its hydrogen bonding to the neighbouring groups. On the other hand, for DL-serine,[15,21] and L–alanine,[63] in which neither the bifurcated bonds N–H···O in the head-to-tail chains can be formed on compression, nor the side chain can change noticeably its orientation, the crystal structures do not undergo phase transitions. At the same time, a proton shift from the carboxylic group to the amino group along N–H···O hydrogen bond in L-alanine plays an important role in the changes in the dynamic properties of this structure with pressure.[63] As was discussed in ref. 11, continuous changes in the hydrogen bond geometry preceding a pressure-induced phase transition may be important, to understand its mechanism. In particular, the formation of a bifurcated N–H···O hydrogen bond in a head-to-tail chain of amino acids zwitterions can be important for the subsequent structural rearrangement. If this is true, the N–H···O hydrogen bonds in the zwitterionic chains of DL-cysteine crystal structure should become completely bifurcated (Fig. 9) at pressures above 1.55 GPa, when the second phase transition occurs.

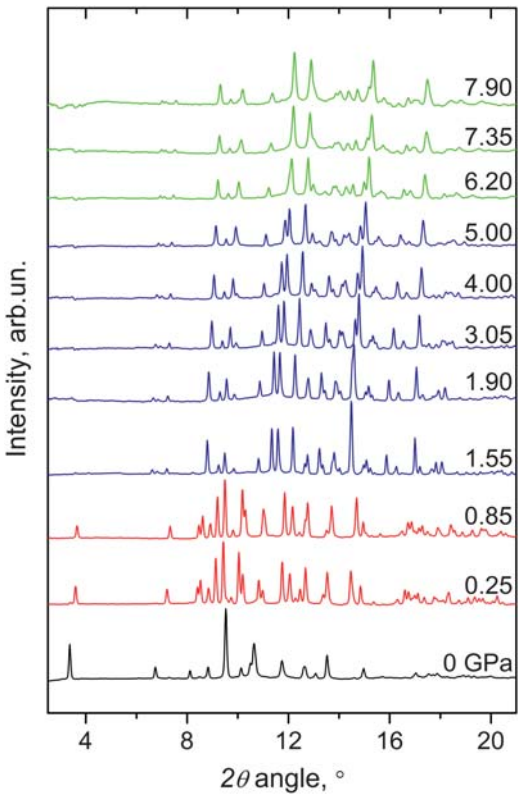

Fig. 9 Powder X-ray diffraction patterns of DL-cysteine on increasing pressure up to 7.90 GPa.

The diffraction pattern of the new phase formed at 1.55 GPa differs noticeably from that of DL-cysteine-II in all the 2θ range. The structure of this new phase is preserved in a relatively large pressure range, until 6.20 GPa (Fig. 9). Some minor structural changes can be observed at about 6.20 GPa (*e.g.* in the $2\theta \sim 12$–$13°$ range), suggesting that one more phase transition occurs, and this is supported by the Raman spectroscopy: the modes corresponding to the stretching vibrations of the groups in the side chain (CS_{str}, CC_{str}, SH_{str} and CH_{str}) split.[23] All these changes are reversible on decompression and have practically no hysteresis. Unfortunately, final structural models of these phases are not available yet: a single crystal is destroyed during the second phase transition, and structure solution and refinement from powder data requires some additional work.

Interestingly enough, although the crystal structure of a structural analog of DL-cysteine, DL-serine, is also layered, it doesn't undergo any phase transitions on cooling or increasing pressure. This fact can be explained by strong hydrogen bonding between terminal hydroxyl and carboxylate groups, which cannot switch to another group, like in L-serine (O–H···O(hydroxyl) hydrogen bonds are substituted for stronger O–H···O(carboxylate) hydrogen bonds).[14–18] As in DL-cysteine, the most compressible direction in DL-serine corresponds to shortening the distance between the layers. However, when an amino group approaches a neighbouring carboxylate group, this does not lead to the formation of a bifurcated N–H···O bond.[15,21] The crystal structure of DL-serine can be thus compressed continuously, without a structural phase transition. The decrease in the volume of DL-serine is much larger, than in DL-cysteine: for the pressure change from ambient to 0.63 GPa it is *ca.* −4.0%, and for the pressure increasing up to 8.6 GPa about −20%.[21]

Conclusions

DL-cysteine provides an example of a crystal, in which the structural response to compression is determined by the dynamics and the interactions of the side $–CH_2SH$ groups, while strain is relatively small (cooling, increasing pressure up to 0.25 GPa), and by the properties of stronger N–H···O hydrogen bonds, when the volume decrease is considerably larger (at 0.85 GPa and higher). The low-temperature and the first high-pressure phase transitions in DL-cysteine-I give the same phase (DL-cysteine-II), and occur not when some of the contacts become too short, and the corresponding atoms/groups start repulsing, but when multiple van der Waals interactions and S–H···O hydrogen bonds start competing successfully with the S–H···S hydrogen bonds, as the cysteine-groups from the neighbouring layers approach each other sufficiently. While the strain values remain comparable, the structural response to variations to temperature and pressure is similar. As the strain induced by pressure reaches the values, which cannot be achieved by cooling even down to 3 K, the response of the structure becomes similar to that previously observed in the crystals of other amino acids, such as β- and γ-glycine.

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