Studies on Molecular Motions and Phase Transition in Pyridinium Tetrachloroiodate(III) Crystals by the Measurements of the Temperature Dependences of Chlorine Nuclear Quadrupole. Resonance Frequencies and Relaxation Times

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To elucidate the phase transition of pyridinium tetrachloroiodate(III) at $T_c = 217$ K, the temperature dependences of the chlorine NQR frequencies and corresponding NQR spin-lattice and spin-spin relaxation times (T_{1Q} and T_{2Q}) have been measured in the range 77–370 K. Above ca. 370 K and between 206 and 223 K no chlorine NQR frequency could be observed, the chlorine relaxation times becoming extremely short (ca. 100 µs). Except for near T_c, the T_{1Q} values below ca. 310 K can be explained by fluctuations of the electric field gradient at the chlorine nuclei due to in-plane reorientations of the cations about their pseudohexad axis. The increase of T_{1Q}^{-1} in the vicinity of T_c suggests a critical slowing down of the orientational fluctuations of the cations and a distortion of the complex anions. The decrease of T_{1Q} above 310 K is considered to be mainly due to the in-plane reorientation of the complex anions. An activation energy of 64 kJ mol^{-1} is evaluated for that motion.

1. Introduction

Previously, we have studied the motion of pyridinium cations (pyH^+) in $(pyH)AuCl_4$ crystals using ^{1}H NMR [1] and chlorine NQR [2]. In order to elucidate the effect of the motion of pyridinium cations on the quadrupolar relaxation of chlorine nuclei and to clarify the motion of the complex anions themselves, we have extended our NMR-NQR studies to $(pyH)ICl_4$ crystals. The $(pyH)ICl_4$ salt, having a square planar anion, is known to undergo a structural phase transition at $T_c = 215$ K [3]. It is also one of the important research aims of the present investigation to obtain information about the mechanism of the phase transition.

2. Experimental

We have used a homemade pulsed NQR spectrometer [4, 5]. The pulse sequences π-τ-$(\pi/2)$-τ_e-π and $(\pi/2)$-τ-π were employed for the determination of the spin-lattice (T_{1Q}) and spin-spin (T_{2Q}) relaxation times, respectively, where τ_e was set constant (ca. 100 µs) for observing echo signals. The signal amplitude decreased exponentially with τ in all measurements. The sample temperatures were controlled within ± 0.5 K by means of a temperature controller [4]. The observed temperatures were estimated to be accurate within ± 1 K. The same sample was employed in the present investigation as that prepared previously for the study of ^{1}H NMR experiments [6]. DTA experiments were carried out by means of a homemade apparatus [7].

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3. Results

Temperature Dependence of Chlorine NQR Frequencies and Phase Transition

The temperature dependence of the ^{35}Cl NQR frequencies is shown in Figure 1. The resonance frequencies were determined with the spin echo method. Some data are listed in Table 1. Our resonance frequencies agree fairly well with those reported in [3].

In the range 223–370 K a single resonance line, ν_I, and below 206 K two resonance lines, ν_{IIh} and ν_{III} of high and low frequency, respectively, were observed. Above 370 K and between 206 K and 223 K, no echo signal could be detected, T_{1Q} and T_{2Q} becoming extremely short (ca. 100 µs).

From our DTA experiments, a phase transition was located at 217 K in the temperature range where no resonance could be observed. When the temperature was increased and decreased in the DTA experiments,

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characteristic endo- and exo-thermic heat anomalies with a long tail on the low-temperature side were recorded, as shown in Figure 2. The peak temperatures of both anomalies were the same within experimental errors and have been assigned to T_c for the reason already reported [7, 8].

The following fact is very interesting. The temperature dependence of the average of ν_{IIh} and ν_{III} agrees well with the extrapolated curve of ν_I (cf. Figure 1).

T_{1Q} *and* T_{2Q} *of Chlorine Nuclei*

The temperature dependences of T_{1Q} and T_{2Q} for the ^{35}Cl and ^{37}Cl nuclei in (pyH)ICl_4 crystals are shown in Figure 3. Some T_{1Q} and T_{2Q} values are also listed in Table 1.

When the sample was warmed from 84 K to ca. 150 K, the ^{35}Cl T_{1Q} values of ν_{IIh} and ν_{III} decreased with increasing temperature, the curves being slightly convex towards the abscissa around ca. 100 K. In the range 150–190 K, T_{1Q} of both lines was almost temperature independent. With increasing the temperature furthermore from 190 to 204 K, both T_{1Q} values decreased very rapidly and the ν_{IIh} and ν_{III} signals

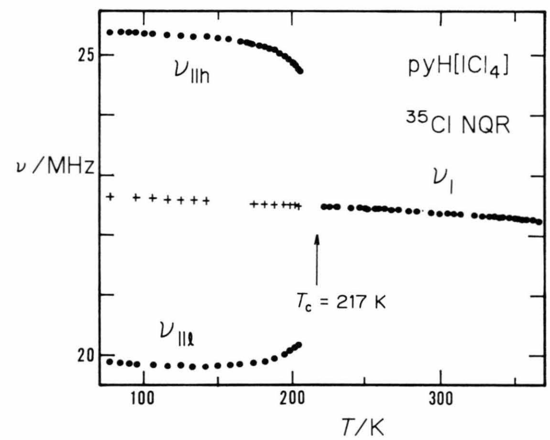

Fig. 1. The temperature dependence of the ^{35}Cl NQR frequencies ν_{IIh}, ν_{III}, and ν_I of (pyH)ICl_4. The averages of ν_{IIh} and ν_{III} are indicated by crosses.

Table 1. Data for the ^{35}Cl NQR lines ν_{IIh} and ν_{III} in the low-temperature phase and ν_I in the high-temperature phase of (pyH)ICl_4. Data for the ^{37}Cl NQR lines corresponding to ν_{III} and ν_I are marked by asterisks. Dashes indicate "no measurements".

T/K	ν/MHz	T_{1Q}/ms	T_{2Q}/ms
84	25.390	530	–
84	19.868	130	0.31
*84	15.658	140	0.41
106	25.364	28	0.23
105	19.852	6.2	0.24
*105	15.648	8.2	0.31
133	25.320	2.0	0.18
132	19.839	1.4	0.17
*131	15.638	1.4	–
178	25.164	0.74	0.16
178	19.904	0.44	0.15
*178	15.675	0.59	–
198	24.933	0.43	0.13
195	20.024	0.39	0.12
*195	15.788	0.35	–
257	22.440	0.50	0.19
*257	17.686	0.90	0.28
355	22.268	0.25	0.14

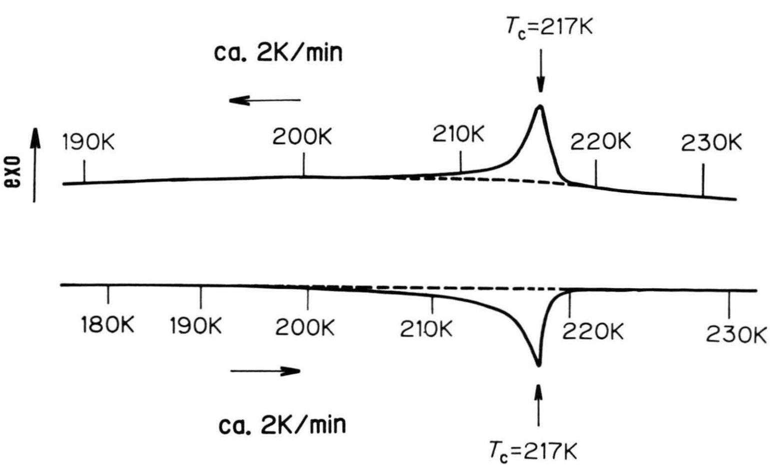

Fig. 2. DTA curves for (pyH)ICl_4 crystals across the phase transition temperature T_c.

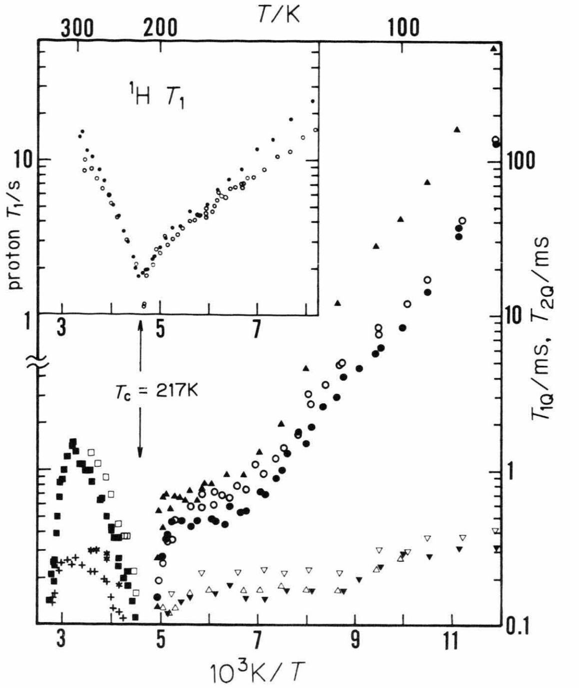

Fig. 3. The temperature dependence of NQR spin-lattice and spin-spin relaxation times T_{1Q} and T_{2Q}. The T_{1Q} values of the ^{35}Cl NQR lines ν_{IIh}, ν_{III}, and ν_I are indicated by ▲, ● and ■, respectively. T_{2Q} of these lines is indicated by △, ▼ and +, respectively. T_{1Q} (T_{2Q}) values of the ^{37}Cl NQR lines corresponding to the ν_{III} and ν_I lines are indicated by ○ (▽) and □ (∗), respectively. In the inset, the temperature dependences of the ^{1}H NMR spin-lattice relaxation times T_1 for the resonance frequencies of 10.5 (○) and 29.5 (●) MHz [6] are shown for comparison.

faded out at 206 K. At 223 K, the ν_I signal appeared and T_{1Q} of ν_I could be determined above this temperature. When the temperature was increased from 223 K, ^{35}Cl T_{1Q} increased with increasing temperature up to ca. 310 K. Above this temperature, T_{1Q} of ν_I showed again a very steep decrease.

The temperature dependence of ^{37}Cl T_{1Q} was also determined for the ν_{III} and ν_I lines. The results were very similar to those of the corresponding ^{35}Cl T_{1Q} lines. The isotope ratios of T_{1Q} (^{37}Cl)/T_{1Q}(^{35}Cl) were 1.1, 1.3, 1.0, 1.3, 1.0, and 1.7 for the temperature ranges 84–95 K, 95–125 K, 125–135 K, 135–190 K, 190–204 K, and 223–280 K, respectively.

4. Discussion

NQR Spectra and Molecular Structure

Although the crystal structure of (pyH)ICl_4 has not been determined as yet, X-ray powder patterns taken at room temperature [6] indicate that its crystal structure is similar to that of (pyH)$AuCl_4$ [9]. The single ^{35}Cl NQR line observed in the high-temperature phase of the present complex indicates that all chlorine atoms in the crystal are crystallographically equivalent. This is consistent with the crystal structure of (pyH)ICl_4 being similar to that of (pyH)$AuCl_4$, in which $[AuCl_4]^-$ forms an approximately square planar complex anion.

The frequency splitting in the low temperature phase (ca. 5 MHz, cf. Fig. 1) is too large to be attributable to a lattice effect of the NQR frequencies or a usual change in the H-bonding scheme of Cl ... H–N type. Most probably the $[ICl_4]^-$ anions are strongly deformed in the low-temperature phase. This may lead to a large difference in I–Cl bond distances in the anion.

Dillon and Waddington [3] reported that the ^{35}Cl NQR frequencies of various salts containing $[ICl_4]^-$ ions are widely spread (over ca. 13 MHz), due probably to a heavy distortion of the complex anion from its D_{4h} symmetry, leading to expansion and contraction of I–Cl bonds. They showed that the I–Cl bond distance in $[ICl_4]^-$ depends linearly on the NQR frequency of ^{35}Cl in question [3]. By applying this relation to the present complex, the I–Cl bond distance can be estimated to be 2.51 Å for the high-temperature phase and 2.54 and 2.47 Å for two different kinds of I–Cl bonds in the low-temperature phase. A structural analysis using a single crystal is now in progress for both high- and low-temperature phases.

Reorientation of Complex Anions

Above ca. 310 K, T_{1Q} decreases according to

$$T_{1Q} \propto \exp(a/T). \tag{1}$$

This experimental result suggests that sudden 90° reorientations of the complex anion about its pseudotetrad (C_4') axis are the main origin for the quadrupolar spin-lattice relaxation. Introducing an activation energy E_a, (1) can be written in the form [10]

$$T_{1Q} = (2/3)\,\tau = (2/3)\,\tau_0 \exp\{E_a/RT\}, \tag{2}$$

where τ denotes the correlation time for the motion.

By use of (2), E_a could be evaluated from the gradient of the linear portion of the log T_{1Q} vs. T^{-1} plot above 310 K to be 64 kJ mol^{-1}. This is very close to the value of 67 kJ mol^{-1} already obtained for (pyH)$AuCl_4$ [2, 11], indicating that the hindering barrier to the C_4' reorientation of the present anion in the crystal is approximately the same as that of $[AuCl_4]^-$ in the (pyH)$AuCl_4$ crystal.

Cationic Motion

The motion of pyH^+ in the present crystals has previously been studied by measuring the ^1H NMR spin-lattice relaxation time T_1 [6] (cf. Figure 3). The temperature coefficients of chlorine T_{1Q} and ^1H T_1 in the range 300–223 K are similar to each other on the $\log T_{1Q}$ vs. T^{-1} and $\log T_1$ vs. T^{-1} plots, respectively. Accordingly, fluctuations of the electric field gradient (EFG) produced at resonant chlorine nuclei through the motion of the cations can be considered as an effective mechanism for the chlorine nuclear relaxation.

The above explanation is supported by the experimental fact that the ratios $T_{1Q}(^{37}Cl)/T_{1Q}(^{35}Cl)$ were 1.1, 1.3, and 1.7 for the temperature ranges 84–95 K, 135–190 K, and 223–280 K, respectively. When chlorine T_{1Q} is determined mainly through the fluctuation of the chlorine EFG due to the motion of the cations, the theoretically derived isotope ratios are 1.00, 1.27, and 1.61 for the cases that the fluctuation of the EFG is slow, comparable, and fast, respectively, as compared with the NQR frequency [12, 13].

As the most probable mode of the cationic motion, in-plane reorientation of the cation about its C_6' axis can be considered. This is because the excitation of the above motion has been suggested from the temperature dependence study of ^1H NMR second moments [6]. This motion leads to the fluctuation of the EFG at the chlorine nuclei mainly through the formation and destruction of H-bonds between chlorine and nitrogen atoms.

In the low-temperature phase, the T_{1Q} vs. T^{-1} curves show a shoulder around 100 K (cf. Figure 3). Approximately the same isotope ratio of 1.3 was obtained in two neighboring temperature ranges closely spaced, namely, 95–125 K and 135–190 K. This fact suggests that at least two different correlation times are responsible for the fluctuation of the EFG at the chlorine nuclei. This conforms with our conclusion in the ^1H NMR study [1, 2] that pyridinium cations perform the C_6' reorientation over unequal potential barriers. On the other hand, the isotope ratio of 1.7 observed in the high-temperature phase indicates that the cationic motion is rapid enough compared with the chlorine NQR frequency.

Phase Transition

When the temperature was increased from ca. 190 K, T_{1Q} decreased very rapidly up to near $T_c = 217$ K. It has been reported that the $\log T_{1Q}$ vs. T^{-1} curves show an anomalous dip near T_c in various crystalline solids [4, 5, 14–19]. In some R_2MX_6 (R = K, NH_4; M = Sn, Os, Re; X = Cl, Br) type complexes, soft mode phase transitions were observed [20–25] and halogen T_{1Q} yielded a dip around T_c because of the softening of the vibrational modes responsible for the fluctuation of the EFG produced at the resonant nuclei [14, 17, 18]. When this mechanism is operative in the phase transition, the isotope ratio $T_{1Q}(^{37}Cl)/T_{1Q}(^{35}Cl)$ is expected to be 1.6 at temperatures nearby T_c on both sides [4, 5].

For the present complex, an isotope ratio of 1.0 was observed at 190–204 K below T_c. Therefore, the relaxation mechanism near T_c can not be explained by the softening of a vibrational mode. The present phase transition is assumed to occur through an order-disorder mechanism in the orientation of the pyridinium cations. However, it is strongly suggested that the $[ICl_4]^-$ anion is heavily distorted below T_c, as discussed above. The ν_{III} and ν_{IIh} lines have positive and negative temperature coefficients, respectively, in the temperature range of 190–204 K. These temperature dependences of the resonance lines are attributable to a gradual distortion of the complex anion below T_c. We suggest that the distortion of the complex anion is deeply related to the order parameter of the phase transition, and the orientational disorder of the pyridinium cations might be combined with an anharmonic vibrational mode involving the complex anions.

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