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Phase Transition in the Ionic Modification of Phosphorus Pentachloride, $[PCl_4][PCl_6]$. Chlorine Nuclear Quadrupole Resonance Study

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Chlorine-35 nuclear quadrupole resonance frequencies in the ionic crystal $PCl_4^+\cdot PCl_6^-$ were redetermined. Ten resonance lines were found and their temperature dependences were measured below the second order phase transition point at 102 K. The splitting $\Delta\nu_i$ in the resonance lines in the low temperature phase showed a similar temperature dependence as the order parameter. This was accounted for by a librational soft mode theory based on an anharmonic coupling between molecular or ionic librational modes in the crystal.

In 1967 we reported on the ^{35}Cl nuclear quadrupole resonance (NQR) and calorimetric studies of both ionic and molecular modifications of phosphorus pentachloride.[1] It was found that the ionic crystal $[PCl_4][PCl_6]$ undergoes a second order phase transition at 102 K, but the mechanism of the phase transition was not fully clarified because of insufficient accuracy in the heat capacity measurement as well as other experimental data concerning the phase transition.

Meanwhile, DiLorenzo and Schneider[2] measured the NQR frequencies in the same substance and observed some resonance lines at different frequencies from those reported by the present authors. Smith and Tong[3] pointed out later that there are altogether nine lines due to ^{35}Cl and that we missed a pair of doublets at 30.05 MHz and one of four lines at about 32.3 MHz. However, they did not report a broad line at 28.6 MHz which we had described previously.[1]

Now it has become evident from the three previous papers that there are ten NQR lines in Phase II (the low temperature phase) of $[PCl_4][PCl_6]$. This fact clearly indicates that all chlorine atoms in the chemical formula unit (P_2Cl_{10}) are at crystallographically non-equivalent sites in Phase II. Since our failure to observe three more resonance lines seems to be due to insufficient sensitivity of the spectrometer used, we attempted to re-examine all the ten resonance lines using a carefully constructed cryostat. In the present paper, we will discuss the NQR spectra in Phase II in relation to the crystal symmetry of both Phase I and II. It will be shown that the temperature dependence of the NQR frequencies can be explained by a librational soft-mode theory[4,5] which is based on an anharmonic coupling between the molecular or ionic librational modes.

Experimental

The NQR frequencies were measured on the same specimen as was used in the previous NQR study.[1] This had been stored in a sealed glass tube at room temperature for about three and half years after the original measurements of the temperature dependence of the NQR frequencies were carried out.

Some modifications were made of the experimental arrangement. The coaxial cable wire connecting the spectrometer and the sample coil was replaced by a thin-walled cupronickel tube running down the axis of a stainless-steel tube. Both tubes were silver-plated in order to improve spectral sensitivity.[6] The NQR frequencies were determined with a Takeda Riken Model TR-5578 digital frequency counter instead of the one used previously.

Results and Discussion

Spectra in Relation to Structure. The stable phase of phosphorus pentachloride contains two types of complex ion, PCl_4^+ and PCl_6^-, in a tetragonal unit cell of the space group P4/n at room temperature (Phase I).[7] The phosphorus atom and two of the six chlorine atoms in PCl_6^- lie on the four-fold axis and the phosphorus atom in PCl_4^+ is on the $\bar{4}$ axis. Other chlorine atoms are at general positions. All the four chlorine atoms in a PCl_4^+ cation are crystallographically equivalent and the four chlorine atoms in the PCl_6^- that lie in the *ac* plane are also equivalent.

Therefore, the number of resonance lines in Phase I observed in the previous work agrees with the number expected from the crystal structure. In Phase II, on the other hand, ten ^{35}Cl NQR lines were observed

TABLE 1. ^{35}Cl NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES OF $[PCl_4][PCl_6]$ AT 20.9 K

	Frequency/MHz	Assignment
ν_1	28.5902±0.0004	PCl_6^-
ν_2	29.7833±0.0009	
ν_3	30.0685±0.0008	
ν_4	30.0772±0.0003	
ν_5	30.6029±0.0009	
ν_6	30.7569±0.0004	
ν_7	32.3827±0.0002	PCl_4^+
ν_8	32.4898±0.0001	
ν_9	32.5639±0.0001	
ν_{10}	32.7695±0.0003	

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

[2] J. V. DiLorenzo and R. F. Schneider, *Inorg. Chem.*, **6**, 766 (1967).

[3] J. A. S. Smith and D. A. Tong, *J. Sci. Instr.*, Ser 2, **1**, (19868).

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

[5] H. Chihara, N. Nakamura, and M. Tachiki, *ibid.*, to be published.

[6] N. Nakamura and H. Chihara, *J. Phys. Soc. Japan*, **22**, 201 (1967).

[7] D. Clark, H. M. Powell, and A. F. Wells, *J. Chem. Soc.*, **1942**, 642.

Table 2. ^{35}Cl nuclear quadrupole resonance frequencies (MHz) at 78 and 109 K compared with previous work

Temperature	Present work	Chihara, *et al.*[a]	DiLorenzo and Schneider[b]	
			unannealed	annealed
78 K	28.3951	28.424	—	—
(Phase II)	29.7111	29.720	29.65	29.61
	30.0272	—	—	—
	30.0602	—	30.08	30.07
	30.4574	30.478	30.47	30.45
	30.5719	—	—	30.62
	32.2791	32.288	32.30	32.28
	32.3843	32.396	—	—
	32.4198	—	32.42	—
	32.6023	32.620	32.63	32.61
109 K	28.0871	28.098		
(Phase I)	29.6377	29.647		
	30.1960	30.203		
	32.2808	32.28		

a) Ref. 1. b) Ref. 2

instead of the seven detected previously. The resonance frequencies at 20.9 K and their assignment are given in Table 1.

The present results are compared with the previous results[1,2] at 78 K (Phase II) and 109 K (Phase I) in Table 2. Our results in the two independent measurements differ slightly, which may be due to some error in the frequency and/or temperature measurements. DiLorenzo and Schneider[2] pointed out that the solid maintained at liquid nitrogen temperature for a period of four weeks gave a spectrum differing from that of a rapidly cooled sample both in the resonance frequency (see Table 2) and intensity. They attributed this aging phenomenon to the remedy of lattice strain by annealing. In an attempt to confirm such an effect of annealing we compared the spectrum of Phase II cooled rapidly down to liquid nitrogen temperature with that of the sample which had been stored at liquid nitrogen temperature for five weeks. No appreciable change in the spectrum due to aging was observed except for slight enhancement in the intensity of ν_5, ν_6, and ν_9.[8]

Temperature Dependence. The temperature dependence of all the resonance frequencies was measured again between 20 and 110K. The result is shown in Fig. 1. Of the four resonance lines in Phase I, the two higher-frequency lines split into four when the crystal was cooled through the transition point ($T_{tr}=103\pm0.6$ K), whereas the other two lines (ν_1 and ν_2 in PCl_6^-) remained unsplit.

As was mentioned above two chlorine atoms in PCl_6^- are in special positions in Phase I (on the 4-fold axis). Therefore we can unambiguously assign ν_1 and ν_2 to these chlorines also in Phase II.

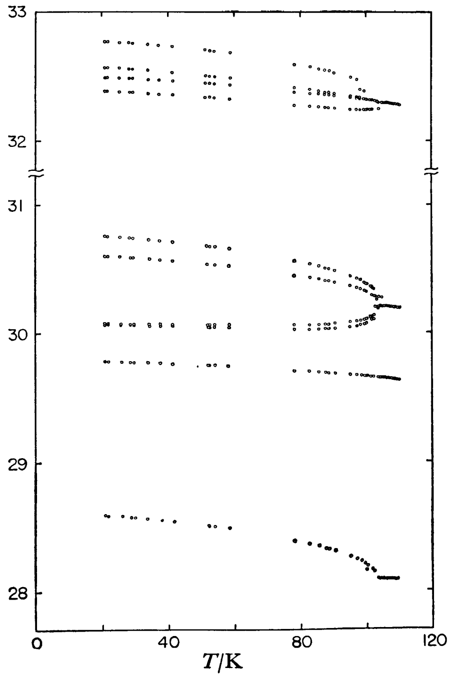

Fig. 1. Nuclear quadrupole resonance frequencies of $[PCl_4]$-$[PCl_6]$ between 20 and 110 K.

The four chlorine atoms in PCl_6^- (in the basal plane) as well as four in PCl_4^+ become non-equivalent in Phase II. This fact shows that both 4 and $\bar{4}$ symmetry axes are not conserved in Phase II. Thus, it is obvious that the transition is of the second order according to Landau's classification.[10] It is interesting to note that each set of four chlorine atoms in PCl_4^+ and PCl_6^- appears to split into quartets symmetrically separated on either side of the average frequency in Phase II. Moreover, ν_1 shows a discontinuous change in slope at T_{tr} whereas ν_2 shows barely discernible anomaly around T_{tr}. In Fig. 2 the splitting $\Delta\nu_i$ (i=3—6) is plotted against the reduced temperature T/T_{tr} for PCl_6^-. The magnitude of the splitting was measured from the averaged frequency of the four lines and reduced by $\Delta\nu_i(0)$, the splitting being extrapolated to 0 K. It can be seen from Fig. 2 that all $\Delta\nu_i$ depend

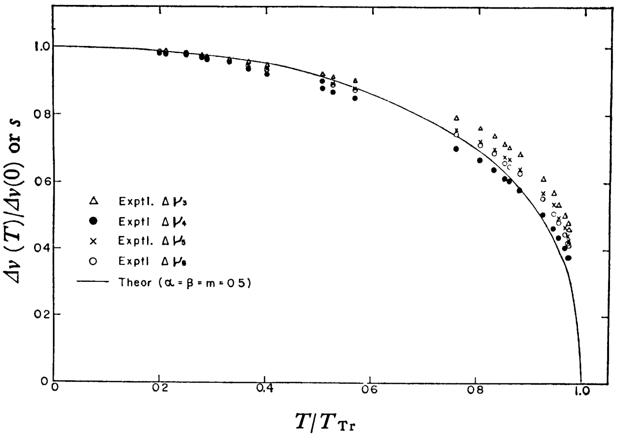

Fig. 2. Separation of lines ν_3 to ν_6 from their average, reduced by the separation at 0 K, as function of temperature (taken as the order parameter s).

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[8] The effect of the sample treatment on the heat capacity has been observed in the phase transition region.[9]

[9] H. Chihara, M. Nakamura, and K. Masukane, This Bulletin, **46**, 97 (1973).

[10] L. D. Landau and E. M. Lifshitz, "Statistical Physics," Pergamon Press, London, (1958).

similarly on temperature, suggesting that the splittings have a common cause.

Mechanism of the Transition. It is reasonable to consider that the phase transition is brought about by some reorientation of a PCl_6^- group about an axis perpendicular to its figure axis. Such a reorientation may be expressed by one parameter, *i.e.*, the angle of rotation θ from a fixed direction in the lattice. The magnitude of separation of the resonance line can be expanded in terms of θ as

$$\Delta\nu_i = A_i\theta + B_i\theta^2 + \cdots, \tag{1}$$

where θ can be measured from the original direction of the figure axis in Phase I. Here the tilt angle θ can be regarded as an order-parameter of the phase transition, and $\Delta\nu_i$ given in Fig. 2 can be taken as the same quantity if we neglect higher order terms of θ in Eq. (1).

In order to explain a similar type of phase transition in a chloranil crystal we have developed a librational soft mode theory which is based on an anharmonic coupling between molecular librational modes.[5,9,11] As the PCl_4^+ and PCl_6^- groups can be considered as rigid bodies, we can apply this theory to the phase transition of P_2Cl_{10}.

The Hamiltonian of the whole libration system is given by

$$H = \frac{P_\theta^2}{2I} + V(\theta) + \sum_i\left(\frac{P_i^2}{2I} + \frac{1}{2}I\omega^2\varphi_i^2\right) + \sum_i f(\theta)\varphi_i^2, \tag{2}$$

where $V(\theta)$ is the potential energy for a uniform mode, P_θ is its conjugate angular momentum, and the last term expresses the anharmonic coupling between the uniform mode and other librational modes φ_i treated as harmonic oscillators with frequency ω. We assume that $V(\theta)$ is of the form

$$V(\theta) = a(\theta^2 - p\theta^4 - q\theta^6), \tag{3}$$

which has a minimum at $\theta=\theta_0$ and satisfies the symmetry conditions in Phase I. The PCl_6^- ion is in the orientation of minimum potential energy θ_0 at 0 K. If the anharmonic coupling is taken into account in such a way as to make the librational frequencies $\Omega(\theta)$ of the Einstein mode to decrease with a decrease in θ, the Helmholtz energy is given by

$$A = V(\theta) + NkT\ln\left[1-\exp\left(-\hbar\Omega(\theta)/kT\right)\right], \tag{4}$$

and the orientation giving the minimal A changes toward smaller θ as the temperature increases. The equilibrium orientation $\bar{\theta}$ can be determined from the condition $\partial A/\partial\theta=0$ at any temperature. The result is

$$\ln\left[\frac{\alpha}{\beta(1-s^2)\{1+(1-2m)s^2\}}+1\right] = (1+\alpha s^2)/t, \tag{5}$$

where $\alpha=If''(0)\theta_0^2/8\omega^2$, $\beta=a\theta_0^2/\hbar\omega$, $t=kT/\hbar\omega$, and $m=p\theta_0^2$ must be treated as adjustable parameters. The order parameter $s=\bar{\theta}/\theta_0$ was then calculated by using a NEAC-2200 electronic computer. The result is shown in Fig. 2 by a solid line, where α, β, and m were chosen so as to give the best fit to the experimental points. The adequacy of the set of parameters has been favorably examined by analyzing the excess heat capacity associated with the phase transition.[9]

On the other hand, the splitting of the resonance line due to PCl_4^+ ion shows no such regularity as is observed for PCl_6^- (Fig. 2) and the extent of the splitting is significantly small compared with the case of PCl_6^-. These facts suggest that the anharmonic coupling between the librational and the uniform modes of PCl_6^- plays a principal role in the cooperative ordering process and the splitting in the resonance line of PCl_4^+ is produced as a result of the second-order effect of ordering.

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11) H. Chihara and N. Nakamura, *J. Chem. Phys.*, to be published.