Low-temperature heat capacity of L- and DL-phenylglycines

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Abstract Heat capacity of crystalline L- and DL-phenylglycines was measured in the temperature range from 6 to 305 K. For L-phenylglycine, no anomalies in the $C_p(T)$ dependence were observed. For DL-phenylglycine, however, an anomaly in the temperature range 50–75 K with a maximum at about 60 K was registered. The enthalpy and the entropy changes corresponding to this anomaly were estimated as 20 J mol^{-1} and 0.33 J K^{-1} mol^{-1}, respectively. In the temperature range 205–225 K, an unusually large dispersion of the experimental points and a small change in the slope of the $C_p(T)$ curve were noticed. Thermodynamic functions for L- and DL-phenylglycines in the temperature range 0–305 K were calculated. At 298.15 K, the values of heat capacity, entropy, and enthalpy are equal to 179.1, 195.3 J K^{-1} mol^{-1}, and 28590 J mol^{-1} for L-phenylglycine and 177.7, 196.3 J K^{-1} mol^{-1} and 28570 J mol^{-1} for DL-phenylglycine. For both L- and DL-phenylglycine, the $C_p(T)$ at very low temperatures does not follow the Debye law $C - T^3$. The heat capacity $C_p(T)$ is slightly higher for L-phenylglycine, than for the racemic DL-crystal, with the exception of the phase transition region. The difference is smaller than was observed previously for the L-/DL-cysteines, and considerably smaller, than that for L-/DL- serines.

Keywords Adiabatic calorimetry · L-phenylglycine · DL-phenylglycine · Heat capacity · Molecular crystals · Chiral/racemic counterparts

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Introduction

A comparison of the properties of the crystals of chiral amino acids and of their racemic counterparts attracts much attention. For example, a pronounced difference in the heat capacity [1], vibrational spectra [2–4], inelastic scattering [4], lattice strain on cooling and with increasing pressure [5, 6], and the stability with respect to pressure- and temperature-induced phase transitions [7–11] was recently reported for chiral and racemic crystals of serine. Different properties including different $C_p(T)$ behavior, were reported also for L- and DL-cysteine [12–18]. The origin of the different properties of the L- and the DL-crystals in the two examples was sought in the different mobility of the –CH$_2$OH and –CH$_2$SH side chains and in their ability to be involved in the formation of different types of intermolecular hydrogen bonds. In the present contribution, we report the results of a comparative study of another couple, namely L- and DL-phenylglycine, $^+$NH$_3$–CH(C$_6$H$_5$)–COO$^-$. The side chain in this amino acid cannot form hydrogen bonds although it can change its orientation (rotate). The value of the heat capacity of D-α-phenylglycine (presumably, at room temperature, since no temperature was indicated in the article) has been reported as 1.173 J K^{-1} g^{-1} = 177.3 J K^{-1} mol^{-1} [19]. Low-temperature heat capacity has not been studied previously.

Experimental

The samples of L- and DL-phenylglycine were purchased from Aldrich and Fluka, respectively (molecular mass 151.16 g, the purity was equal to 99 mass% for L- and 98 mass% for DL-phenylglycine). The mass of the sample was equal to 2.7042 g for L- and 0.76856 g for DL-phenylglycine. Heat capacity measurements of L-phenylglycine were carried out using a computerized vacuum adiabatic calorimeter of an internal volume equal to 6 cm^3 as described previously [20]. In order to improve the heat transfer during the calorimetric measurements, gaseous helium (with pressure up to 70 Hgmm (3.0 × 10^3 Pa) was input into the calorimeter. Since the amount of helium in the calorimeter during the calorimetric measurements was substantially larger, than that during the calibration of the empty calorimeter, a special correction was applied to the measurement results at very low temperatures. The value of this correction was about 1.2% at 6 K and fell down to 0.1% at 20 K. At higher temperatures, it was less than the scatter of experimental data and was ignored. The experiments were carried out in a pulse mode. The temperature increment during a calorimetric experiment was about ∼10% of the absolute temperature of the experiment in the range between 6 and 100 K, and did not exceed 10 K above this temperature. In order to measure the heat capacity of DL-phenylglycine, a small calorimeter

ampoule of internal volume of 2 cm^3 was used [21]. The technique of measurements and calculation of the correction for extra helium in the calorimeter cell were similar to that used by the heat capacity measurements for L-phenylglycine.

Results and discussion

Thermodynamic properties of L-phenylglycine were studied in 68 calorimetric experiments in the temperature range 5.7–304.7 K. No anomalies were observed. The experimental data in the order of measurement are summarized in Table 1. Average deviation of the experimental points from the smoothed $C_p(T)$ curve was equal to 0.13, 0.08 and 0.02% at 6–20, 20–75, and 75–300 K, respectively. Thermodynamic functions were calculated extrapolating the measured $C_p(T)$ curve down to 0 K. The smoothed values of the C_p and the calculated thermodynamic parameters at selected temperatures are summarized in Table 2.

Thermodynamic properties of DL-phenylglycine were studied in 73 calorimetric experiments in the temperature range 6.5–305.0 K. The experimental data in the order of measurements are summarized in Table 3. Average deviation of the experimental points from the smoothed $C_p(T)$ curve is equal to 0.6, 0.4, and 0.15 at 6–10, 10–60, and 60–300 K, respectively. The smoothed values of the C_p

Table 1 Experimental data on the heat capacity of L-phenylglycine

T/K	C_p^0/J K^{-1} mol^{-1}	T/K	C_p^0/J K^{-1} mol^{-1}	T/K	C_p^0/J K^{-1} mol^{-1}	T/K	C_p^0/J K^{-1} mol^{-1}
Series 1		183.84	116.4	7.27	1.785	21.04	13.81
301.76	181.29	193.77	121.5	8.84	2.847	23.40	16.27
304.71	183.06	203.66	126.7	10.47	4.063	26.01	18.90
Series 2		213.59	132.0	12.09	5.323	28.59	21.48
82.60	63.27	223.48	137.3	13.72	6.742	31.17	24.12
87.66	66.22	233.26	142.6	15.30	8.204	33.74	26.67
92.71	69.07	243.13	148.0	16.88	9.655	36.30	29.15
97.79	71.94	253.10	153.5	18.47	11.24	38.89	31.55
103.91	75.21	260.55	157.6	20.07	12.88	41.46	33.81
110.95	78.92	265.46	160.3	*Series4*		44.03	36.15
117.87	82.54	270.32	163.1	6.40	1.281	47.64	39.15
124.83	86.17	275.24	165.8	7.96	2.229	52.22	42.84
131.84	89.75	280.20	168.7	9.54	3.359	56.77	46.21
138.81	93.28	285.13	171.5	11.24	4.649	61.33	49.58
145.75	96.82	292.51	175.8	14.58	7.540	65.88	52.80
154.16	101.1	302.39	181.4	16.21	9.076	70.42	55.82
164.05	106.2	*Series 3*		17.83	10.64	74.95	58.61
173.94	111.3	5.74	0.947	19.45	12.23	79.46	61.34

Table 2 Smoothed values of heat capacity and thermodynamic functions of L-phenylglycine

T/K	$C_{p,m}^0(T)$/J K^{-1} mol^{-1}	$S_m^0(T) - S_m^0(0)$/J K^{-1} mol^{-1}	$H_m^0(T) - H_m^0(0)$/J mol^{-1}
5.74	0.9460	0.3153	1.512
10	3.698	1.479	8.203
15	7.915	3.744	34.44
20	12.78	6.677	86.61
25	17.87	10.08	166.5
30	22.93	13.78	273.7
35	27.88	17.69	406.8
40	32.55	21.72	564.2
45	36.95	25.81	745.1
50	41.07	29.92	948.7
60	48.63	38.09	1,420
70	55.51	46.11	1,963
80	61.70	53.93	2,563
90	67.55	61.54	3,218
100	73.11	68.95	3,927
120	83.66	83.22	5,501
140	93.89	96.88	7,276
160	104.1	110.1	9,253
180	114.4	122.9	11,430
200	124.8	135.5	13,810
220	135.4	147.9	16,390
240	146.3	160.2	19,180
260	157.3	172.3	22,200
280	168.6	184.4	25,440
298.15	179.1	195.3	28,570
300	180.2	196.4	28,900
304.71	182.9	199.2	29,810

and the calculated thermodynamic parameters at selected temperatures are summarized in Table 4. The resulting $C_p(T)$ curves for L- and DL-phenylglycine are plotted in Fig. 1.

The value of heat capacity reported in [19] for D-phenylglycine (177.3 J K^{-1} mol^{-1}) is close to that obtained in our study for DL-phenylglycine at 298.15 K (177.7 J K^{-1} mol^{-1}), and differs noticeably from the value determined in our study for L-phenylglycine at the same temperature (179.1 J K^{-1} mol^{-1}). Since the data of chemical and phase analysis of the sample studied in [19] were not reported, and neither was the procedure of measuring heat capacity described in details (seems to have been calculated from the measured value of the enthalpy at room temperature), it is difficult to interpret the origin of this discrepancy.

At very low temperatures (6–10 K), the $C_p(T)$ dependences for both L- and DL-phenylglycines do not follow the Debye's law, $C_p \sim AT^3$; the function C_p/T (T^2) is not a straight line. The Debye's law may be, however, valid at even lower temperatures, below 6 K (the straight lines connecting the two lowest points go through the origin) (Fig. 2). Therefore, the extrapolation of $C_p(T)$ curve down to zero temperature has been made following Debye function.

In the $C_p(T)$ measured for DL-phenylglycine, an anomaly in the temperature range 50–75 K with a maximum at about 60 K was registered as a small bulge exceeding the background at about 5% at the maximum point (Fig. 3). The enthalpy and the entropy increments corresponding to this anomaly were estimated as 20 J mol^{-1} and 0.33 J K^{-1} mol^{-1}, respectively. In the temperature range 205–225 K, an unusually large dispersion of the experimental points and a slight increase in the slope of the $C_p(T)$ curve were noticed. The anomalies at the $C_p(T)$ curve can be visualized better, if the derivative $dC_p/dT(T)$ is plotted (Fig. 3). In the absence of any anomalies, this curve should have a maximum at low temperatures and then decrease steadily with temperature according to Debye function. In the case of DL-phenylglycine, a pronounced peculiarity in the dC_p/dT function is observed in the temperature range 50–75 K. Between 100 and 200 K, the derivative dC_p/dT is practically constant, and at higher temperatures the values of $dC_p/dT(T)$ somewhat increase. The similar increase of the derivative dC_p/dT takes place for L-phenylglycine as well, but in this case the derivative rises more gradually and, therefore, it is not visible in the initial curve $C_p(T)$. Such changes in the $dC_p/dT(T)$ curves indicate that the heat capacity of both L- and DL-phenylglycines at temperatures above 100 K and up to the ambient temperature does not follow the Debye law.

An anomaly at low temperatures, similar to that revealed in $C_p(T)$ of DL-phenylglycine, was observed previously for a phase transition in L-cysteine related to the disordering in the thiol side chains [12, 13]. In the crystal structure of DL-phenylglycine [22], zwitter-ions of the amino acid form hydrogen-bonded infinite head-to-tail chains further linked into double centrosymmetrical bands with the phenyl rings forming the hydrophobic outer-part and the hydrophilic amino acid backbone being "hidden" inside the band (Fig. 4).

One can suppose the observed low-temperature anomaly in DL-phenylglycine to be related to the changes in the orientation of the phenyl rings in the structure and, as a consequence, in the interaction between them. It is worth noting, that the values of the entropy and the enthalpy of the low-temperature anomaly of DL-phenylglycine are much smaller than those obtained for L-cysteine, thus indicating that a disordering in the thiol groups resulting in a change in the type of their hydrogen bonding is related to a larger structural reconstruction than that of the phenyl rings, which do not form any hydrogen bonds. At higher

Table 3 Experimental data on the heat capacity of DL-phenylglycine

| T/K	C_p^0/J K^{-1} mol^{-1}	T/K	C_p^0/J K^{-1} mol^{-1}	T/K	C_p^0/J K^{-1} mol^{-1}	T/K	C_p^0/J K^{-1} mol^{-1}
Series 1		204.60	126.1	Series 4		31.21	25.57
301.92	179.6	214.52	131.3	6.91	1.136	33.79	27.93
304.95	180.9	224.50	136.8	8.47	1.964	36.95	30.94
Series 2		234.55	142.2	10.04	3.074	40.62	34.27
84.21	64.95	244.79	148.0	11.62	4.387	44.20	37.50
89.26	67.85	254.98	153.6	13.22	5.887	49.35	41.89
94.26	70.68	265.03	159.0	14.81	7.492	54.43	46.73
99.22	73.29	275.15	164.9	16.43	9.344	59.46	51.48
105.18	76.28	285.24	171.0	18.07	11.14	64.49	54.33
112.15	79.75	295.30	176.7	19.65	12.85	69.52	56.46
119.07	83.19	301.91	179.7	21.49	14.87	74.54	59.38
125.95	86.63	305.03	181.7	Series 5		79.58	62.42
132.92	90.22	Series 3		6.45	0.946	Series 6	
139.80	93.72	206.60	126.9	8.03	1.700	54.88	47.25
146.70	97.23	209.72	128.8	9.61	2.748	57.94	50.19
155.09	101.4	212.82	130.2	11.17	3.987	60.99	52.29
164.98	106.3	215.90	131.9	12.75	5.404	64.03	53.49
174.88	111.4	218.97	133.2	23.42	17.01	67.08	55.19
184.66	116.3	222.03	135.4	26.01	19.84	70.12	57.10
194.60	121.2	225.06	137.4	28.62	22.68		

temperatures, a higher rate of the increase in heat capacity with temperature, than could be expected, if the Debye law was followed, may indicate at the increase in the anharmonicity in the vibrational spectrum of this crystal. Further variable-temperature Raman spectroscopy studies will be helpful to understand better the nature of the observed anomalies in DL-phenylglycine.

In the case of the L- and DL-cysteine counterparts, low-temperature phase transitions could be observed in all the two forms, although at different temperatures and different in manifestations [12–16, 18]. Both crystal structures have also shown phase transitions with increasing pressure [17, 23]. The difference between the heat capacity of L-cysteine and that of DL-cysteine was positive in the region of phase transition in L-cysteine (50–150 K). At higher temperatures, the heat capacity of DL-cysteine grows faster than that of L-cysteine and exceeds it several times near the temperature of phase transition in DL-cysteine. In the case of L- and DL-serine, phase transitions at low temperatures and with increasing pressure were observed for L-serine only [3–6, 11]. The heat capacity of chiral serine was higher than that of DL-serine in all the temperature range studied (5.5–300 K)[1]. On the contrary, in case of phenylglycine, the low-temperature phase transition was observed for DL-form, and not for L-phenylglycine (Fig. 1). Unfortunately, the crystal structure of L-phenylglycine remains unknown, and it is not possible at this stage to interpret the higher phase stability of the crystal structure of L-phenylglycine as compared with that of DL-phenylglycine. The difference between the heat capacity of the racemic form and that of the chiral form is positive in the region of the phase transition and slightly negative at other temperatures (Fig. 5). At temperatures above 160 K, this difference is about 0.8%, and between 110 and 160 K the two curves practically coincide. At 25–40 K, the discrepancy becomes as high as 4% (the $C_p(T)$ of DL-phenylglycine being higher). At 15 K, the two curves cross each other, and at the lowest temperatures the discrepancy reaches 20%, the $C_p(T)$ of DL-phenylglycine becoming lower. As for the entropies at 298.15 K, they coincide within 0.5%, and the enthalpies at this temperature are also practically the same. Thus, for all the three pairs of chiral–racemic counterparts studied up to now (serine, cysteine, and phenylglycine), the heat capacity $C_p(T)$ is higher for L-forms, as compared with the racemic DL-crystals, with the exception of the phase transition regions. The smallest difference is observed for phenylglycine, the side chains of which cannot be involved in any hydrogen bond formation, and the largest one—for serine, in which the side chains form strong OH…O intermolecular hydrogen bonds in the crystal.

**Table 4** Smoothed values of heat capacity and thermodynamic functions of DL-phenylglycine

| T/K	$C_{p,m}^0(T)$/J K^{-1} mol^{-1}	$S_m^0(T) - S_m^0(0)$/J K^{-1} mol^{-1}	$H_m^0(T) - H_m^0(0)$/J mol^{-1}
6.45	0.9378	0.3126	1.512
10	3.038	1.106	8.203
15	7.704	3.170	34.44
20	13.20	6.134	86.61
25	18.74	9.677	166.5
30	24.08	13.57	273.7
35	29.10	17.66	406.8
40	33.85	21.86	564.2
45	38.14	26.12	745.1
50	42.62	30.40	948.7
60	51.56	38.98	1,420
70	56.88	47.33	1,963
80	62.59	55.33	2,563
90	68.27	63.04	3,218
100	73.57	70.51	3,927
120	83.73	84.83	5,501
140	93.81	98.49	7,276
160	103.9	111.7	9,253
180	113.8	124.5	11,430
200	123.8	137.0	13,810
220	134.2	149.3	16,390
240	145.2	161.4	19,180
260	156.4	173.5	22,200
280	167.7	185.5	25,440
298.15	177.7 ± 0.4	196.3 ± 0.4	28,570 ± 60
300	178.7	197.4	28,900
305.03	181.5	200.4	29,810
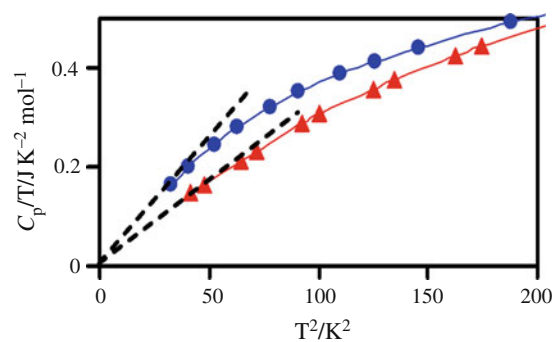
Fig. 2 $C_p(T)/T$ versus T^2 at very low temperatures: *circle* L-phenylglycine, *triangle* DL-phenylglycine
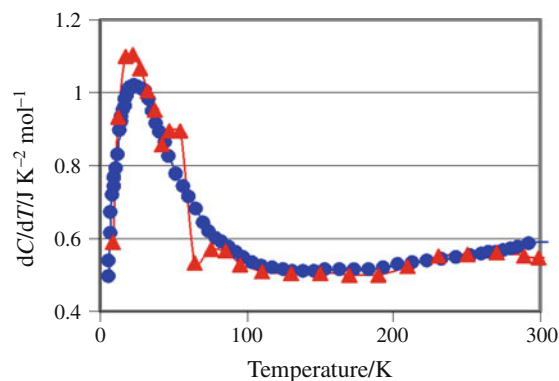
Fig. 3 Manifestations of the heat capacity anomaly in the derivative $\mathrm{d}C_p/\mathrm{d}T(T)$: *circle* L-phenylglycine, *triangle* DL-phenylglycine
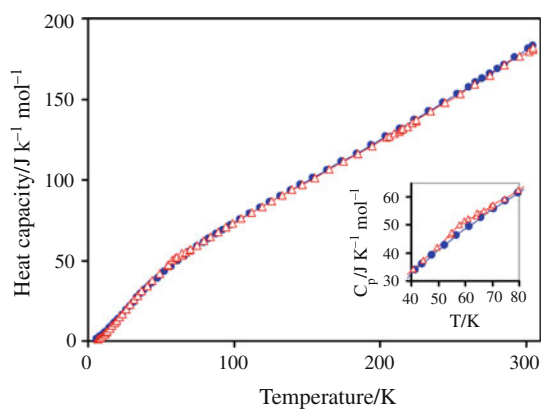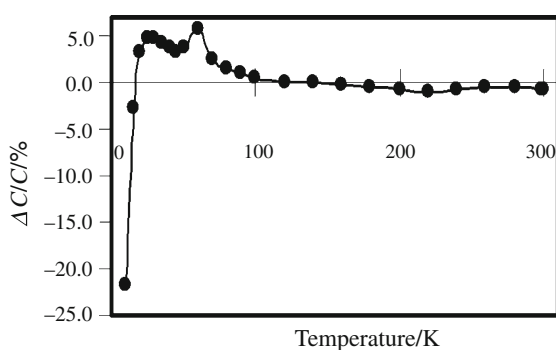

Fig. 1 $C_p(T)$ in a wide temperature range: *closed circle* L-phenylglycine, *open triangle* DL-phenylglycine
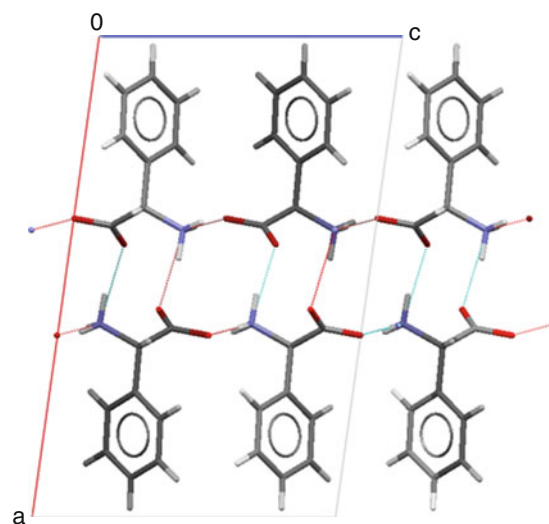
Fig. 4 A fragment of the crystal structure of DL-phenylglycine [22]

Fig. 5 The difference between smoothed heat capacities of DL- and L-phenylglycine related to the heat capacity of DL-phenylglycine

Conclusions

L- and DL-phenylglycine provide one more example of a pronounced difference in the thermodynamic properties of the chiral crystals of amino acids and their racemic counterparts. In contrast to serine, the DL- and not the L-form showed a low-temperature phase transition. We can suppose that the same form may undergo also a phase transition with increasing pressure. Further Raman spectroscopy and diffraction studies of the two forms at variable-temperature conditions will be helpful to achieve a better understanding of the nature of the anomalies observed for DL-phenylglycine in the present study.

References

1. Drebushchak VA, Kovalevskaya YuA, Paukov IE, Boldyreva EV. Heat capacity of L- and DL-serine in a temperature range of 5.5 to 300 K. J Therm Anal Calorim. 2007;89(2):649–54.
2. Chesalov YuA, Chernobay GB, Boldyreva EV. Temperature effects on the IR spectra of crystalline amino acids, dipeptides, and polyamino acids. II. L- and DL-serines. J Struct Chem. 2008;49:627–38.
3. Kolesov BA, Boldyreva EV. Difference in the dynamic properties of chiral and racemic crystals of serine studied by Raman spectroscopy at 3–295 K. J Phys Chem B. 2007;111(51):14387–97.
4. Bordallo HN, Kolesov BA, Boldyreva EV, Juranyi F. Different dynamic of chiral and racemic (L- and DL-) serine crystals: Evidenced by incoherent inelastic neutron and Raman scattering. J Am Chem Soc (Commun). 2007;129(36):10984–5.
5. Boldyreva EV, Kolesnik EN, Drebushchak TN, Ahsbahs H, Beukes JA, Weber HP. A comparative study of the anisotropy of lattice strain induced in the crystals of L-serine by cooling down to 100 K or by increasing pressure up to 4.4 GPa. Z Kristallogr. 2005;220:58–65.
6. Boldyreva EV, Kolesnik EN, Drebushchak TN, Sowa H, Ahsbahs H, Seryotkin YuV. A comparative study of the anisotropy of lattice strain induced in the crystals of DL-serine by cooling down to 100 K or by increasing pressure up to 8.6 GPa. A comparison with L-serine. Z Kristallogr. 2006;221:150–61.
7. Kolesnik EN, Goryainov SV, Boldyreva EV. Different behavior of L- and DL-serine crystals at high pressures: Phase transitions in L-serine and stability of the DL-serine structure. Doklady Phys Chem. 2005;404:61–4 (Rus), or 169–72 (Engl).
8. Moggach SA, Allan DR, Morrison CA, Parsons S, Sawyer L. Effect of pressure on the crystal structure of L-serine-I and the crystal structure of L-serine-II at 5.4 GPa. Acta Cryst B. 2005;61:58–68.
9. Boldyreva EV, Sowa H, Seryotkin YuV, Drebushchak TN, Ahsbahs H, Chernyshev V, et al. Pressure-induced phase transitions in crystalline L-serine studied by single-crystal and high resolution powder X-ray diffraction. Chem Phys Lett. 2006;429:474–8.
10. Drebushchak TN, Sowa H, Seryotkin YuV, Boldyreva EV, Ahsbahs H. L-Serine III at 8.0 GPa. Acta Cryst. 2006;E62:o4052–4.
11. Moggach SA, Marshall WG, Parsons S. High-pressure neutron diffraction study of L-serine-I and L-serine-II, and the structure of L-serine-III at 8.1 GPa. Acta Cryst B. 2006;62:815–25.
12. Paukov IE, Kovalevskaya YuA, Drebushchak VA, Drebushchak TN, Boldyreva EV. An extended phase transition in crystalline L-cysteine near 70 K. J Phys Chem B. 2007;111(31):9186–8.
13. Paukov IE, Kovalevskaya YuA, Boldyreva EV. Low-temperature thermodynamic properties of L-cysteine. J Therm Anal Calorim. 2008;93:423–8.
14. Paukov IE, Kovalevskaya YuA, Boldyreva EV. Low-temperature thermodynamic properties of DL-cysteine. J Therm Anal Calorim. 2010;100:295–301.
15. Minkov VS, Chesalov YuA, Boldyreva EV. Temperature effects on the IR spectra of crystalline amino acids, dipeptides, and polyamino acids. IV. L-cysteine and DL-cysteine. J Struct Chem. 2008;49:1022–34.
16. Kolesov BA, Minkov VS, Boldyreva EV, Drebushchak TN. Phase transitions in the crystalline cysteine on cooling: the role of the intermolecular hydrogen bonds and side-chain motions. 1. L-cysteine. J Phys Chem B. 2008;112:12827–39.
17. Minkov VS, Krylov AS, Boldyreva EV, Goryainov SV, Bizyaev SN, Vtyurin AN. Pressure-induced phase transitions in crystalline L- and DL-cysteine. J Phys Chem B Lett. 2008;112:8851–4.
18. Minkov VS, Tumanov NA, Kolesov BA, Boldyreva EV. Phase transitions in the crystalline cysteine on cooling: the role of the side-chain motions. 2. DL-cysteine. J Phys Chem B. 2009, in the press.
19. Sabbah R, Skoulika S. Thermodynamique de composés azotés. Partie VI. Étude thermochimique de la N-phénylglycine et de la d-α-phénylglycine. Thermochim Acta. 1980;36:179–87.
20. Paukov IE, Kovalevskaya YuA, Rahmoun NS, Geiger CA. A low-temperature heat capacity study of synthetic anhydrous Mg-cordierite (Mg₂Al₄Si₅O₁₈). Am Mineral. 2006;91:35–8.
21. Paukov IE, Belitsky IA, Kovalevskaya YuA. Thermodynamic properties of natural zeolite gmelinite at low temperatures. J Chem Thermodyn. 2001;33:1687–96.
22. Dalhus B, Gorbitz CH. DL-aminophenylacetic acid. Acta Cryst C. 1999;55:IUC9900061.
23. Moggah SA, Allan DR, Clark SJ, Gutmann MJ, Parsons S, Pulham CR, et al. High-pressure polymorphism in L-cysteine: the crystal structures of L-cysteine-III and L-cysteine-IV. Acta Cryst B. 2006;62:296–309.