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Calorimetric Study of Phase Transitions in the Thiourea Carbon Tetrachloride Inclusion Compound*

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Abstract. Heat capacities of the inclusion compound $(\text{thiourea})_{3.00}CCl_4$ have been measured in the temperature range 15–300 K. A first-order phase transition was found at 41.3 K and a second-order transition at 67.17 K. The enthalpy and entropy of the transition are 149 J mol^{-1} and 3.7 J K^{-1} mol^{-1} for the former, and 241 J mol^{-1} and 3.9 J K^{-1} mol^{-1} for the latter. A divergent expression $\Delta C = A\{(T_c - T)/T_c\}^{-\alpha}$ was fitted to the excess heat capacity of the upper phase transition. The best-fit parameters were $A = 7.4$ J K^{-1} mol^{-1}, $T_c = 67.166$ K and $\alpha = 0.31$. Possible types of molecular disorder in the high temperature phase are discussed in relation to the transition entropy and the molecular and site symmetries of the guest molecule. The heat capacity of the lowest temperature phase was unusually large and may indicate the existence of very low frequency vibrational modes or labile configurational excitation of the guest molecule. Standard thermodynamic functions were calculated from the heat capacity data and are tabulated in the appendix.

Key words. Thiourea inclusion compound, phase transition, entropy of transition, orientational disorder, guest-guest interaction.

1. Introduction

It has long been known that thiourea forms inclusion compounds of the channel type with many organic molecules of intermediate size. Adductible molecules known so far are mostly alicyclic or branched aliphatic hydrocarbons [1]. The compounds offer possibilities of studying host-guest and guest-guest interactions in structurally well-defined crystalline lattices. The host-guest interaction is the primary mechanism stabilizing the clathrate lattice and accounts for the greater part of the enthalpy of enclathration. Guest-guest interactions play a secondary role in the formation and stability of the inclusion compounds because the guest molecules are not in direct contact with each other and hence the interaction between them is much weaker than the host-guest interaction. This interaction has been neglected in the thermodynamics of clathrate formation except in a few theoretical papers [2–4]. However, in some cases the guest-guest interaction reveals itself in a striking way at low temperatures when the inclusion compounds undergo phase transitions [5–12].

Cope *et al.* measured the heat capacities of the urea inclusion compounds of four hydrocarbons and found a complicated series of phases in all of them [11]. The disorder implied by the large transition entropies indicates that inter- and intramolecular conformational degrees of freedom contribute to the entropy term of the free energy of enclathration.

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Carbon tetrachloride is one of the few non-hydrocarbon molecules that form thiourea inclusion compounds [1, 13] and, in fact, it is the only rigid molecule known to be adductible with thiourea. Because of its chemical and structural simplicity, it provides an ideal case for the detailed study of molecular motions and phase transitions due to the host-guest and guest-guest effects. In the present paper we report the heat capacities of this compound, which show the occurrence of two phase transitions at low temperature. There has been ambiguity as to the stoichiometry of the compound. The independent determinations of the composition are also reported here to show that the stoichiometry is $(\text{thiourea})_{3.00}CCl_4$ within the accuracy of our experiment.

2. Experimental

2.1. SAMPLE PREPARATION

The sample was prepared according to the phase diagram of the system CCl_4–thiourea–acetic acid [13] as follows. Carbon tetrachloride and acetic acid were mixed in a 1 : 1 ratio by mass. The mixed solvent was heated to 75°C and saturated with thiourea. As the solution slowly cooled down, colorless needle-like crystals of the inclusion compound separated out. They were stored in a desiccator oven with KOH pellets.

The composition of the crystal was detemined in two different ways. First, the compound was decomposed with boiling water and dried to constant weight. The decrease in the mass gave the amount of CCl_4 in the sample crystal. Sublimation of thiourea during the drying was shown to be negligible in a separate experiment. The host/guest ratio thus determined was 3.005, 2.968 and 3.044: average 3.006. Second, the stoichiometric ratio was also determined by elemental analysis, $C = 12.57\%$, $H = 3.13\%$, $S = 24.96\%$, $N = 21.81\%$ and $Cl = 36.18\%$. The most probable host/guest ratio calculated from these values was 3.00, in agreement with the thermal decomposition experiment. A slightly different value of 2.86 has been reported [13].

2.2. HEAT CAPACITY MEASUREMENT

The heat capacities were measured between 15 and 300 K with a computer-controlled adiabatic calorimeter [14]. The thermometer had been calibrated on IPTS-68. The mass of the calorimetric sample was 2.1654 g. The temperature increment of one heat capacity determination was ca. 2 K. It decreased to about 0.08–0.1 K near the transition temperature. The accuracy of the data was estimated to be better than 1% below 30 K and 0.3% above 30 K.

3. Results and Discussion

The heat capacity data are given in Tables I and II and plotted in Figure 1. Two heat capacity peaks due to the phase transitions occur at 41.3 K and 67.17 K. The former is a first-order phase transition, for the entropy increased discontinuously at the transition temperature, as shown below. The latter is basically a higher-order transition characterized by a large anomalous heat capacity below the transition

Table I. Molar heat capacities of $(\text{thiourea})_{3.00}CCl_4$. ($R = 8.3144\ J\ K^{-1}\ mol^{-1}$, $m_r = 382.18\ g\ mol^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}R$	T/K	$C_{p,m}/R$
16.03	5.282	55.47	17.54	160.69	31.02
17.08	5.670	57.00	18.02	163.64	31.32
18.11	6.076	58.54	18.47	166.56	31.68
19.15	6.457	60.07	18.99	169.47	32.02
20.22	6.835	61.57	19.53	172.35	32.35
21.21	7.192	63.04	20.12	175.21	32.61
22.13	7.522	64.51	20.86	178.06	32.97
23.07	7.831	66.09	22.36	180.88	33.28
24.04	8.168	67.72	24.12	183.69	33.62
24.99	8.494	69.37	19.72	186.48	33.96
25.91	8.785	71.07	19.96	189.25	34.27
26.84	9.109	72.78	20.23	192.01	34.57
27.79	9.425	74.47	20.46	194.75	34.86
28.71	9.744	76.13	20.73	197.48	35.23
29.61	10.06	77.81	20.97	200.19	35.56
30.57	10.41	79.50	21.22	202.89	35.81
31.77	10.85	81.18	21.46	205.57	36.20
32.17	10.97	81.40	21.44	208.24	36.52
33.09	11.32	82.84	21.67	210.90	36.80
33.28	11.38	84.51	21.92	213.54	37.12
34.35	11.76	85.05	21.93	216.88	37.42
34.50	11.83	86.20	22.17	220.90	37.89
35.40	12.14	87.88	22.40	224.89	38.35
35.98	12.35	88.56	22.41	228.85	38.85
36.46	12.51	89.54	22.61	232.79	39.26
37.42	12.86	91.96	22.86	236.71	39.65
37.35	12.89	95.25	23.33	240.60	40.20
38.57	13.28	98.45	23.75	244.47	40.54
38.83	13.36	101.58	24.13	248.33	40.89
39.58	13.65	104.63	24.46	252.16	41.32
40.18	14.46	107.63	24.81	255.97	41.71
40.56	18.00	110.57	25.14	259.76	42.11
41.31	27.31	113.45	25.51	263.53	42.56
41.42	26.40	116.29	25.84	267.28	42.88
42.34	13.74	119.43	26.25	271.02	43.32
42.47	13.80	122.86	26.63	274.73	43.68
43.75	14.11	126.23	27.01	278.44	44.02
43.94	14.16	129.56	27.40	282.12	44.43
45.49	14.61	132.83	27.77	285.79	45.11
45.55	14.62	136.07	28.17	289.44	45.49
46.98	15.06	139.26	28.54	293.07	45.89
47.32	15.16	142.41	28.89	296.69	46.03
48.46	15.51	145.53	29.24	297.00	46.07
49.02	15.67	148.62	29.60	298.80	46.18
50.65	16.14	151.68	29.95	300.61	46.35
52.28	16.59	154.71	30.32	302.40	46.72
53.90	17.08	157.71	30.65	304.20	46.78

Table II. Molar heat capacities of $(\text{thiourea})_{3.00}\text{CCl}_4$ around the upper phase transition. ($R = 8.3144\ \text{J K}^{-1}\ \text{mol}^{-1}$, $m_r = 382.12\ \text{g mol}^{-1}$)

T/K	$C_{p,\text{m}}/R$	T/K	$C_{p,\text{m}}/R$
62.18	20.27	70.99	20.40
62.48	20.30	71.91	20.54
62.78	20.32	72.81	20.71
63.08	20.56	73.70	20.82
63.37	20.76		
63.66	20.85		
63.95	21.00	65.15	21.23
64.24	21.17	65.33	21.19
64.53	21.33	65.45	21.38
64.81	21.55	65.57	21.51
65.09	21.68	65.68	21.61
65.37	21.91	65.80	21.65
65.65	22.25	65.91	21.88
65.88	22.39	66.03	21.92
66.05	22.59	66.14	22.17
66.22	22.95	66.25	22.40
66.40	23.13	66.37	22.43
66.57	23.64	66.48	22.74
66.74	24.17	66.59	22.93
66.90	24.82	66.70	23.32
67.07	26.56	66.82	23.74
67.22	43.35	66.93	24.40
67.35	39.99	67.03	25.26
67.51	19.99	67.14	29.37
67.69	20.01	67.23	55.15
67.86	20.12	67.31	46.80
68.03	19.93	67.41	19.77
68.21	20.04	67.53	19.43
68.38	20.59	67.76	19.48
68.55	19.92	68.14	19.53
69.11	20.16	68.53	19.59
70.06	20.26	68.94	19.60

temperature. At the final stage of the transition there was a small discontinuous increase of the entropy. The heat capacity around the transition temperature is shown on an enlarged scale in Figure 2. For the determination of the transition enthalpies and entropies, the normal heat capacity was calculated by interpolation using a 5th order polynomial in temperature that reproduced the experimental points to $\pm 0.1\%$ in the temperature intervals 15–30 K and 90–130 K. Transition enthalpies thus determined were $149\ \text{J mol}^{-1}$ and $241\ \text{J mol}^{-1}$ for the transitions at 41.3 K and 67.17 K, respectively. The corresponding transition entropies were $3.7\ \text{J K}^{-1}\ \text{mol}^{-1}$ and $3.9\ \text{J K}^{-1}\ \text{mol}^{-1}$. Figure 3 shows the temperature dependence of the transitional entropies. The discontinuous parts of the entropy increments were 78% and less than 19% of the transition entropies for the low and high temperature transitions, respectively. Thus the low temperature phase transition is a strong first-order type, whereas the high temperature transition is very close to a second- or higher-order transition.

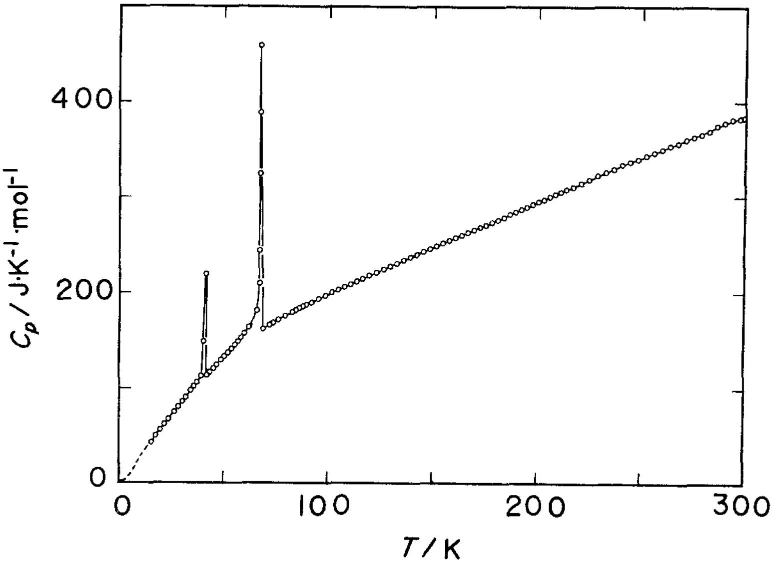

Fig. 1. Molar heat capacities of the (thiourea)$_{3.00}$CCl$_4$ inclusion compound.

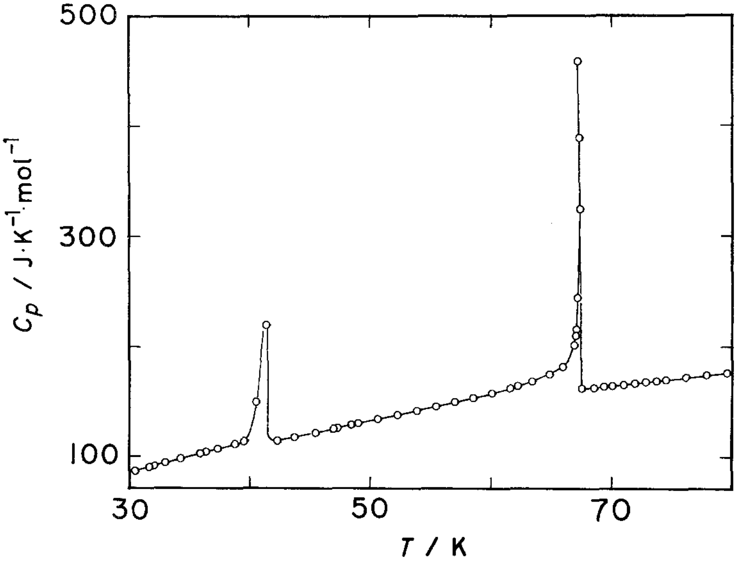

Fig. 2. Molar heat capacities of the (thiourea)$_{3.00}$CCl$_4$ inclusion compound around the two phase transitions.

Since the transition temperature could be approached closely in the heat capacity measurement, an attempt was made to fit a divergent function to the heat capacity near the upper transition temperature. The function fitted was [15]

$$\Delta C = A((T_c - T)/T_c)^{-\alpha} \qquad (T < T_c) \tag{1}$$

The best fit parameters were $A = (7.4 \pm 0.4)$ J K^{-1} mol^{-1}, $\alpha = (0.31 \pm 0.1)$ and $T_c = (67.166 \pm 0.003)$ K. Figure 4 shows the comparison between the experimental

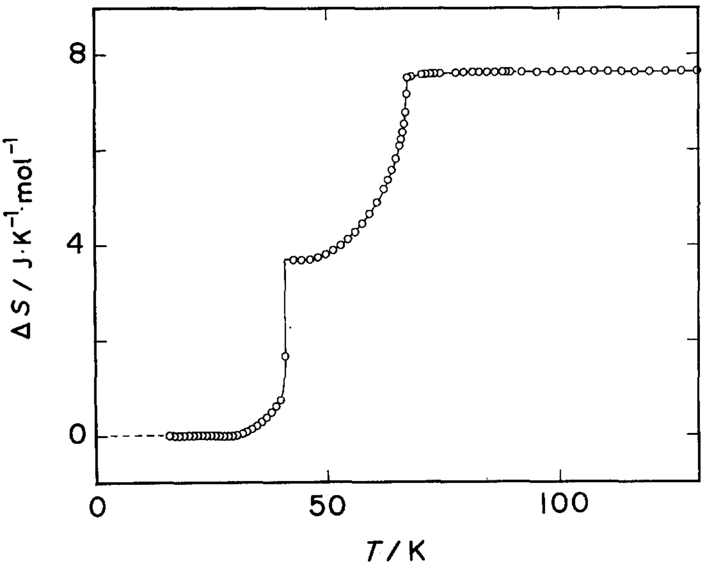

Fig. 3. Excess entropy of the (thiourea)$_{3.00}$CCl$_4$ inclusion compound

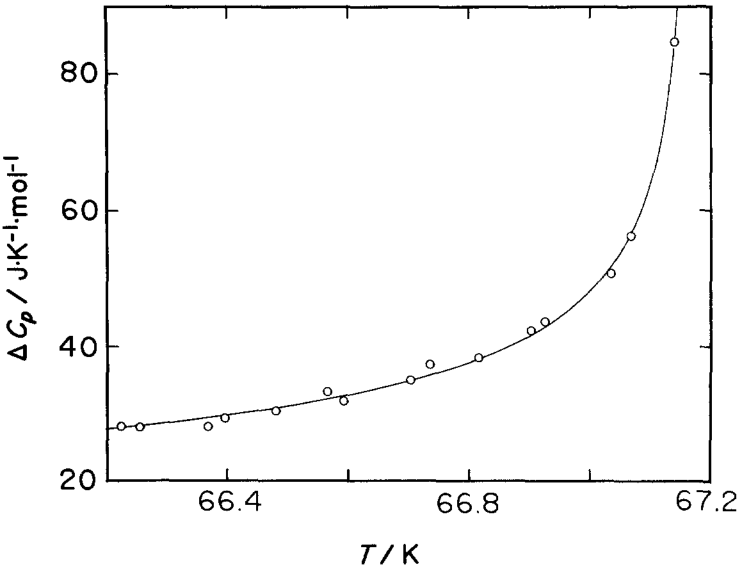

Fig. 4. Excess heat capacities of the (thiourea)$_{3.00}$CCl$_4$ inclusion compound close to the upper transition and the best-fit power law function represented by the solid curve.

and calculated heat capacities. The data used for the fitting were those between 66.2 K and 67.16 K. The two points closest to the transition temperature were excluded from the fitting because distortion of the data by the latent heat was suspected. For $T > T_c$ the excess heat capacity was very small and could not be reproduced by Equation (1). The critical exponent $\alpha(T < T_c)$ is smaller than the mean field value of 0.5. The non-classical value of $\alpha = 0.31$ is reasonable in view of the channel structure of the crystal in which each guest molecule has a small number of nearest neighbors. However, the absence of significant excess heat capacity above T_c indicates that the short range ordering is not important. Since it is generally true that the short range effect is less significant in a system in which each molecule interacts with a large number of neighbors, the effective number of the neighboring CCl_4 molecules with which each of the CCl_4 molecules interact appears much larger than the value of 2 suggested by the channel structure. In fact the phase transition would not occur if the interactions were restricted to those between the nearest neighbors in the channel.

It is customary to relate the transition entropy ΔS to the ratio W_h/W_l of the numbers of the allowed molecular orientations in the high and low temperature phases by the following equation.

$$\Delta S = R \ln(W_h/W_l). \tag{2}$$

This supposes that the phase transition is an order–disorder type, which is reasonable for the present case in view of the large value ($7.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$) of the total transition entropy. We accept this view and furthermore set $W_l = 1$ assuming that the molecules are ordered in the low temperature phase. The experimental value of W_h is given by $\exp(\Delta S/R) = 2.8$. In the following discussion this is compared with model values based on the molecular and site symmetries. The molecular symmetry of CCl_4 is T_d and the site symmetry D_3. The latter is assumed to be the same as in the thiourea cyclohexane adducts [16].

For the molecular orientation in which the molecular and site triad axes coincide, one need not (though one may) assume orientational disorder around the axis to satisfy the symmetry requirement. However, one has to invoke a two-fold disorder as to the orientation (up or down) of the molecular triad axis. This model has $W_h = 2$ and the corresponding entropy is $R \ln 2 = 5.76\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

A set of three equivalent orientations (i.e. $W_h = 3$) is also possible: the orientations in which the diad axes of the molecule and the site coincide. There are three such orientations. The entropy predicted by this model is $R \ln 3 = 9.13\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

For a general orientation in which none of the molecular and site symmetry elements coincide, the disorder required by the symmetry is six-fold. Thus the symmetry restricts the disorder to 2-, 3- or 6-fold. The second possibility is the closest to the experiments ($\Delta S = 7.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$). The first possibility may also be compatible with the experiment, if one takes into account other degrees of freedom (e.g., vibrational) that may contribute to the transition entropy and the probable error in the estimation of the normal heat capacity. The third possibility $W_h = 6$ ($\Delta S = 14.9\ \mathrm{J\ K^{-1}\ mol^{-1}}$) is outside the range of the uncertainty ($\sim 10\%$) of the experimental transition entropy and thus is untenable. The mechanism by which the phase transition proceeds in two steps is not understood at present.

In a nuclear quadrupole spectroscopic measurement to be reported separately [17], the chlorine resonance lines were detected only below 28 K. This observation indicates an extremely large mobility which the guest molecule has even at low temperature. The large motional freedom is doubtless related to the nonspecific and isotropic character of the host-guest interaction in this compound. In some other inclusion compounds of CCl_4 the chlorine resonance was observed at temperatures as high as 150 K, e.g., in CCl_4–Dianin's compound and CCl_4–Fe(AcAc)$_3$ [18]. It is also relevant here that the low temperature heat capacity of an analogous inclusion compound containing $C_2H_2Cl_4$ is smaller than that of the present compound [19]. The facile thermal excitation of the guest CCl_4 molecule indicated by the fading-out of the quadrupole resonance signal and the large heat capacity at low temperature may be related to subtle differences in the host-guest and guest-guest interactions in these inclusion compounds.

Appendix

Standard thermodynamic functions of the (thiourea)$_{3.00}$ CCl_4 inclusion compound were calculated from the heat capacity data and are presented in reduced forms in

Table A-I. Standard thermodynamic functions of (thiourea)$_{3.00}$ CCl_4. (R = 8.3144 J K^{-1} mol^{-1})

T/K	$C^\circ_{p,\mathrm{m}}/R$	$\Delta_0^T H^\circ_\mathrm{m}/RT$	$\Delta_0^T S^\circ_\mathrm{m} R$	$\Phi^\circ_\mathrm{m}(T)/RT$
5	0.755	0.199	0.267	0.067
10	2.957	1.030	1.466	0.436
15	4.892	1.999	3.036	1.036
20	6.760	2.957	4.700	1.743
25	8.485	3.893	6.396	2.503
30	10.20	4.800	8.093	3.292
35	12.00	5.701	9.800	4.099
50	15.94	8.511	15.14	6.629
60	18.96	9.996	18.31	8.312
70	19.83	11.61	21.58	9.972
80	21.28	12.73	24.33	11.60
90	22.62	13.75	26.91	13.16
100	23.90	14.71	29.36	14.65
110	25.11	15.60	31.69	16.10
120	26.30	16.44	33.93	17.49
130	27.46	17.24	36.08	18.84
140	28.61	18.01	38.16	20.14
150	29.76	18.76	40.17	21.41
160	30.91	19.48	42.13	22.65
170	32.06	20.19	44.04	23.85
180	33.21	20.88	45.90	25.02
190	34.37	21.56	47.73	26.17
200	35.52	22.23	49.52	27.29
210	36.66	22.89	51.28	28.40
220	37.80	23.54	53.02	29.48
230	38.92	24.18	54.72	30.54
240	40.03	24.82	56.40	31.58
250	41.12	25.45	58.06	32.61
260	42.19	26.08	59.69	33.62
270	43.25	26.69	61.30	34.61
273.15	43.58	26.88	61.81	34.92
280	44.30	27.30	62.89	35.59
290	45.35	27.91	64.47	36.56
298.15	46.21	28.39	65.74	37.34
300	46.40	28.50	66.02	37.52

Table A-I. For the calculation the data were extrapolated below 15 K by the use of the Debye and Einstein functions. For $T > 15$ K, polynomial interpolation functions were employed to represent the heat capacity data, except in the transition regions where direct numerical integration was performed. The molar mass was taken to be 382.18 g mol^{-1}.

References

1. L. C. Fetterly: in *Non-stoichiometric Compounds* (ed. L. Mandelcorn), p. 491. Academic Press, New York (1964).
2. V. E. Schneider, E. E. Tornau, and A. A. Vlasova: *Chem. Phys., Lett.* **93**, 188 (1982).
3. V. E. Schneider, E. E. Tornau, A. A. Vlasova, and A. A. Gurskas: *J. Incl. Phenom.* **3**, 235 (1985).
4. V. R. Belosludov, Yu. A. Dyadin, G. N. Chekhova, and B. A. Kolesov: *J. Incl. Phenom.* **3**, 243 (1985).
5. T. Matsuo, H. Suga, and S. Seki: *J. Phys. Soc. Jpn.* **30**, 785 (1971).
6. T. Matsuo: *J. Phys. Soc. Jpn.* **30**, 794 (1971).
7. R. C. Pemberton and N. G. Parsonage: *Trans. Faraday Soc.* **61**, 2112 (1965).
8. R. C. Pemberton and N. G. Parsonage: *Trans. Faraday Soc.* **62**, 553 (1966).
9. F. G. Cope and N. G. Parsonage: *J. Chem. Thermodyn.* **1**, 99 (1969).
10. H. Ukegawa, T. Matsuo, H. Suga, A. J. Leadbetter, R. Ward and J. W. Clark: *Can. J. Chem.* **66**, 943 (1988).
11. A. F. G. Cope, D. J. Gannon, and N. G. Parsonage: *J. Chem. Thermodyn.* **4**, 829 (1972).
12. M. Sorai, K. Ogasahara, and H. Suga: *Mol. Cryst. Liq. Cryst.* **73**, 231 (1981).
13. G. N. Checkhova, Yu. A. Dyadin, and T. B. Rodionova: *Izv. Sib. Otd. Akad. Nauk. -Ser. Khim.* N5, 78 (1979). *Chem. Abstr.* **92**, 100212P (1980).
14. T. Matsuo and H. Suga: *Thermochim. Acta* **88**, 149 (1985).
15. H. E. Stanley: *Introduction to Phase Transition and Critical Phenomena*, Clarendon Press, Oxford (1971).
16. H-U. Lenne: *Acta Crystallogr.* **7**, 1 (1954).
17. T. Matsuo, M. Sekii, H. Suga, N. Nakamura, and H. Chihara: *International Conference on Nuclear Quadrupole Resonance*, Takayama, 1989. *Z Naturforsch.* **A45** (1990) in press.
18. L. Pang and E. A. C. Lucken: *J. Incl. Phenom.* **5**, 245 (1987).
19. M. Sekii, T. Matsuo, and H. Suga: to be presented at the 25th Annual Meeting of the Japanese Society of the Calorimetry and Thermal Analysis, Osaka (1989). Abstract P. 31.