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LOW-TEMPERATURE HEAT CAPACITY OF β-GLYCINE AND A PHASE TRANSITION AT 252 K

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Low-temperature heat capacity of unstable β-glycine was measured in a temperature range 5.5 to 295 K, and thermodynamic functions were calculated. At very low temperatures, heat capacity fits a sum of cubic (Debye) and linear terms: $C_p=aT+bT^3$. The linear contribution increases with temperature and disappears at the second-order phase transition near 252 K which was observed for the first time.

Keywords: *adiabatic calorimetry, Gibbs free energy, glycine, heat capacity, phase transition, polymorphism*

Introduction

Recently, we investigated relative thermodynamic stability of α and γ polymorphs of glycine, NH_2CH_2COOH [1]. The polymorphs differ significantly in structure (α is monoclinic and γ is trigonal) and properties (γ is piezoelectric, but α not). Surprisingly, at ambient conditions the two polymorphs turned out to be very similar in thermodynamic functions. The difference in the Gibbs energy is nearly equal to the experimental error in calorimetric experiments. This is the reason why for a long time no one could define with certainty which polymorph is stable at ambient conditions and which one is metastable [2].

There exists the third polymorph of glycine, the monoclinic β-form. It is evidently unstable transforming spontaneously into either α or γ polymorphs [3]. A new procedure of its synthesis allowed us to receive the substance in amount large enough to conduct low-temperature calorimetric measurements [4]. Thermodynamic functions of all three polymorphs of glycine are very important for the investigation of the relationship between structure and energy of interaction among molecules in molecular crystals.

The objective of this work was to measure low-temperature heat capacity of unstable β-polymorph of glycine and to compare the results with the data for other polymorphs, α- and γ-forms.

Experimental

The crystals of β-glycine were precipitated in several portions from the solution according to the procedure described in [4]. The portions were tested by means of X-ray powder diffraction. Those with impurity of γ-polymorph were rejected, only portions consisting of pure β polymorph were used in calorimetric measurements.

X-ray powder diffraction was carried out using GADDS D8 Bruker, CuK_α, 2θ=5–60°. Unit cell parameters for monoclinic β-polymorph were measured as follows: a=0.5096(3), b=0.6276(4), c=0.5386(3) nm, β=113.21(3)°.

Calorimetric measurements were carried out using low-temperature adiabatic calorimetric system working over the temperature range of 4.2–320 K, described in the previous report [1]. Mass of the sample in the calorimeter of 5.7 cm^3 was 3.25008 g. This is less than the amount of α and γ polymorphs placed into the same calorimeter, 5.6988 and 3.3513 g, respectively. The reason, we think, is the same as for the difference in sample mass for α and γ polymorphs: piezoelectric needle-like crystals of β-glycine repel from each other preventing close-packing of the powder [4].

A single-crystal X-ray diffraction in the temperature range 100–300 K was carried out using a STADI-4 four-circle diffractometer (STOE, Darmstadt, Germany) with an Oxford Cryostreams cooling device.

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Results and discussion

Heat capacity and a low-temperature phase transition

Heat capacity of β-glycine was measured at 111 points over the temperature range of 5–295 K. The temperature range was limited with the value close to ambient temperature at which the sample was crystallized, for even slight heating above it can start transformation of β into α or γ polymorphs. The experimental points are listed in Table 1. The standard deviation of the experimental points from the smoothed curve is 2.1% for $T<10$ K, 0.38% for $10<T<50$ K, and 0.04% for $T>50$ K.

At low temperatures, heat capacity of β polymorph fits polynomial $C_p=aT+bT^3$. Here, the cubic term is the lattice contribution corresponding to the Debye model. The linear term is typical of metals but not of isolators, for it is connected with 'free' electrons. This linear contribution to the heat capacity will be discussed below. The straight line in axes C_p/T and T^2 calculated over 12 first experimental points fits

Table 1 Experimental heat capacity of β-polymorph of glycine

T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}
Series 1		Series 3		Series 4		Series 6	
293.35	97.305	226.11	79.790	259.62	88.862	5.72	0.05721
294.74	97.705	228.26	80.485	260.73	88.973	6.88	0.09699
Series 2		230.39	81.049	261.83	89.270	8.12	0.1433
82.84	36.742	232.32	81.643	262.98	89.530	9.18	0.2093
87.34	38.665	233.98	82.231	269.66	91.623	10.35	0.2841
92.23	40.621	235.63	82.797	270.68	91.603	11.55	0.3950
97.67	42.717	237.32	83.319	271.70	91.472	12.71	0.5545
102.98	44.659	239.04	83.922	272.75	91.783	14.09	0.8271
108.18	46.481	240.75	84.511	273.76	92.196	15.60	1.1273
113.29	48.205	242.21	85.006	Series 5		17.09	1.5215
118.58	49.929	243.39	85.501	6.43	0.07917	18.59	1.9794
124.15	51.709	244.57	86.055	7.52	0.1201	20.34	2.5500
130.74	53.707	245.74	86.579	8.57	0.1678	22.28	3.2926
138.36	55.945	246.91	87.186	9.53	0.2234	24.16	4.1111
146.03	58.138	248.08	87.882	10.71	0.3193	25.96	4.9619
153.82	60.324	249.24	88.538	11.87	0.4300	27.74	5.8587
161.81	62.570	250.39	89.195	12.89	0.5832	29.56	6.8373
169.94	64.857	251.58	89.882	13.95	0.8034	31.91	8.1848
178.16	67.057	252.81	90.186			34.72	9.8339
186.59	69.281	254.02	90.252			37.50	11.534
195.16	71.468	255.21	90.117			40.11	13.173
203.85	73.778	256.39	89.789			43.28	15.167
212.75	76.180	257.57	89.318			47.14	17.572
221.84	78.632	258.72	89.064			51.63	20.371
230.96	81.321	259.90	88.986			56.67	23.360
240.06	84.386	262.48	89.327			61.68	26.186
249.20	88.616	263.98	89.835			66.77	28.921
258.33	89.610	265.47	90.304			71.90	31.536
267.46	90.933	266.96	90.749			76.93	33.972
276.57	92.988	268.44	91.234			81.90	36.248
285.65	95.371	269.92	91.679				
		272.73	91.821				
		274.89	92.513				
		277.05	93.105				

them with a standard deviation of 1.76% (Fig. 1). Thermodynamic functions of β glycine were calculated using smoothed values of heat capacity above 10 K and extrapolation function $C_p=0.00231T+0.000239T^3$ from 0 to 10 K. The results are shown in Table 2.

A phase transition in β-glycine was observed at 252 K (to the best of our knowledge – for the first time). It looks like a smooth protuberance (~4%) on a plot $C_p(T)$ but is evident on the diagram $C_p(\beta,T)–C_p(\alpha,T)$, where the difference in heat capacity between β- and α polymorphs is shown (Fig. 2). This phase transition is characterized with the excess heat capacity of about 3.5 J mol^{-1} K^{-1} at temperature 252 K. The data in Table 2 were calculated using smoothed C_p values 'as measured', the anomalous contribution of the phase transition to the regular heat capacity was not extracted.

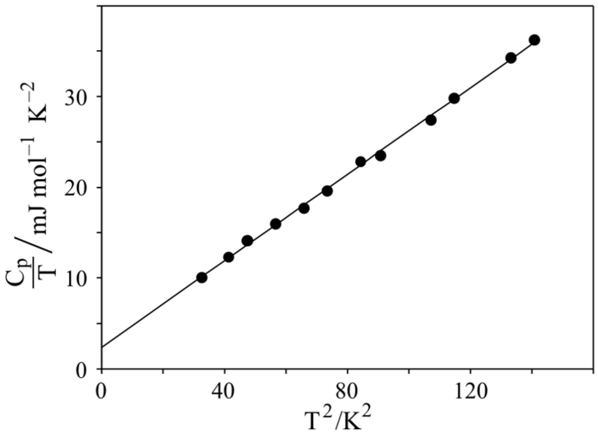

Fig. 1 Testing heat capacity on obeying the Debye model. Fitting line does not cross the zero point indicating that a linear term exists

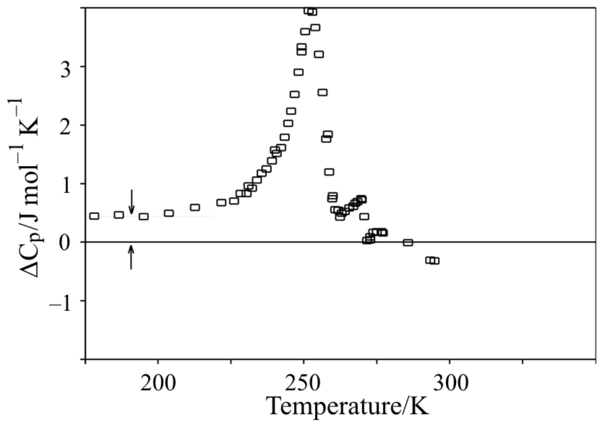

Fig. 2 The difference between heat capacities of β- and α-polymorphs, $C_p(\beta,T)–C_p(\alpha,T)$, near the phase transition point. Solid line at T>310 K is the result of DSC measurements [4]. Arrows indicate the difference equivalent to the linear contribution defined at the fitting in Fig. 1

Table 2 Thermodynamic functions for β-polymorph of glycine

T/ K	C_p/ J mol^{-1} K^{-1}	H/ J mol^{-1}	S/ J mol^{-1} K^{-1}
(5)	(0.041)	(0.066)	(0.022)
10	0.262	0.712	0.103
15	1.021	3.55	0.322
20	2.437	11.88	0.792
25	4.490	28.94	1.545
30	7.094	57.71	2.586
35	10.005	100.4	3.896
40	13.098	158.1	5.433
45	16.251	231.5	7.158
50	19.362	320.5	9.031
60	25.250	544.0	13.09
70	30.585	823.7	17.39
80	35.412	1154	21.79
90	39.741	1530	26.22
100	43.586	1947	30.61
110	47.103	2401	34.93
120	50.382	2889	39.17
130	53.481	3408	43.33
140	56.434	3958	47.40
150	59.262	4536	51.39
160	62.084	5143	55.31
170	64.848	5778	59.15
180	67.535	6440	62.94
190	70.164	7128	66.66
200	72.772	7843	70.32
220	78.118	9351	77.51
240	84.241	10972	84.55
260	88.944	12733	91.60
273.15	91.954	13923	96.06
280	93.934	14560	98.37
295	97.769	15997	103.37
(298.15)	(98.692)	(16307)	(104.41)

During a recent variable-temperature X-ray diffraction study [5] no indications at a structural phase transition at 252 K could be noticed. Since in [5] temperature was changed in rather large (50 K) steps, after a phase transition was discovered at about 250 K calorimetrically, we have undertaken a revised variable-temperature X-ray diffraction study specially in the vicinity of the phase transition point. In the whole temperature range 100–300 K the changes in cell parameters and cell volume of β-glycine were continuous (Fig. 3). This argues in favor of the second-order phase transition. No evident changes in the symmetry of the crystal structure were detected. No changes in the time of heat relaxation at pulse heating near the

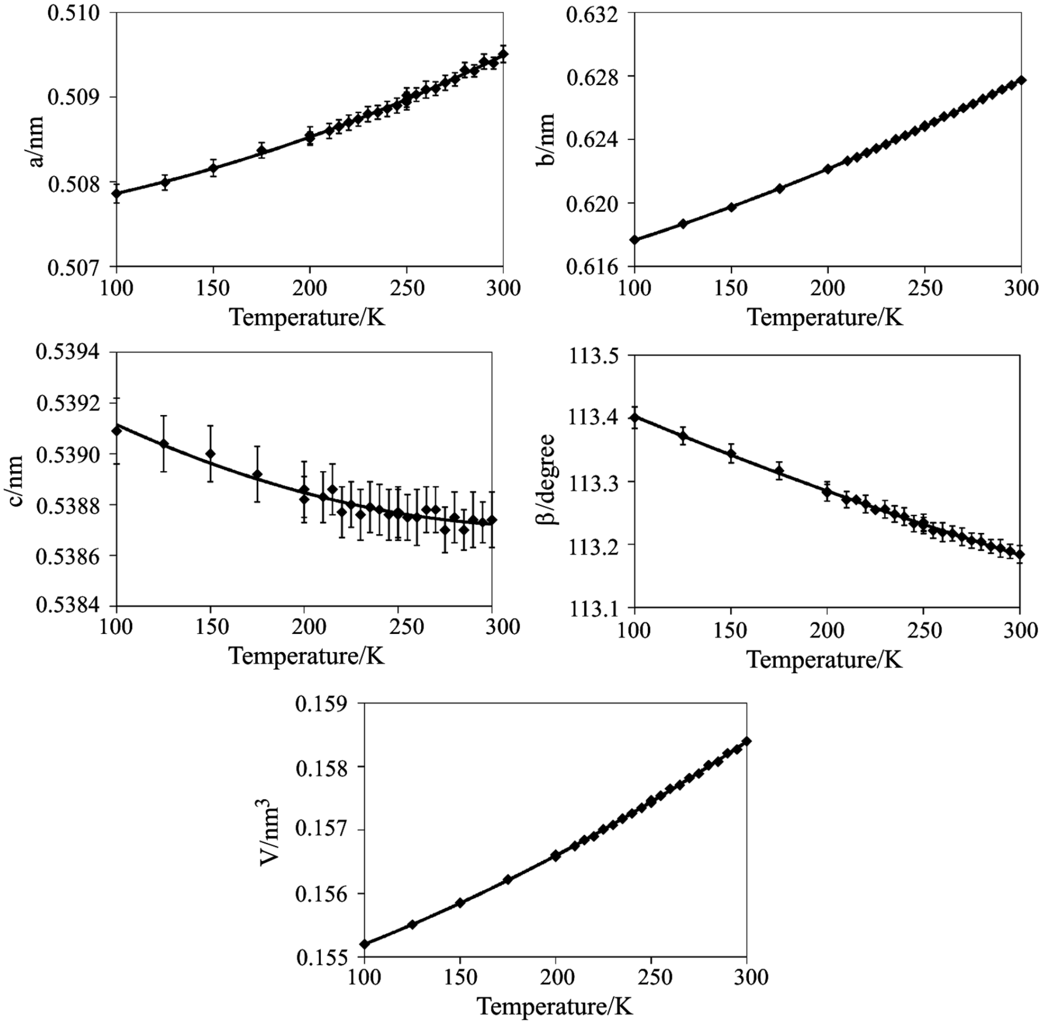

Fig. 3 Cell parameters and cell volume of β-glycine over the temperature range near the phase transition

phase transition were observed. It is also typical of a second-order phase transition, for heat capacity is a continuous function of temperature except the very point of a maximum in $C_p(T)$ where its fluctuations are virtual. Finally, we came to the conclusion that the anomalous increase in heat capacity of β-glycine near 252 K is due to a second-order phase transition. Probably, this is the ferroelectric-paraelectric transition.

After the heat capacity was measured over the whole temperature range allowing us to evaluate thermodynamic functions, we have tried to measure $C_p(T)$ in the vicinity of the phase transition more accurately and made several heating-cooling cycles near 250 K. Unexpectedly, a heat process started inside the calorimeter manifesting itself as a drift in temperature. New values of heat capacity turned out to differ from the previous curve and we took the sample from the calorimeter. X-ray diffraction showed that β-polymorph transformed completely into the mixture of α- (major) and γ- (minor) polymorphs.

In the single-crystal X-ray diffraction experiments we have also observed the repeated cyclic variation of temperature around the phase transition point (252 K) to result eventually in the deterioration of crystal quality and a β–α polymorphous transformation. It is worthy noting, that a simple cooling of a crystal of β-polymorph from ambient temperature down to 100 K and then a reverse heating back to ambient temperature did not induce any polymorphous transformations, and the crystals preserved their quality [5].

Additional contribution to the heat capacity of β-polymorph

At very low temperatures, heat capacity of β polymorph fits polynomial $C_p=aT+bT^3$, where a=0.00231 J mol^{-1} K^{-2} and b=0.000239 J mol^{-1} K^{-4}. Of two other polymorphs, γ does not fit Debye model and α fits to the polynomial $C_p=bT^3$, where b=0.000238 J mol^{-1} K^{-4}. Thus, the values of b coefficients for α and β are identical within the limits of experimental error and one may anticipate that the vi-

Table 3 Thermodynamic data for three polymorphs of glycine

	α	β	γ
Space group	$P2_1/n$	$P2_1$	$P3_1$
ρ at 294 K/g cm^{-3} [5]	1.608	1.576	1.591
C_p(T)/J mol^{-1} K^{-1} at			
50 K	19.25	19.36	19.81
100 K	43.38	43.59	43.37
200 K	72.36	72.77	71.34
298.15 K	99.23	98.69	96.00
H(298.15)–H(0)/kJ mol^{-1}	16.19	16.31	15.99
ΔH_s(298.15)/kJ mol^{-1} [6]	14.52	14.20	14.79
S(298.15)/J mol^{-1} K^{-1}	103.7	104.4	103.4
$G(i$,298.15)–G(γ,298.15)/J mol^{-1} K^{-1}	157	277	0

bration spectra are almost identical for α and β-polymorphs.

Linear term in the fitting polynomial is the additional contribution to the heat capacity produced by unknown additional interaction among $^{+}NH_3$–CH_2–COO^{-} zwitter-ions forming layers in the crystal structure of the two glycine polymorphs. $^{+}NH_3$ tails of zwitter-ions stick out of the layers uniformly either up (↑) or down (↓) bonding with oxygen of zwitter-ions in a neighboring layer. The tails in the neighboring layers are paired (↑↓↑↓↑↓) in α-glycine and unpaired (↑↑↑↑↑↑) in β-glycine. The main difference in physical properties between α and β polymorphs is the non-zero electric moment of the unit cell in β-glycine. This is the difference that makes β-polymorph piezoelectric and α-polymorph non-piezoelectric. The electric interaction among zwitter-ions in the β-polymorph could be responsible for the phase transition, and the linear term in the polynomial fitting the heat capacity could be, in fact, the 'electric' contribution. The difference in heat capacity between β and α polymorphs at 200 K (before the phase transition) is about 0.42 J mol^{-1} K^{-1}. If extrapolated to that point, the low-temperature linear contribution ($0.00231T$) produces 0.46 J mol^{-1} K^{-1}. This should be considered as an excellent agreement. After the phase transition, the difference in heat capacity between β and α polymorphs decreases and changes in sign. At ambient temperature, heat capacity of β-polymorph is less than that of α-polymorph. Excess 'electric' interaction in β-polymorph is destroyed at the phase transition, and the 'electric' contribution to the heat capacity ceases.

Relationship between structure and thermodynamic functions

Now we have complete information on structure and thermodynamic functions of all three polymorphs of glycine. Table 3 contains a digest of the information. The values of heat capacity for three polymorphs are very close. At selected temperatures, the greatest difference is about 3.5% (between α and γ at 298.15 K). Similarly, enthalpy and entropy of the polymorphs differ insignificantly. Enthalpies of polymorph transitions are very small compared to the enthalpies of formation or even enthalpies of dissolution. The latter are listed in Table 3 as ΔH_s(298.15). It is not the crystal structure in general, that affects thermodynamic properties. The arrangement of $^{+}NH_3$ tails of zwitter-ions is the factor that governs physical properties. It produces additional interaction among zwitter-ions. The greatest difference in heat capacity between polymorphs is observed at phase transition points (at ~10 K for γ- and at ~252 K for β-polymorphs). Since the difference in the vibrational (Debye) contributions to the heat capacity between the polymorphs is very small, any additional contribution produces quite significant changes in thermodynamic functions. Thus, when comparing the polymorphs of molecular crystals, one should first identify what peculiarities in the structure can produce an additional contribution to heat capacity.

The difference in Gibbs energy $G(i$,298.15)–G(γ,298.15) was evaluated for the transformation from polymorph i into polymorph γ. These values are positive for both i=α and i=β indicating that γ-polymorph is stable at 298.15 K and the rest polymorphs are metastable at this temperature.

Conclusions

The measurements of low-temperature heat capacity of β-glycine have shown that the second order phase transition occurs at 252 K. Heat capacity of β-polymorph differs from that of the α-form by a linear contribution aT. The contribution disappears right after the phase transition.

For all the three polymorphs, heat capacities are very close. Enormous differences in the crystal structures hardly affect thermodynamic functions of molecular crystals. It is impossible to predict a priori, just looking at the structure, which molecular arrangement is preferable and gives the most stable polymorph. In the case of glycine, and, possibly, of other related compounds, it is the arrangement of charged tails of zwitter-ions that produces additional interaction between zwitter-ions and an extra contribution to the heat capacity, thus affecting the relative stability of the polymorphs.

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