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LOW-TEMPERATURE HEAT CAPACITY OF α AND γ POLYMORPHS OF GLYCINE

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Abstract

Low-temperature heat capacity of two polymorphs of glycine (α and γ) was measured from 5.5 to 304 K and thermodynamic functions were calculated. Difference in heat capacity between polymorphs ranges from +26% at 10 K to –3% at 300 K. The difference indicates the contribution into the heat capacity of piezoelectric γ polymorph, probably connected with phase transition and ferroelectricity. Thermodynamic evaluations show that at ambient conditions γ polymorph is stable and α polymorph is metastable.

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

Introduction

Relative stability of the polymorphs and the preferable growth of a particular polymorph in real experiments do not necessarily correlate directly. This is a reason why much confusion and contradictory statements can be found in the literature about glycine, NH_2CH_2COOH. It forms three crystalline polymorphs: two monoclinic (α and β) and one trigonal (γ). Two of them are stored unchanged for a long time at ambient conditions – α and γ. At heating, γ polymorph transforms into α polymorph at about 165°C. At cooling, the reverse transformation was never observed. β polymorph transforms at heating or long-term storage at ambient conditions either into α or γ polymorph. Inspecting the literature, we found several works stating that α polymorph is stable but other works stated that γ polymorph is stable. Neither paper contains thermodynamic justification of the statement. Moreover, in spite of a long history of glycine investigation, there are no reliable thermodynamic data that can be used for the justification.

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It is very strange that published data on thermodynamic properties of crystalline glycine have no indication on the structure of the sample investigated. Specific heat, heat of combustion, heat of solution, energy of crystalline lattice, etc., always refer to 'glycine' in general, not to the specific (α, or β, or γ) polymorph. The only exception is the recent work on heat of dissolution in water [1]. At 298.15 K, the solution enthalpies for α, β and γ polymorphs were found to be 14523±76, 14198±73, and 14791±84 J mol^{-1}. These data are not sufficient to conclude with certainty which polymorph is stable at ambient conditions: the values of entropy are needed. These can be derived only from the data on low-temperature heat capacity.

For the first time heat capacity of glycine was measured over the temperature range of 93–300 K by means of adiabatic calorimetry [2]. Later, the measurements were repeated over the temperature range of 11–305 K to diminish the temperature range (93 to 0 K) of the extrapolation of heat capacity and to evaluate entropy and enthalpy more correctly [3]. Experimental values of heat capacity in the two papers agree well coinciding with one another within the limits of experimental error: $C_\mathrm{p}(298.15)=99.2\pm0.2$ J mol^{-1} K^{-1}.

Later, heat capacity of glycine was measured using drop calorimetry in a temperature range of 293.15–305.15 K [4]. The results were compared with those of [3] to check the accuracy of the calorimetric technique in the measurements of partial molar heat capacity of some amino acids in aqueous solution. The values measured agree well with those published in [3]: $C_\mathrm{p}(298.15)=99.3\pm0.1$ J mol^{-1} K^{-1}.

Heat capacity of a chemical 'chromatographically homogeneous glycine' supplied by Reanal (Hungary) was measured by means of differential scanning calorimetry together with other peptides and their solutions with a relative error of 0.01 J g^{-1} K^{-1} [5]. For glycine, heat capacity at 298 K was found to be 95 J mol^{-1} K^{-1} (with a relative error of 0.8 J mol^{-1} K^{-1}). The value differs evidently from those in [2–4]. The discrepancy was not discussed.

This paper contains a part of the results of a systematic investigation of polymorphism in amino acids. The objective of this work was to measure heat capacities of α and γ polymorphs of glycine in a wide range of temperature in order to determine which polymorph is stable at ambient conditions and which one is metastable. The measurements were also expected to elucidate the reason of the discrepancy between C_p in [2–5] (experimental errors or a difference in the crystal structures of the samples).

Experimental

First, we tested the chemicals 'glycine' received from different chemical companies. Neither company indicates crystalline polymorph of glycine. Usually, the reagents contain a mixture of both polymorphs (α and γ). The polymorph content of different chemicals ranges from α with an admixture of γ to γ with an admixture of α. Pure α polymorph can be received after recrystallization in water but chemical composition of the crystals is uncontrolled. Thus, we can use either the reagents of high chemical purity containing two polymorphs or single polymorph of unknown purity. We have chosen the first way.

Glycine 'Analytical Reagent' of Riedel-de Haën (Sigma-Aldrich Laborchemikalien GmbH) was used in our calorimetric measurements. The chemical mainly consists of α polymorph with γ polymorph impurity of 6%. The content was determined with X-ray powder diffraction of α–γ binary mixtures. To convert α polymorph into γ polymorph, we used special procedure of recrystallization in a gas, developed at the Novosibirsk State University and the Institute of Solid State Chemistry and Mechanochemistry (to be published). After the treatment, the sample consists of pure γ polymorph of the same composition but without traces of α polymorph. The samples were characterized by means of X-ray powder diffraction (GADDS D8 Bruker, CuK_{α}, 2Θ 10–40°). Unit cell parameters are $a=0.511$, $b=1.200$, $c=0.547$ nm, $\beta=111.52°$ for monoclinic α polymorph and $a=0.705$, $c=0.549$ nm for trigonal γ polymorph.

Calorimetric measurements were carried out using low-temperature adiabatic calorimetric system working over the temperature range of 4.2–320 K [6]. Nickel calorimeter has internal volume of 5.7 cm^3. Mass of a sample in the calorimeter was 5.6988 g (α polymorph) and 3.3513 g (γ polymorph). Both polymorphs have similar density and the difference in the mass is due to the difference in the packing of small crystals forming the powder. The difference in sample mass produces the difference in accuracy of the heat capacity measured (Results). Test measurements of benzoic acid show that the difference between our and reference data on heat capacity is within the limits of 0.5% for T>20 K and 3% over the temperature range of 6 to 20 K [7].

Results

Heat capacity was measured at 62 points over the temperature range of 6.5–305 K for α polymorph and 66 points over the temperature range of 5.7–305 K for γ polymorph. The experimental points are listed in Tables 1 and 2. For the α polymorph, the standard deviation of the experimental points from the smoothed curve is 0.35% for $10<T<50$ K, 0.02% for $50<T<200$ K, and 0.03% for $T>200$ K. For the γ polymorph, those values are 0.4% for $T<50$ K, 0.03% for $50<T<200$ K, and 0.08% for $T>200$ K.

Experimental data on heat capacity of α polymorph were corrected for the impurity of γ polymorph. The greatest value of the correction is about +1.5% near 10 K decreasing with temperature down to –0.2% at 300 K with a change of the sign at 100 K. Experimental point at 269.5 K contains a contribution from ice melting. It increases heat capacity by 0.28% at a temperature increment ΔT of 8.6 K. Thus, the water content of the reagent estimated is 0.006 g per mole of glycine. In [3], the increase in heat capacity at 269.27 K was 1.1% at a temperature increment of 7.5 K and the water content was estimated 0.022 g per mole of glycine.

At low temperatures, heat capacity of α polymorph agrees well with the Debye model ($C_p=aT^3$). The straight line calculated in axes C_p/T and T^2 over 4 first experimental points fits them with a standard deviation of 1.7% (Fig. 1). Thermodynamic functions of α polymorph of glycine were calculated using smoothed values of heat capacity above 10 K and extrapolation function $C_p=0.000238T^3$ from 0 to 10 K. The results are shown in Table 3.

Table 1 Experimental heat capacity of α 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}
6.52	0.06424	42.79	14.77	149.23	58.73
7.69	0.1104	45.92	16.75	157.29	60.97
8.77	0.1612	50.02	19.29	165.52	63.23
9.72	0.2217	54.12	21.79	173.98	65.50
10.84	0.3132	58.25	24.20	182.61	67.79
12.19	0.4716	63.31	27.02	191.36	70.05
13.75	0.7405	69.21	30.11	200.20	72.31
15.28	1.041	74.96	32.95	209.15	74.71
16.55	1.344	80.56	35.53	217.99	76.92
17.82	1.690	82.43	36.38	226.56	79.21
19.44	2.208	87.70	38.62	235.10	81.47
21.32	2.891	92.48	40.54	243.67	83.78
23.18	3.648	97.37	42.41	252.26	86.14
25.05	4.492	101.98	44.10	260.90	88.45
26.84	5.358	106.31	45.62	269.51	91.09
28.56	6.254	110.74	47.13	278.06	93.23
30.87	7.542	115.26	48.62	286.57	95.66
33.51	9.071	119.95	50.12	295.05	98.12
35.93	10.52	126.14	52.04	298.58	99.15
38.24	11.93	133.69	54.30	304.23	100.85
40.56	13.39	141.37	56.52		

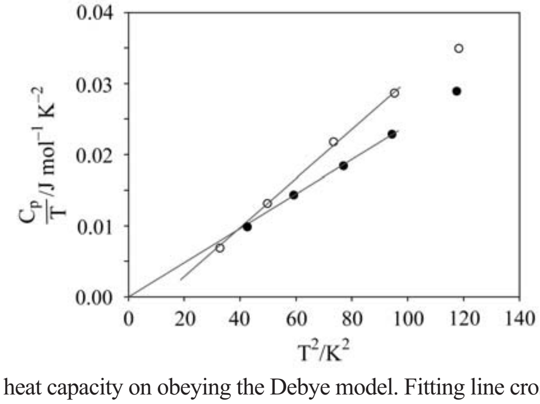

Fig. 1 Testing heat capacity on obeying the Debye model. Fitting line crosses the zero point for α polymorph (filled circles) but goes down for γ polymorph (open circles)

For γ polymorph, heat capacity does not fit the Debye model. Below 6 K, its heat capacity is lower than that of α polymorph but increases with temperature rapidly, according to the power greater than 3. It makes impossible to use the cubic polynomial for the extrapolation of heat capacity to zero temperature. To perform extrapolation, we have to use the Einstein model. Thermodynamic functions of γ polymorph of glycine were calculated using smoothed values of heat capacity above 7.05 K and extrapolation function $C_p=1182T^{-2}\exp(-39.12/T)$ from 0 to 7.05 K.

Table 2 Experimental heat capacity of γ 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}
5.74	0.03932	32.11	8.651	135.01	54.32
7.05	0.09249	34.65	10.18	145.36	57.16
8.57	0.1864	37.22	11.77	155.94	60.02
9.76	0.2795	39.59	13.27	166.76	62.92
10.88	0.3800	41.80	14.67	177.76	65.80
12.38	0.5871	45.30	16.89	188.97	68.61
13.82	0.8708	50.01	19.81	199.42	71.15
15.30	1.191	54.60	22.56	208.98	73.65
15.43	1.211	59.02	25.07	218.65	75.83
15.49	1.224	64.19	27.87	228.38	78.40
16.20	1.401	69.92	30.78	238.14	80.84
16.71	1.547	75.43	33.42	247.93	83.35
16.73	1.555	81.01	35.94	257.65	85.75
17.71	1.819	84.37	37.40	267.36	88.32
17.92	1.888	89.07	39.32	276.97	90.71
19.22	2.314	94.50	41.39	286.43	93.13
19.57	2.446	100.61	43.59	295.88	95.50
21.53	3.175	106.11	45.47	297.06	95.71
23.45	4.005	111.16	47.14	297.11	95.64
25.32	4.897	116.30	48.78	302.70	97.16
27.17	5.836	121.59	50.42	302.85	97.16
29.52	7.150	127.04	52.04	305.33	97.88

Discussion

The difference between heat capacity of α and γ polymorphs over the whole temperature range of the measurements, $100(C_p(\gamma)-C_p(\alpha))/C_p(\alpha)$ *vs*. T, is shown in Fig. 2 (circles). The polymorphs differ evidently in heat capacity. Squares show the difference between published heat capacity of the unspecified sample of glycine [3] and smoothed data for α

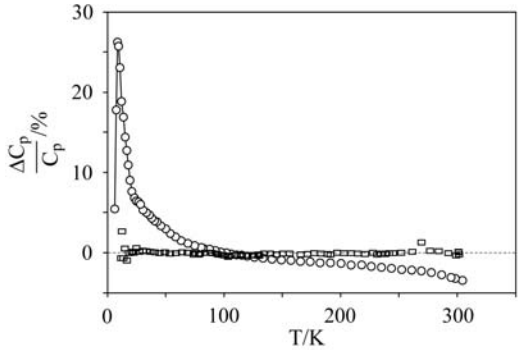

Fig. 2 Difference between heat capacities of γ and α polymorphs (both this work, circles) and between unspecified sample of glycine ([3]) and α polymorph (this work, squares)

polymorph (this work): $100(C_p([3])–C_p(\alpha))/C_p(\alpha)$. Two points with the greatest difference are at 12.4 K (+2.68%) and 269.27 K (1.29%). The rest points deflect from the smoothed curve by less than 1%. The averaged difference is 0.13±0.80% at temperatures below 50 K, –0.19±0.14% for $50<T<200$ K, and +0.01±0.33% for $T>200$ K. These values are within the limits of experimental error. Heat capacity of α polymorph at 298.15 K is 99.2 J mol^{-1} K^{-1} (Table 3). One can conclude that the unspecified sample of glycine investigated in [3] was in fact α polymorph. For heat capacity of γ polymorph at 298.15 K is 96.0 J mol^{-1} K^{-1} (Table 4), the chemical ‘chromatographically homogeneous glycine’ supplied by Reanal (Hungary) was probably γ polymorph. Finally, the difference in heat capacity of glycine at 298.15 K between [3–5] can be the result of different polymorphs measured.

The difference in heat capacity between γ and α polymorphs is large enough near 10 K. It looks like a peak of the phase transition in γ polymorph. Deflection of its heat capacity from the Debye model at temperatures below 6 K argues also in favor of the phase transition. We know nothing about the nature of the interaction resulting the anomalous difference in the heat capacity. Nevertheless, we can suppose this is the dipole interaction between flat glycine molecules (zwitterions) packed in the structure. In contrast to α polymorph, γ and β polymorphs are piezoelectric. Probably, electric repulsion among crystals of γ glycine prevented them to fill the calorimeter with the mass as much as α polymorph (Experimental). Anyway, the mechanism of the anomalous heat capacity at low temperatures in γ polymorph is outside the scope of this report. It is of interest for us only because the additional contribution to the heat capacity of γ polymorph turned out to increase its thermodynamic stability with respect to the transformation into α polymorph. In relation to a possible phase transition in γ-glycine at low temperature, it is interesting to note that a pressure-induced polymorph transition of unknown nature was mentioned in [8]. Some reversible spontaneous changes in the powder diffraction patterns of γ-glycine that might be an indication of a phase transition above 4 GPa were also described in [9].

Table 3 Thermodynamic functions for α polymorph of glycine

T/K	C_p/J mol^{-1} K^{-1}	H/J mol^{-1}	S/J mol^{-1} K^{-1}
(5)	(0.030)	(0.037)	(0.010)
10	0.238	0.592	0.079
15	0.970	3.36	0.293
20	2.388	11.46	0.750
25	4.448	28.30	1.493
30	7.020	56.79	2.525
35	9.932	99.07	3.822
40	12.996	156.3	5.348
45	16.132	229.2	7.059
50	19.246	317.6	8.921
60	25.162	540.1	12.96
70	30.490	818.8	17.25
80	35.277	1148	21.64
90	39.552	1523	26.04
100	43.384	1938	30.41
110	46.888	2389	34.71
120	50.148	2875	38.93
130	53.225	3392	43.07
140	56.159	3939	47.12
150	58.984	4514	51.09
160	61.757	5118	54.99
170	64.481	5749	58.82
180	67.149	6408	62.58
190	69.757	7092	66.28
200	72.357	7803	69.92
220	77.564	9302	77.06
240	82.896	10906	84.04
260	88.346	12618	90.89
273.15	92.000	13804	95.34
280	93.926	14441	97.64
298.15	99.226	16193	103.70
300	99.778	16377	104.32

Of three polymorphs, only monoclinic β glycine is known with certainty metastable. Its exothermic transformation into α polymorph was investigated by DSC [10]. The enthalpy of transformation is extremely small: 200 J mol^{-1}. It was not known so far which polymorph of the rest two (α or γ) is stable at ambient conditions and which one is metastable.

Table 4 Thermodynamic functions for γ polymorph of glycine

T/K	C_p/J mol^{-1} K^{-1}	H/J mol^{-1}	S/J mol^{-1} K^{-1}
(5)	(0.019)	(0.012)	(0.003)
10	0.299	0.669	0.083
15	1.119	3.91	0.334
20	2.595	12.88	0.840
25	4.735	30.94	1.637
30	7.416	61.15	2.731
35	10.402	105.6	4.096
40	13.528	165.4	5.688
45	16.699	241.0	7.464
50	19.806	332.3	9.385
60	25.617	559.9	13.52
70	30.821	842.5	17.87
80	35.507	1175	22.29
90	39.675	1551	26.72
100	43.371	1966	31.10
110	46.763	2417	35.39
120	49.928	2901	39.60
130	52.889	3415	43.71
140	55.700	3958	47.73
150	58.429	4529	51.67
160	61.132	5127	55.53
170	63.757	5751	59.31
180	66.326	6402	63.03
190	68.869	7078	66.69
200	71.341	7779	70.28
220	76.271	9255	77.31
240	81.299	10830	84.16
260	86.377	12507	90.87
273.15	89.766	13665	95.21
280	91.522	14286	97.46
298.15	95.995	15988	103.35
300	96.465	16166	103.94

Solution enthalpies of the three polymorphs were measured in [1]. The authors discussed the results as lattice energies. We are to use them in thermodynamic evaluations, for difference in solution enthalpies is, in fact, the difference in the enthalpies of formation. The enthalpy of the reaction of dissolution at temperature T is

$$\Delta_r H(i,T)=\Delta_f H(\text{solution},T)-\Delta_f H(\text{solvent},T)-\Delta_f H(\text{solute } i,T),$$

where i is the polymorph (i=α, β, γ), $\Delta_f H$ is the enthalpy of formation of a substance at temperature T. If the reaction for all polymorphs is carried out at the same experimental conditions, for any two polymorphs

$$\Delta_r H(i,T)-\Delta_r \mathrm{H}(j,T)=\Delta_f H(\text{solute } j,T)-\Delta_f H(\text{solute } i,T).$$

Before using experimental data on solution enthalpies from [1], we have to solve two problems. First, the results of [1] contradict ours partly. These are to be discussed mainly in the next paper dealing with the phase transition γ→α. Here, it is very important that β polymorph in [1] remains unchanged after heating to and isothermal treating at 220°C. Contrary, we found β polymorph to transform into α polymorph at heating to 140°C. Second, the experimental errors of the enthalpies published in [1] are too large. For the differences in the enthalpies of formation, the errors are of the same order as the values themselves:

$$\Delta_r H(\beta,298.15)-\Delta_r H(\alpha,298.15)=-325\pm149 \text{ J mol}^{-1}$$

$$\Delta_r H(\gamma,298.15)-\Delta_r H(\alpha,298.15)=268\pm160 \text{ J mol}^{-1}$$

We have analyzed information about the experiments in [1] and found that the differences can be derived from the experimental data with less errors. Experimental error in calorimetric measurements consists of two parts: 1) random error of a run and 2) uncertainty in the calibration coefficient.

Random error in a series of N runs is treated according to conventional procedure: evaluations of the mean ($\bar{x}$), estimated standard deviation (s), and estimated standard deviation of the mean ($s_m=s/\sqrt{N}$). A 95 percent confidence limit in the mean is

$$\Delta=t_{0.95,N-1}s_m$$

where t is the critical value of the Student distribution. After data published in [1], the values of Δ for the solution enthalpies are 47, 35, and 58 J mol^{-1} for α, β, and γ polymorphs, respectively.

Uncertainty in the calibration coefficient is derived from the calibration experiments (KCl in water): ±0.29% (17225±50 J mol^{-1}). The values of the calibration error in $\Delta_r H(i,298.15)$ are 42, 41, and 43 J mol^{-1} for α, β, and γ polymorphs, respectively. Finally, the solution enthalpies of three polymorphs have the total experimental errors of 89, 77, and 101 J mol^{-1} instead of 76, 73, and 84 J mol^{-1} published. On the other hand, the error in the calibration coefficient for their differences is less than 1 J mol^{-1}, and the total uncertainty is 83 J mol^{-1} for $\Delta_r H(\beta,298.15)-\Delta_r H(\alpha,298.15)$ and 104 J mol^{-1} for $\Delta_r H(\gamma,298.15)-\Delta_r H(\alpha,298.15)$. This consideration is valid as all the experiments were carried out using the same equipment with the same calibration coefficient.

Comparing difference in the solution enthalpies for β and α polymorphs with the enthalpy of the transition β→α, one can test how calorimetric data in various sources relay with one another. Enthalpy of transition changes with temperature according to equation

$$\Delta_{\mathrm{tr}}H(T)-\int_{T_0}^{T}\Delta C_{\mathrm{p}}\mathrm{d}T=\Delta_{\mathrm{tr}}H(T_0)$$

Evaluation of the solution enthalpies at 298.15 K [1] gives

$$\Delta_{\mathrm{tr}}H(298.15)=\Delta_{\mathrm{r}}H(\beta,298.15)-\Delta_{\mathrm{r}}H(\alpha,298.15)=-325\pm83\ \mathrm{J\ mol^{-1}}$$

Using the results of scanning calorimetry [10], we have

$$\Delta_{\mathrm{tr}}H(390)-\int_{298.15}^{390}\Delta C_{\mathrm{p}}\mathrm{d}T=-287\pm39\ \mathrm{J\ mol^{-1}}$$

The value was derived from experimental function $C_{\mathrm{p}}(\beta,T)-C_{\mathrm{p}}(\alpha,T)$ over temperature range 310–415 K, extrapolated (15 mJ $\mathrm{g^{-1}\ K^{-1}}$) onto the range 298.15–310 K. Peak temperature is 390 K. The 95 percent confidence limit (±39 J $\mathrm{mol^{-1}}$) was calculated after the reproducibility of the calorimetric runs (the estimated standard deviation after 7 runs is 5 mJ $\mathrm{g^{-1}\ K^{-1}}$). The values 325±83 and 287±39 agree well with one another.

For the reaction γ→α, the change in the Gibbs free energy is

$$\Delta G(T)=\Delta H(T)-T\Delta S(T),$$

where

$$\Delta H(T)=\Delta_{\mathrm{f}}H(\alpha,T)-\Delta_{\mathrm{f}}H(\gamma,T)=\Delta_{\mathrm{r}}H(\gamma,T)-\Delta_{\mathrm{r}}H(\alpha,T)$$

At T=298.15 K, the solution enthalpies yield

$$\Delta H(298.15)=268\pm105\ \mathrm{J\ mol^{-1}}$$

On the other hand,

$$\Delta_{\mathrm{f}}H(i,T)=\Delta_{\mathrm{f}}H(i,0)+H(i,T)-H(i,0),$$

where $H(i,T)-H(i,0)$ is the increment in enthalpy of ith polymorph derived from its low-temperature heat capacity. The values for α and γ polymorphs of glycine are listed in Tables 3 and 4, respectively. The accuracy of the low-temperature calorimetric data was estimated after the root-mean-square of difference between experimental points and smoothed values. The values of uncertainty in enthalpy for α and γ polymorphs are 1.1 and 1.3 J $\mathrm{mol^{-1}}$ at 50 K, 2.6 and 3.6 J $\mathrm{mol^{-1}}$ at 200 K, and 5.2 and 10.5 J $\mathrm{mol^{-1}}$ at 300 K. For the entropy, these values are 0.031 and 0.035 J $\mathrm{mol^{-1}\ K^{-1}}$ at 50 K, 0.043 and 0.053 J $\mathrm{mol^{-1}\ K^{-1}}$ at 200 K, 0.053 and 0.080 J $\mathrm{mol^{-1}\ K^{-1}}$ at 300 K.

The enthalpy of the reaction γ→α at T=0 K is

$$\Delta H(0)=\Delta_{\mathrm{f}}H(\alpha,0)-\Delta_{\mathrm{f}}H(\gamma,0)=57\pm121\ \mathrm{J\ mol^{-1}}$$

Now we can calculate the change in the Gibbs free energy for the γ→α transition:

$$\Delta G(T)=\Delta H(0)+H(\alpha,T)-H(\gamma,T)-T\,(S(\alpha,T)-S(\gamma,T)).$$

The results are shown in Fig. 3. Dashed line indicates the limits of error. Over the temperature range from 0 to 300 K function $\Delta G(T)$ is positive. At 298.15, $\Delta G=157\pm145$ J mol^{-1}. This means that the γ→α transition will not occur, but inverse transition α→γ will. The latter is the reaction that was used for the preparation of γ polymorph for the calorimetric measurements (Experimental). Thus, γ polymorph is stable at ambient conditions and α is metastable.

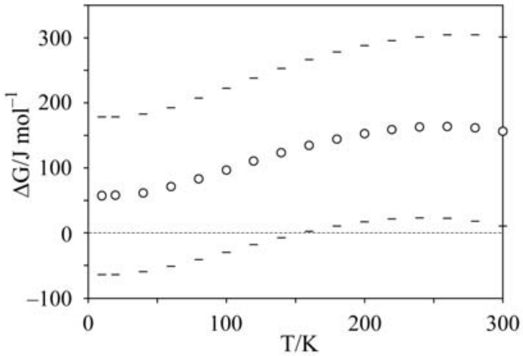

Fig. 3 Change in the Gibbs free energy for the γ→α transition (circles for the values calculated, dashed lines for the limits of error)

At heating above room temperature, the change in the Gibbs free energy for the γ→α transition decreases. The derivative

$$\mathrm{d}\Delta G/\mathrm{d}T=S(\gamma)-S(\alpha)$$

is certainly negative starting from 260 K (Tables 3 and 4). The second derivative

$$\mathrm{d}^2\Delta G/\mathrm{d}T^2=(C_\mathrm{p}(\gamma)-C_\mathrm{p}(\alpha))/T$$

is also negative starting from 110 K. Thus, relative stability of the two polymorphs will change at elevated temperatures. This agrees with the fact that γ polymorph transforms into α polymorph near 440 K.

Conclusions

The measurements of low-temperature heat-capacity have shown that below 300 K γ polymorph of glycine is more stable than α polymorph. Difference in the heat capacity between the polymorphs and their thermodynamic functions indicate the change in the relative stability of the polymorphs at elevated temperatures: α polymorph is getting stable and γ metastable.

The reason of the discrepancy between C_p in [2–5] is the difference in the crystal structures of the samples measured.

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