Heat Capacity of Solid Phosphorus Pentachloride between 4 and 150 K. Nature of the Transition at 102 K.

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Molar heat capacity of solid P_2Cl_{10} was measured between 4 and 150 K with an adiabatic calorimeter, with particular attention to the phase transition at 102.0 ± 0.2 K. The heat and entropy of the transition were 148 ± 3 $\mathrm{J mol^{-1}}$ and 1.67 ± 0.03 $\mathrm{JK^{-1}mol^{-1}}$. Shape and magnitude of the anomalous heat capacity depend on the method of preparation. Anomaly in the heat capacity begins at about 75 K, rises gradually to a maximum of 9.12 ± 0.08 $\mathrm{JK^{-1}mol^{-1}}$ at 102.0 K and tails off at about 110 K. The shape of the excess heat capacity curve can be explained satisfactorily by the librational soft-mode theory which assumes that PCl_6 anions tend to change equilibrium orientation with temperature.

Stable ionic form (P_2Cl_{10}) of phosphorus pentachloride has a higher-order phase transition at about 102 K. A detailed study of nuclear quadrupole resonance in ionic and molecular forms of P_2Cl_{10} was reported together with a preliminary heat capacity measurement.[1] Reinvestigation of the nuclear quadrupole resonance and precision measurements of the solid heat capacities have now been carried out with particular attention to the phase transition. The present paper describes the heat capacity and its relation to the soft-mode theory of phase transition. The quadrupole resonance part has been revised and presented in the preceding paper.[2]

Experimental

Material. Solid phosphorus pentachloride (reagent grade, Yashima Chemicals Co.) was pulverized and subjected to fractional vacuum sublimation to remove phosphorus oxychloride $POCl_3$ which had contaminated the specimen through hydrolysis by humid air. Sublimation in a vacuum of 10^{-2}—10^{-3} Torr at 60°C onto a glass wall at room temperature gave about 100 g of Sample I out of 250 g of the original material. After the heat capacity measurements were concluded with Sample I in 1966, it was found that the results were not entirely consistent with the preliminary results. In view of the recent observations in the case of chloranil[3] that a broad phase transition is extremely sensitive to crystal imperfections, it was decided to prepare another specimen, Sample II, of well-developed crystallinity. Sample II differed from Sample I in that it was obtained by slow vacuum sublimation onto a glass wall maintained at liquid nitrogen temperature. This procedure gives rise to molecular modification, which upon warming to room temperature is transformed into the stable ionic modification.[1] In fact Sample II gave a sharp, intense quadrupole resonance spectrum both at room temperature and at liquid nitrogen temperature.[2] Unfortunately, Sample I was not examined by quadrupole spectroscopy when its heat capacity was determined, but it showed a perfectly normal quadrupole spectrum four years after its preparation.

The heat capacities of Sample I and II differed only in the transition region. Charging of the calorimeter with the specimen was done in a dry-box in nitrogen atmosphere and the calorimeter was sealed by use of Woods' alloy after about 2—3 Torr of He gas replaced the air in the calorimeter.

Heat Capacity Measurements. The calorimeter vessel is made of gold and has an inner volume of about 50 $\mathrm{cm^3}$. A Leeds & Northrup platinum thermometer was inserted into the reentrant well at the center of the calorimeter using Wood's alloy to fill in the void space. Six radiant vanes inside the calorimeter improved thermal diffusivity in the specimen. Heater wires (♯36 manganin) were wound both round the entire length of the platinum thermometer and round the lower quarter of the outside wall of the calorimeter. A carbon resistor (Allen-Bradley, 1/8W, 10 Ω at room temperature) was used for the temperature below 11K. Gold-plated, thin copper sheath which covered the lower part of the calorimeter and the head of the platinum thermometer was used to reduce the heat exchange due to radiation.

The temperature scale above 11K is based on the 1948 International Temperature Scales and the U.S. National Bureau of Standards Scale. The working scale below 11K has been described in a previous paper.[4] The measuring circuitry including control of the adiabatic mantles is the same as reported earlier.[5]

Results and Discussion

Measured Heat Capacities. The measured heat capacity values are given in Tables 1 and 2 for Samples I and II, respectively.[6] The measurements for Sample I extend between 4.6 and 134.2 K, whereas those for Sample II cover only the region between 55 and 150 K because the two separate measurements agreed quite satisfactorily (to within ±0.3%) below 85 K and above 107 K. The results for either sample were internally consistent with scatter of points within ±0.1% except for those of Sample I below 11 K where maximum scatter amounted to about 5%. Figure 1 gives a plot of the two measurements; In the transition region, Sample I gives smaller heat capacities than Sample II, the maximum difference being as large as about 5.23 $\mathrm{JK^{-1}mol^{-1}}$ at 102 K. The most pronounced qualitative difference lies in the fact that the Sample I heat

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[1] H. Chihara, N. Nakamura, and S. Seki, This Bulletin, **40**, 50 (1967).

[2] H. Chihara and N. Nakamura, *ibid.*, **46**, 94 (1973).

[3] H. Chihara and K. Masukane, *J. Chem. Phys.*, to be published.

[4] H. Chihara and M. Nakamura, This Bulletin, **45**, 133 (1972).

[5] T. Atake and H. Chihara, *J. Chem. Thermodynamics*, **3**, 51 (1971).

[6] The values refer to one mole of P_2Cl_{10}.

Table 1. Heat capacity of solid P_2Cl_{10} (Sample I).
(Weight of sample 54.241 g, Molecular weight 416.48)

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
Series I		45.392	88.39	96.505	164.01	99.500	166.72
12.257	13.44	47.368	91.48	97.527	165.22	100.110	168.23
13.420	16.46	49.311	94.75	98.542	166.48	100.716	169.22
14.282	18.71	51.297	97.95	99.551	167.60	101.321	169.29
14.661	20.19	53.229	101.30	100.556	168.78	101.924	170.03
15.468	22.42	55.271	104.69	101.554	169.62	102.526	170.37
16.261	24.76	Series III		102.563	170.40	103.126	170.96
16.980	26.73	56.959	106.85	103.585	170.99	103.725	170.98
17.803	28.96	59.016	110.52	104.610	171.43	104.310	171.21
18.718	31.76	61.006	113.55	Series V		104.906	171.71
19.663	34.42	62.995	116.09	103.980	171.06	105.509	171.77
20.708	37.21	64.988	119.27	104.992	171.57	106.118	172.81
21.770	40.07	66.987	122.04	106.001	172.48	106.726	172.71
22.825	42.88	68.982	124.89	107.005	172.89	107.333	172.91
Series II		70.976	127.63	108.006	173.70	107.946	173.26
21.561	39.67	72.958	130.50	109.003	174.34	108.556	174.44
22.669	42.58	74.959	133.40	110.489	175.91	Series VII	
23.599	44.97	77.035	136.51	112.457	177.43	4.590	0.649
24.602	47.73	79.194	139.69	114.408	179.70	5.379	0.910
25.511	49.77	Series IV		116.376	181.02	5.685	1.231
26.465	52.03	80.676	141.81	118.359	182.77	5.959	1.636
26.831	52.72	82.827	144.82	120.325	184.63	6.568	2.185
28.485	56.91	84.939	148.30	122.277	186.30	7.368	3.212
30.250	60.59	87.043	151.42	124.248	187.59	7.949	4.114
32.126	64.59	89.147	154.18	126.236	189.80	8.588	5.184
33.793	67.88	89.817	155.07	128.209	191.55	9.387	6.648
34.873	70.13	91.371	157.06	130.200	193.25	10.275	8.581
36.755	73.80	92.395	158.70	132.209	195.05	11.133	10.573
38.854	77.27	93.414	159.28	134.216	197.11	11.934	12.523
41.155	81.22	94.443	161.21	Series VI		12.895	15.067
43.327	84.87	95.478	162.60	99.023	166.16	14.017	18.553

Table 2. Heat capacity of solid P_2Cl_{10} (Sample II).
(Weight of sample 40.053 g, Molecular weight 416.48)

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
Series I		84.060	148.05	106.546	172.88	147.729	208.05
55.067	103.87	85.098	149.44	Series III		149.821	209.56
56.212	105.70	86.129	151.20	105.783	172.66	Series IV	
57.337	107.50	87.150	152.75	106.675	172.51	94.595	163.40
58.507	109.27	88.162	154.48	107.608	173.24	95.556	165.12
59.725	111.22	89.168	155.68	108.525	173.61	96.510	167.08
60.988	113.29	90.166	157.22	109.516	174.21	97.458	167.92
62.293	115.35	91.158	158.60	110.532	175.08	98.400	169.73
63.579	117.27	92.143	160.10	111.543	176.27	99.149	171.16
64.844	119.37	93.122	161.41	112.701	177.07	99.713	172.24
66.089	120.91	94.046	162.49	113.954	178.32	100.270	172.96
67.317	123.02	94.867	164.02	115.329	179.60	100.827	173.82
68.528	124.66	95.636	165.22	116.826	180.95	101.334	174.51
69.607	126.40	96.403	166.81	118.315	182.18	101.793	174.94
70.614	127.78	97.163	167.89	119.796	183.69	102.252	175.33
71.611	129.33	97.921	169.10	121.437	185.37	102.665	175.53
72.540	130.44	98.674	170.14	123.237	186.94	103.031	175.34
73.464	131.68	99.424	171.53	125.027	188.00	103.444	174.89
74.440	133.28	100.170	172.92	126.806	190.10	103.951	173.73
75.460	134.71	100.912	173.92	128.574	191.62	104.505	172.86
Series II		101.652	174.79	130.567	193.32	105.057	172.91
75.398	134.19	102.297	175.52	132.775	195.29	105.608	172.87
76.520	136.51	102.849	175.49	134.962	197.32	106.251	172.89
77.630	137.81	103.402	174.66	137.132	199.16	106.995	173.02
78.728	139.56	103.957	173.93	139.283	201.11	107.750	173.37
79.816	141.20	104.511	173.20	141.421	203.05	108.493	173.59
80.893	142.86	105.111	172.77	143.548	205.00	109.223	174.13
81.959	144.55	105.806	172.77	145.643	206.13	109.942	174.28
83.015	146.28						

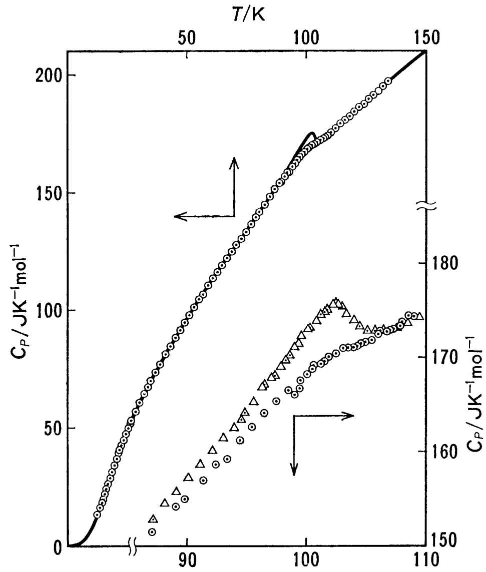

Fig. 1. Molar heat capacity of solid P_2Cl_{10}; ⊙ Sample I, △ Sample II; Solid curve above 50 K represents the result for Sample II.

capacity has nowhere a negative temperature coefficient, while the Sample II heat capacity shows a broad but distinct maximum at about 102 K. The behavior of the former is quite unlike the preliminary results obtained by use of a smaller calorimeter.[1] This is why we redetermined the heat capacities with the use of Sample II after about three years. In the following, we will use only the results of Sample II in discussing the effect of phase transition.

Table 3. Fundamental intra-ionic vibrations in P_2Cl_{10} (after Carlson).

Ion	Wave number/cm^{-1} (degeneracy)	Symmetry	Description
PCl_6^-	360 (1)	a_{1g}	P–Cl stretch
	281 (2)	e_g	P–Cl stretch
	449 (3)	f_{1u}	P–Cl stretch
	62 (3)	f_{1u}	Deformation
	150 (3)	f_{2g}	Deformation
	— (3)	f_{2u}	Deformation
PCl_4^+	459 (1)	a_1	P–Cl sym. stretch
	171 (2)	e	P–Cl sym. bend
	658 (3)	f_2	Degenerate stretch
	252 (3)	f_2	Degenerate bend

Separation of Anomalous Part of Heat Capacity. In order to amplify the extra heat capacity associated with the phase transition, contributions from the intra-ionic oscillations were calculated by the Einstein approximation and subtracted from the measured heat capacity values because all these contributions combined were expected to give a monotonous temperature dependence. Table 3 lists the relevant information on

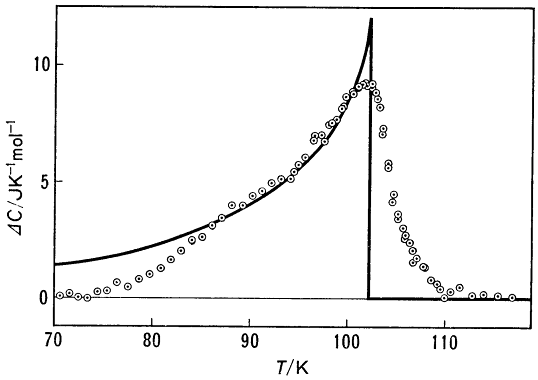

Fig. 2. Anomalous part of the heat capacity (Sample II). Solid curve represents Eq. (1) with α-β-m=0.5 as parameters determined by nuclear quadruplle resonance.

Table 4. Estimates of 'normal heat capacity' in the transition region

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^1
70	126.9	100	163.5
76	135.2	106	170.2
82	143.0	112	176.1
88	150.6	118	181.0
94	157.4		

the vibrational spectra of PCl_4^+ cation having T_d symmetry and of PCl_6^- anion having O_h symmetry according to Carlson.[7] The wave numbers given in Table 3 are those at room temperature. We assumed that they do not change with temperature. Such contributions[8] having been subtracted, the residual heat capacity values were plotted on a large graph paper and a smooth 'normal' heat capacity curve was drawn to obtain the anomalous part, which is shown in Fig. 2. Estimates of the 'normal' heat capacity (including intra-ionic contributions) are given in Table 4. We see from Fig. 2 that the maximum extra heat capacity is 9.12±0.08 J K^{-1} mol^{-1} at 102.0±0.2 K,[9] the transition point being slightly lower than that determined from Fig. 1. The anomaly starts at about 75 K, gradually rises to maximum over a range of 27 K, and tails off at about 110 K. A shoulder centering at 90 K in Fig. 2 is not considered to be real but is probably due to some inadequacy in the tempreature scale. Since the temperature increments used in the measurements are about 0.6 K in the vicinity of the maximum, the transition is apparently of higher order than the second order transition in the Ehrenfest definition.[10] The heat of transition is 148±3 Jmol^{-1} and the entropy of transition is 1.67±0.03 J K^{-1} mol^{-1}.

Comparison with the Soft-mode Theory. As discussed

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[7] G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963).

[8] The heat capacities corresponding to ν=62 cm^{-1} (f_{1u}) and to an unknown frequency (f_{2u}) were not taken into account for the reason discussed earlier.[1]

[9] Extrapolation of the order parameter to zero gives 103~0.6 K as determined by quadrupole resonance but the difference is considered trivial.

[10] From nuclear quadrupole resonance study,[2] symmetry elements appear abruptly at the transition and thus this is a second-order transition according to Landau's classification.[11]

[11] L. Tisza, "On the General Theory of Phase Transitions" in "Phase Transformations in Solids" edited by R. Smoluchowski, *et al.*, John Wiley & Sons, Inc., New York, (1951).

in the preceding paper,[2] the transition in P_2Cl_{10} is related to a cooperative change in the orientation θ of the figure axis of PCl_6^- anions. The broad nature of the transition as well as the very small entropy of transition suggest that it is due to a kind of soft librational mode for which a simple theory has been developed.[12] By use of Eq. (4) of the preceding paper, we have

$$\varDelta C = -Nk\frac{\alpha s x}{2\sinh^2(x/2)}\cdot\frac{\mathrm{d}s}{\mathrm{d}t},$$

where

$$x = (1+\alpha s^2)/t$$

and

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\alpha x/2s}{\alpha^2-8\beta t\{m+(1-2m)s^2\}\sinh^2(x/2)}.$$

The significance of the parameters is the same as in Ref. 2. Numerical calculation of the excess heat capacity $\varDelta C$ was made by using the parameter values

$$\alpha = \beta = m = 0.5$$

which give the best fit to the temperature dependence of the order parameter s as shown in Fig. 2 of Ref. 2. The result is shown in Fig. 2 by a solid curve. The theoretical curve, which was scaled down by a factor of 0.668, reproduces the important portion of the experimental $\varDelta C$. In view of the difficulty in estimating the 'normal' heat capacity values particularly below 90 K, the agreement between theory and experiment is considered excellent below the transition point. The scaling factor may be interpreted as indicating that only such librational modes that have small k, the wave vector, can couple with the uniform mode. Lack of agreement above the transition point is obviously due to inadequacy of the theory and may suggest the existence of some other lattice vibrational modes that play an important role in the transition phenomenon.

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12) H. Chihara, N. Nakamura, and M. Tachiki, *J. Chem. Phys.*, **54**, 3640 (1971).