^{35}Cl Nuclear Quadrupole Relaxation in Pyridinium Hexachlorostannate(IV)

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The temperature dependence of the ^{35}Cl quadrupole spin-lattice relaxation time T_{1Q} is reported for the three known resonance lines of pyridinium hexachlorostannate(IV). With increasing temperature, a sharp decrease of T_{1Q} is observed below the phase transition temperature of 331 K. This decrease can be explained by reorientational motions of the complex anions. The activation energy for the motions is determined as 97 and 63 kJ mol^{-1} from the T_{1Q} data obtained from the highest-frequency resonance line and the remaining two lines, respectively. The two different barriers observed for the reorientation of a single anion suggest the existence of anisotropy of the anionic motion. An anomalous T_{1Q} vs. T^{-1} relation observed in an intermediate-temperature region is discussed by referring to the cationic motion.

1. Introduction

Ionic dynamics and phase transitions in crystals have been studied for the complexes $[(CH_3)_2NH_2]_2MCl_6$ (M = Sn, Te) by means of NQR and NMR techniques [1–4]. In these studies, a reorientation of the bulky octahedral anion was observed even at low temperatures (ca. 200 K). To obtain information about the anionic motion, ^{35}Cl NQR frequencies and quadrupolar relaxation times T_{1Q} were determined as a function of temperature for pyridinium hexachlorostannate(IV) [abbreviated to $(pyH)_2SnCl_6$]. In this type of complexes, consisting of the planar cation and octahedral anions, we expect that the cations can rotate rather freely in crystals and, hence, some coupled anionic motion should be excited. When almost all our measurements had been done, ^{35}Cl NQR temperature dependence and X-ray studies of this complex were reported by Borchers and Weiss [5]. Since their NQR results agree well with those obtained by us, we report our results mainly from the dynamical aspect of the anion in crystals.

2. Experimental

The ^{35}Cl spin-lattice and spin-spin quadrupolar relaxation times T_{1Q} and T_{2Q} were determined using a homemade pulsed spectrometer constructed with a transmitter from Matec Inc. [4]. The pulse sequences 180°-τ-90° and 90°-τ-180° were employed for the determination of T_{1Q} and T_{2Q}, respectively. Temperatures were controlled to within ±1 K with a proportional temperature regulator EC-61 from Ohkura Denki Co. To obtain information about the nature of the phase transition reported in [5], and also to confirm the transition temperature T_{tr}, DTA measurements were carried out using a homemade apparatus already reported [6]. The sample was prepared as described in [7] and identified by conventional elementary analysis.

3. Results and Discussion

At 77 K, three ^{35}Cl NQR lines (ν_a, ν_b, and ν_c in the order of decreasing frequency) were observed. With increasing temperature, ν_b and ν_c disappeared at ca. 285 K and ν_a at 343 K.

The temperature coefficient of ν_c was positive whereas those of ν_a and ν_b were negative. The temperature dependence curve of ν_a showed a cusp at 331 K.

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These results agree well with Ref. [5]. DTA measurements were performed in the temperature range 100–570 K; a heat anomaly appeared at 331 K, measured with increasing temperature at the peak point. The heat anomalies have a long tail on the low-temperature side as shown in Fig. 1 and yield the same peak temperature for both heating and cooling runs. This feature is typical for a second-order phase transition [8].

The temperature dependence of T_{1Q} is shown in Figure 2. With increasing the temperature from 77 K to ca. 120 K log T_{1Q} for the chlorine sites labeled as *a*, *b*, and *c*, showing ν_a, ν_b, and ν_c, respectively, decreased gradually. Above ca. 285 and 245 K for chlorines at the sites *a* and *b* (or *c*), respectively, log T_{1Q} decreased very sharply and almost linearly with $10^3 \times T^{-1}$. The T_{1Q} curves between ca. 120 and 230 K were slightly concave downward. The free induction decay signals became too weak to provide T_{1Q} values precisely when T_{1Q} decreased below ca. 200 μs. The temperature dependence of T_{2Q} for ν_a is also shown in Figure 2. Above ca. 300 K, the values of T_{2Q} were approximately equal to those of T_{1Q}, whereas T_{2Q} was almost temperature independent below that temperature.

When the sample was cooled from ca. 120 K, T_{1Q} increased gradually in conformity with $T_{1Q} \propto T^{-2}$. This relation usually holds for the quadrupolar relaxation of nuclei with nuclear spin 3/2, when librational fluctuation of the electric field gradient (EFG) formed at the nuclei governs the nuclear relaxation [11, 12].

The sharp decreases of T_{1Q} observed above ca. 285 and 245 K for chlorines at the sites *a* and *b* (or *c*), respectively, can be interpreted in terms of reorientational motions of the complex anions by assuming a thermal process of Arrhenius type for the motion [12, 13]. From the gradient of log T_{1Q} vs. $10^3 \times T^{-1}$ plots, the activation energy for the motion was evaluated as 97 ± 10 and 63 ± 5 kJ mol^{-1} for chlorines at *a* and *b* (or *c*) sites, respectively. These values are larger than those reported for $[(CH_3)_2NH_2]_2SnCl_6$ (35 kJ mol^{-1}) [4], $[(CH_3)_2NH_2]_2TeCl_6$ (27 kJ mol^{-1}) [3], and K_2SnCl_6 (49 kJ mol^{-1}) [14], whereas they are similar to that of $(NH_4)_2SnCl_6$ (83 kJ mol^{-1}) [15]. This suggests that the ions in the present compound are rather closely packed in the crystalline lattice. The relaxation rate due to the reorientation of the pseudo-octahedral anions is faster for chlorines located on site *b* (or *c*) than those on site *a*. This leads to the conclusion that the complex anion reorients more freely about the pseudo-tetrad axis through two chlorines at site *a* than the others.

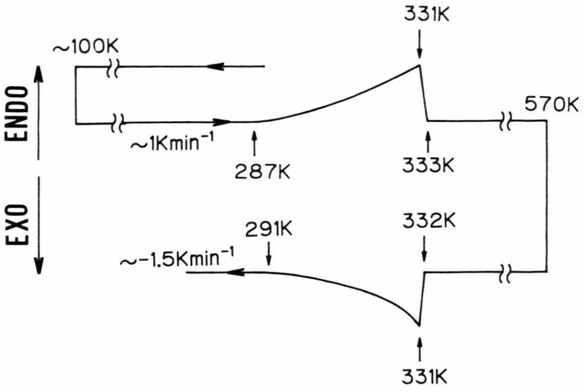

Fig. 1. Heat anomalies appearing in DTA curves recorded for $(C_5H_6N)_2SnCl_6$.

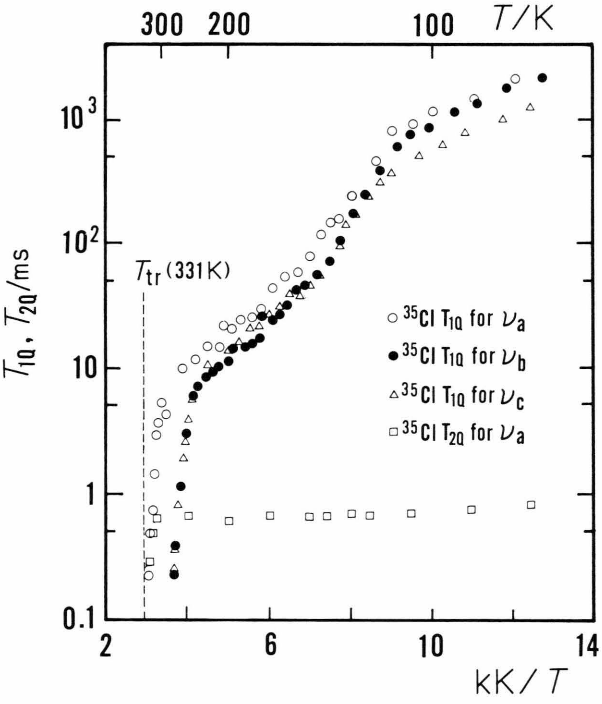

Fig. 2. Temperature dependences of the quadrupolar spin-lattice relaxation time T_{1Q} of ^{35}Cl NQR in $(C_5H_6N)_2SnCl_6$. This complex yields three lines ν_a, ν_b, and ν_c for which the T_{1Q} values are indicated by the symbols ○, ●, and △, respectively. The temperature variation of the spin-spin quadrupolar relaxation time T_{2Q} of ν_a is also shown by the symbol □.

In the temperature range 120–230 K, all three NQR lines showed anomalous T_{1Q} values looking like a shoulder superposed on the background T_{1Q} curve.

To explain these results, it can be considered that the EFG at the resonant nuclei fluctuates by the motion of the surrounding ions, and this provides an appreciable relaxation mechanism [16–18] for the present case. For nuclei having the nuclear spin 3/2, the quadrupolar spin-lattice relaxation rate resulting from the fluctuation of the external EFG can be given as

$$1/T_{1Q} = (1/12)(e^2Q\,q/\hbar)^2 (q'/q)^2\, \tau/(1+\omega_Q^2 \tau^2). \quad (1)$$

Here, (q'/q) is the fluctuation fraction of the EFG and τ is the correlation time of the ionic motion which yields the fluctuating EFG at the resonant nuclei. $e^2 Q\,q/\hbar$ and ω_Q, respectively, denote the quadrupole coupling constant and the angular resonance frequency.

For the present salt, containing pyridinium cations with a large electric dipole moment, the motion of the cation must play an important role for the production of the fluctuating EFG at the resonant nuclei. For (pyH)AuCl$_4$, it is known that the dominant spin-lattice relaxation mechanism of chlorine nuclei below ca. 350 K can be attributed to the fluctuation of the EFG experienced by the chlorine nuclei due to the motion of the surrounding cations [9]. As for the present salt, a 60° flipping motion of the cation is suggested from the study of ^{1}H NMR [10] to be easily excited. This motion may be the origin of the fluctuating EFG. We can explain the observed anomalous behavior of T_{1Q} by superimposing the T_{1Q} curve given by (1) on the gradually changing T_{1Q} due to the lattice vibrations mentioned above.

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