

Nuclear Quadrupole Relaxation and PCl_3 Group Reorientations in Crystals

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The nuclear quadrupole relaxation time T_1 temperature dependence is studied experimentally for the ^{35}Cl nuclei in some $\text{Cl}_3\text{P}=\text{NR}$ -type crystals. The conventional additive libration–reorientation scheme of the relaxation mechanism is accepted. Using this scheme, the T_1 temperature dependence experimental data are analyzed. The results obtained make it possible to prove the existence of the PCl_3 group autonomous reorientations and to find the values of all the parameters characterizing the relaxation processes.

It is well known that different kinds of inner motions are of great importance to the nuclear quadrupole relaxation processes in molecular crystals, which makes it possible to study these motions by means of nuclear quadrupole relaxation measurements. The mobility of the CCl_3 group, possessing a threefold symmetry axis, has recently been widely investigated by the nuclear quadrupole relaxation method (1, 2). The PCl_3 group, which has the same symmetry, has not been studied so widely. A peculiar feature of the reorientation motions of the PCl_3 group is that they occur with respect to the direction of a “formally double” bond (as in the $\text{Cl}_3\text{P}=\text{NR}$ type compounds, for example). The PCl_3 group motions in the $\text{Cl}_3\text{P}=\text{NSO}_2\text{Cl}$ crystal have been investigated (3) using NQR line width measurements. In this paper, the inner motions in some $\text{Cl}_3\text{P}=\text{NR}$ -type crystals are studied using T_1 temperature dependence measurements for ^{35}Cl nuclei. The mobility types are identified and the numerical values of the corresponding parameters are found.

The experimental curves $T_1(T)$ have been obtained using the progressive pulse saturation method (4); here T is temperature in the interval between 77 K and the melting point. The curves having no phase transition singularities, it is natural to accept the well-known additive libration–reorientation scheme of the relaxation mechanism (1, 5):

$$(T_1^{-1})_{\text{obs}} = (T_1^{-1})_{\text{libr}} + (T_1^{-1})_{\text{reor}} = aT^n + b \exp\left(-\frac{V_0}{RT}\right). \quad [1]$$

To get the parameters a , n , b , V_0 , the experimental data have been fitted by means of the conventional least-squares method using computer techniques. Two procedures are possible: one can use the curve Eq. [1] as a whole (1), or get the term $(T_1^{-1})_{\text{reor}}$ as the difference between $(T_1^{-1})_{\text{obs}}$ and $(T_1^{-1})_{\text{libr}}$, the latter being obtained from the low-temperature data (4). Both procedures give practically the same values of the parameters,

TABLE 1
THE ^{35}Cl NQR SPECTRAL AND RELAXATION PARAMETERS FOR PCl_3 GROUPS IN TRICHLOROPHOSHAZO COMPOUNDS

Compound	Melting point temperature (K)	PCl_3 group resonance frequencies at 77 K (MHz)	T_1 at 77 K (msec)	Parameters of Eq. (1)					T_f (K)	λ_f (sec^{-1})
				a ($\text{sec}^{-1} \text{deg}^{-m}$)	n	b (sec^{-1})	V_0 (kcal/mole)			
$\text{Cl}_3\text{P}=\text{NCCl}(\text{CCl}_3)_2$	326	29.442	51	3.31×10^{-3}	1.99	3.10×10^{11}	6.8 ± 0.2	180	2×10^3	
		29.481	42	4.68×10^{-3}	1.95					
		29.764	62	4.78×10^{-3}	1.86					
$\text{Cl}_3\text{P}=\text{NPO}(\text{CCl}_3)_2$	395	29.718	79	1.12×10^{-4}	2.66	1.35×10^{11}	5.1 ± 0.1	145	2×10^3	
		30.070	79	1.12×10^{-4}	2.66					
		30.320	105	1.50×10^{-4}	2.53					
$\text{Cl}_3\text{P}=\text{NCOCF}_3$	245	29.600	68	8.32×10^{-4}	2.24	2.00×10^{11}	6.2 ± 0.2	175	3×10^3	
		30.085	96	3.39×10^{-4}	2.37					
		30.762	88	1.23×10^{-3}	2.10					
$\text{Cl}_3\text{P}=\text{NSO}_2\text{N}=\text{PCl}_3$	314	29.302	52	5.75×10^{-3}	1.90	5.10×10^{12}	6.8 ± 0.1	184	3×10^4	
		29.500	72							
		30.468	44							
		29.355	104							
		29.526	101							
30.897	153	1.90	1.87	6.61×10^{12}	6.6 ± 0.1	177	4×10^4			
$\text{Cl}_3\text{P}=\text{NSO}_2\text{Cl}$	308	30.133	161	1.82×10^{-3}	1.83	5.75×10^{11}	7.3 ± 0.1	225	4×10^4	
		30.254	163							
		31.780	192							
$\text{Cl}_3\text{P}=\text{NCCl}_2\text{CCl}_3$	295	29.075	190	8.01×10^{-4}	2.00	2.82×10^9	3.4 ± 0.2	134		
		29.645	245	6.65×10^{-4}	2.00	1.24×10^9	3.4 ± 0.2	151		
		31.152	192	8.01×10^{-4}	2.00	2.82×10^9	3.4 ± 0.2	134		

but the second one makes it possible to transform the functions $(T_1^{-1})_{\text{libr}} = \phi(T)$ and $(T_1^{-1})_{\text{reor}} = \psi(T^{-1})$ into linear ones, which is profitable from the point of view of the error calculation. In this paper both procedures have been utilized.

Table 1 gives the values of the parameters a , n , b , V_0 obtained in the way described above together with some other data of importance: melting points, NQR frequencies, and T_1 values at 77 K, and fade out temperatures T_f and corresponding reorientation rates estimated as

$$\lambda = \frac{3}{4}(T_1^{-1})_{\text{reor}} \quad [2]$$

[see (1)]. To check the correctness of the values obtained, in some cases the curve for Eq. [1] has been calculated using these values and compared with the experimental curve (see Figs. 1 and 3).

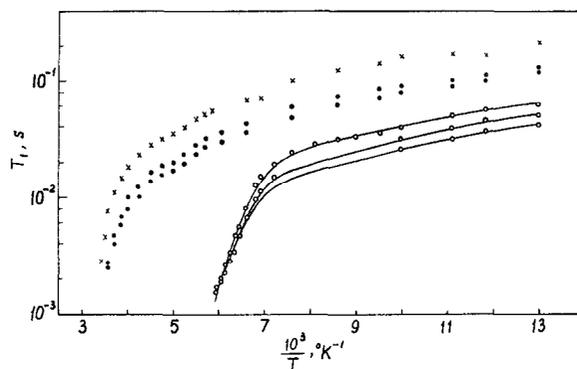


FIG. 1. Temperature dependence of the relaxation time for the ^{35}Cl nuclei in different molecular fragments in $\text{Cl}_3\text{P}=\text{NCCl}(\text{CCl}_3)_2$ (two low-frequency lines of the PCl_3 group coalesce at high temperatures). The solid lines represent the calculated curves with the parameter values from Table 1. \circ , PCl_3 ; \bullet , CCl_3 ; \times , CCl .

The values of the parameters a , n , b , V_0 provide us with important quantitative characteristics of the inner motions in the crystals considered. In addition to that, some interesting qualitative conclusions concerning these motions may be drawn from the results obtained.

First of all, the existence of the PCl_3 group autonomous reorientations may be taken for granted in some crystals. In fact, according to Fig. 1, showing the $T_1(T)$ curve for $\text{Cl}_3\text{P}=\text{NCCl}(\text{CCl}_3)_2$ there are two circumstances: (1) In the temperature interval where the curves corresponding to the ^{35}Cl nuclei in the PCl_3 group become practically exponential, those corresponding to the ^{35}Cl nuclei in the remainder of the molecule are far from being like that; and (2) in the temperature interval mentioned the PCl_3 group curves are very near to one another. No doubt the first circumstance gives an argument for the existence of separate reorientations of the PCl_3 group. The second one does also if the possible reorientation axes of the molecule as a whole do not coincide with the symmetry axes of the PCl_3 group; this coincidence does not take place for the substances considered. In the $\text{Cl}_3\text{P}=\text{NPO}(\text{CCl}_3)_2$ crystal the situation is the same. In the $\text{Cl}_3\text{P}=\text{NCOCF}_3$, $\text{Cl}_3\text{P}=\text{NSO}_2\text{N}=\text{PCl}_3$, and $\text{Cl}_3\text{P}=\text{NSO}_2\text{Cl}$ cases only the second one of the two circumstances mentioned above takes place (for $\text{Cl}_3\text{P}=\text{NSO}_2\text{N}=\text{PCl}_3$

see Fig. 2). In $\text{Cl}_3\text{P}=\text{NSO}_2\text{N}=\text{PCl}_3$ and $\text{Cl}_3\text{P}=\text{NSO}_2\text{Cl}$, this is the only argument for the existence of the PCl_3 group autonomous reorientations: The point is that in the $\text{Cl}_3\text{P}=\text{NSO}_2\text{N}=\text{PCl}_3$ molecule all the ^{35}Cl nuclei are in the PCl_3 groups, and in the $\text{Cl}_3\text{P}=\text{NSO}_2\text{Cl}$ case the NQR signal from the S-Cl fragment fades out before that from

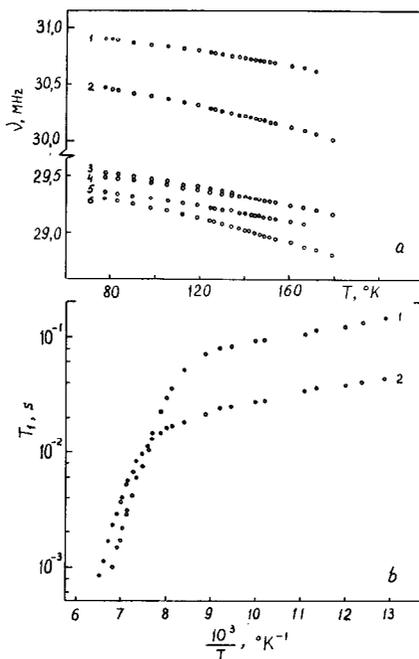


FIG. 2. Temperature dependence of the resonance frequencies (a) and relaxation times (b) for the ^{35}Cl nuclei in $\text{Cl}_3\text{P}=\text{NSO}_2\text{N}=\text{PCl}_3$. Two sets of curves: 1, 3, 5 and 2, 4, 6 concern two PCl_3 groups in the same molecule. Relaxation data are given only for the upper frequency lines corresponding to each of the two sets.

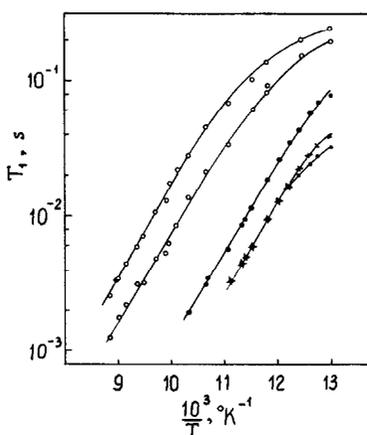


FIG. 3. Temperature dependence of the relaxation time for the ^{35}Cl nuclei in different molecular fragments in $\text{Cl}_3\text{P}=\text{NCCl}_2\text{CCl}_3$ (the PCl_3 solid lines represent the calculated curves with the parameter values from Table 1). ○, PCl_3 ; ●, CCl_3 ; ×, CCl_2 .

the PCl_3 group (3). In the $\text{Cl}_3\text{P}=\text{NCOCF}_3$ case there is a complementary argument given by some ^{19}F NMR data (6).

On the other hand, situations are possible where the separate reorientations of the PCl_3 group cannot be observed, because the NQR signal disappears early due to the reorientations of the molecules as a whole. For example, this occurs in the $\text{Cl}_3\text{P}=\text{NCCl}_2\text{CCl}_3$ crystal (see Fig. 3) where the $T_1(T)$ curves for different molecular fragments give the same reorientation potential barrier values.

In the cases where the separate reorientations of the PCl_3 group have been found, the corresponding barrier values lie in the interval 5–7 kcal/mole (see Table 1). Taking into account the fact that the barrier in question is due to the inner interactions in molecules on the one hand and to the intermolecular interactions on the other hand, one sees that the hindering potential for the PCl_3 group reorientations due to the formally double bond $\text{P}=\text{N}$ is rather low.

The nuclear quadrupole relaxation time T_1 is highly sensitive to the reorientation motions; for example, in the case of the ^{35}Cl nuclei in the PCl_3 group the essential shortening of T_1 begins at reorientation rate values from the interval 2–10 sec^{-1} , see Fig. 1 and 2b.

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