Temperature Dependences of NQR Frequencies and Nuclear Quadrupole Relaxation Times of Chlorine in 2,6-Lutidinium Hexachlorotellurate(IV) as Studied by Pulsed NQR Techniques*

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The temperature dependences of the $^{35}\text{Cl}$ NQR frequencies $v_\text{Q}$ and the nuclear quadrupole spin-lattice relaxation times $T_1\text{Q}$ in 2,6-lutidinium hexachlorotellurate(IV) was observed at various temperatures between 80 and 343 K. This crystal undergoes a phase transition at $T_c = 229$ K. A single and three pairs of $^{35}\text{Cl}$ NQR frequencies were observed above and below $T_c$, respectively. The hysteresis of the phase transition and a discontinuity in the temperature dependence of the resonance frequencies at $T_c$ indicate that this phase transition is of first order. Although the resonance frequencies of the pairs in the low temperature phase are very close to one another, $T_1\text{Q}$ and $v_\text{Q}$ below $T_c$ could be accurately determined by measuring the Fourier transform spectra of each line. Above ca. 250 K, $T_1\text{Q}$ showed an exponential decrease which is attributable to the overall reorientational motion of [TeCl$_6$]$_{2-}$ with an activation energy of 82 kJ mol$^{-1}$.

Introduction

We have studied the ionic dynamics of molecular ions and structural phase transitions in pyridinium hexachlorometallates(IV) by chlorine NQR and $^1$H NMR experiments [1–3]. In these complexes, nuclear relaxations of chlorine and hydrogen resulting from the fluctuation of the electric and magnetic interactions due to the motions of cations and anions were investigated by observing the $^{35}\text{Cl}$ nuclear quadrupole spin-lattice relaxation time $T_1\text{Q}$ and $^1$H spin-lattice relaxation time $T_1$. To study these phenomena when hydrogens in the pyridinium ions are substituted by methyl groups, in the present paper the $^{35}\text{Cl}$ NQR technique was applied on 2,6-lutidinium hexachlorotellurate(IV) [2,6-lutH]$_2$TeCl$_6$.

In previous work we have used a pulsed Fourier transform (FT) NQR spectrometer [4–7], this having a higher resolution than the usual superregenerative spectrometer, thus allowing for the observation of the subtle changes of line shapes and line splittings often occurring at phase transitions. Moreover, the frequencies of signals which are closely spaced can be better determined with this spectrometer.

Experimental

The sample was synthesized by dissolving 2,6-lutidine and tellurium(IV) oxide in conc. hydrochloric acid with molar ratio 2:1 and identified by observing the $^{35}\text{Cl}$ NQR frequency at 298 K, which agreed well with the reported one [8].

The temperature of the specimen was controlled within ±0.5 K, and determined with an accuracy of ±1 K. Besides the homemade FT-NQR spectrometer [4], a modified Dean-type superregenerative spectrometer was used to observe NQR spectra at room temperature. DTA measurements were done with a homemade apparatus [9].

$T_1\text{Q}$ above $T_c$ was measured by the $180^\circ$–$\tau$–$90^\circ$ pulse sequence. $T_1\text{Q}$ and $v_\text{Q}$ below $T_c$ were determined by measuring FT-NQR spectra calculated from free induction decay (FID) signals. The $90^\circ$–$\tau$–$90^\circ$ pulse sequence was used to measure $T_1\text{Q}$ by observing the FT
power spectrum which needs no phase corrections. Practically speaking, \( T_{1Q} \) was determined by plotting \( (F_\text{p} - F_\text{r})/F_\text{r} \) vs. \( \tau \), where \( F_\text{p} \) and \( F_\text{r} \) are the peak-heights of the FT spectrum obtained from FID signals after a 90° pulse and the 90°-τ-90° pulse sequence, respectively.

**Results**

**DTA Measurements**

DTA curves were recorded in the range 140–430 K. A sharp peak was observed at 228 K with decreasing temperature and at 229 K with increasing temperature. We call the high and low temperature phases HTP and LTP, respectively.

### \( ^{35}\text{Cl NQR Frequencies} \)

The temperature dependence of the \( ^{35}\text{Cl NQR frequencies} \) in \((\text{2,6-lutH})_2\text{TeCl}_6\) is shown in Figure 1. Resonance frequencies observed at various temperatures are listed in Table 1. Frequency scanning was made at room temperature in the range 14–19 MHz; only a single signal was observed. However, three pairs of NQR signals were observed at 80 K. Hereafter we call these lines such as indicated in Figure 1. Judging from the peak height of the FT spectra, the intensities of the two component lines of each pair are equal. It is difficult to compare the intensity of three pairs to each other owing to the lines spread over a wide range (ca. 400 kHz at 80 K), but the integrated intensity ratio of the three pairs seems to be nearly 1:1:1.

\( \nu_1 \) was almost temperature independent, \( \nu_2 \) decreased most drastically and \( \nu_3 \) and \( \nu_4 \) decreased linearly with increasing temperature. The intensity of all six signals except \( \nu_2 \) decreased gradually with increasing temperature while \( \nu_2 \) decreased more rapidly. Although the intensity ratio of \( \nu_1 \) and \( \nu_2 \) remained nearly the same even at 180 K, only \( \nu_2 \) could not be observed at 228 K. The intensity of the all lines except \( \nu_2 \) became very weak at 229 K compared with that at 228 K, and the HTP signal \( \nu_h \) appeared at the same temperature. When measurements were made at 229 K, in the course of time the intensity of \( \nu_h \) became strong whereas that of \( \nu_3 \) and \( \nu_4 \) became weak. The spectra were recorded after the specimen had been held at 229 K for one hour. The results are shown in Figure 2. At 230 K, the lines \( \nu_3 \) and \( \nu_4 \) disappeared completely (see Fig. 2), although \( \nu_1 \), \( \nu_5 \), and \( \nu_6 \) were still observable with very weak intensity. The lines \( \nu_5 \) and \( \nu_6 \) disappeared at ca. 231 K, but \( \nu_1 \) could be observed up to 232 K.

\( \nu_6 \) decreased monotonously with increasing temperature, and its intensity became gradually weak on heating and disappeared at ca. 350 K. On decreasing the temperature, the HTP was slightly supercooled.

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( \nu_h/	ext{MHz} )</th>
<th>( \nu_2 )</th>
<th>( \nu_3 )</th>
<th>( \nu_4 )</th>
<th>( \nu_5 )</th>
<th>( \nu_6 )</th>
</tr>
</thead>
</table>

![Fig. 1. The temperature dependence of \( ^{35}\text{Cl NQR frequencies} \) in 2,6-lutidinium hexachlorotellurate(IV). The broken line indicates the phase transition temperature \( T_c = 229 \text{ K} \).]
Temperature variation of \( v_3 \) and \( v_4 \) peaks around \( T_c \) with increasing temperature. These three Fourier transform power spectra are obtained from FID signals which were accumulated by 1024 times. The same irradiated frequency \( \nu_{irr} \) (16.560 MHz) was employed for the measurements made at three temperatures. Although \( v_3 \) and \( v_4 \) look close owing to fold back of \( v_3 \), \( v_3 \), and \( v_4 \) are separated by ca. 40 kHz.

Table 2. \( ^{35} \text{Cl} \) nuclear quadrupole spin-lattice relaxation times \( T_{1Q} \) determined for 2,6-lutidinium hexachlorotellurate(IV) crystals at several temperatures.

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( T_{1Q}/\text{ms} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_h )</td>
<td>( v_1 )</td>
</tr>
<tr>
<td>100</td>
<td>900</td>
</tr>
<tr>
<td>140</td>
<td>775</td>
</tr>
<tr>
<td>220</td>
<td>315</td>
</tr>
<tr>
<td>298</td>
<td>140</td>
</tr>
<tr>
<td>343</td>
<td>0.505</td>
</tr>
</tbody>
</table>

* Values measured at 160 K.

The lines \( v_3 \) and \( v_4 \) appeared at 226 K, and \( v_h \) disappeared completely at 225 K. These results clearly indicate that this phase transition is of first order.

**\( ^{35} \text{Cl Nuclear Quadrupole Spin-Lattice Relaxation Time} **

The temperature dependence of \( ^{35} \text{Cl} \) \( T_{1Q} \) is shown in Fig. 3 and the values at some temperatures are given in Table 2. In the LTP, \( T_{1Q} \) of all lines decreased with increasing temperature, but that of \( v_2 \) decreased more rapidly than the others.

In the HTP, \( T_{1Q} \) of \( v_h \) decreased markedly with increasing temperature. log \( T_{1Q} \) of \( v_h \) was proportional to \( T^{-1} \) above ca. 300 K.

**Discussion**

The Measurements of \( T_{1Q} \) by Use of the FT Spectra

When many lines exist in a narrow frequency range, it is difficult to measure \( \nu_Q \) and/or \( T_{1Q} \) of each line precisely. The frequencies of \( v_3 \) and \( v_4 \) were closely spaced in the range 80 and 229 K, and the frequency difference of these lines was at most ca. 40 kHz. The
same is true for the \( v_5 \) and \( v_6 \) lines. In such cases, the FT-NQR spectra of each line make it possible to determine \( v_Q \) and/or \( T_{1Q} \) exactly.

Preliminary measurements of \( T_{1Q} \) for the same spectrum with the FT method and the usual method show that the linearity of \( (F_x - F_z)/F_x \) vs. \( \tau \) plots obtained with the FT method is poor as compared with that derived with the usual method. As can be seen from the results of this study (Fig. 3), the error of the experimental values seems to be somewhat large. Thus, \( T_{1Q} \) measured by use of FT-NQR spectra seems to be less accurate than that evaluated by the usual method.

\( v_Q \) and \( T_{1Q} \) in the Low Temperature Phase

The \(^{35}\text{Cl} \) NQR lines observed in the LTP are probably assignable to the six chlorines in one octahedral complex anion by considering the intensity ratio of the two lines belonging to each pair mentioned above. The temperature dependences of \( v_1 \) and \( v_2 \) are different from that of the other signals. This can be explained by the effect of H-bonding between chlorines of the complex anion and hydrogens in the 2,6-lutidinium ion as follows. In the present complex crystal, the temperature dependence of \( v_1 \) and \( v_2 \) may involve two terms, i.e., the usual Bayer term [10] and the term relating to H-bonding. It is well known that, when a hydrogen atom approaches the resonant chlorine from the direction perpendicular and parallel to the principal \( z \) axis of the EFG produced at the resonant nucleus, the NQR frequency of the nucleus decreases and increases, respectively [11]. H-bonding is usually weakened due to the activation of thermal vibrations. In view of the foregoing discussion, it is reasonable that \( v_1 \) is nearly temperature independent, because of the cancellation of the Bayer term by the term responsible for H-bonding, which has a positive temperature coefficient. The steep temperature coefficient of \( v_2 \) is thought as due to the fact that the H-bonding term contributes additively to that of the usual Bayer term. As already mentioned above, \( v_2 \) faded out near \( T_c \). Because \( T_{1Q} \) of \( v_2 \) is in the order of 10 ms near \( T_c \), this fade-out phenomenon can be attributed to a static effect. Atoms and/or ions which create a partial EFG at the chlorine nuclei in question are responsible for the fade-out of the signal. Hydrogens in the 2,6-lutidinium ions which form H-bonds with the chlorines meet the above requirements if these hydrogens (or the cations as a whole) are slightly disordered, and the disorder is expected to be excited with increasing temperature.

Theoretically, \( T_{1Q} \) is proportional to \( T^{-2} \) when the relaxation mechanism is mainly attributable to lattice vibrations [12, 13]. Our results, however, could be approximated by

\[
T_{1Q} \propto T^{-n},
\]

where \( n \) is a parameter to be fitted. The most probable values of \( n \) are given in Table 3.

The values of \( n \) for all lines except \( v_2 \) are nearly equal to 2. The value of 3.7 obtained for \( v_2 \) seems to be somewhat larger than the usual experimental ones [7]. It may be possible to fit the observed values to other functions, but the log \( T_{1Q} \) vs. log \( T \) plot yield a good linear relation within the experimental errors (Figure 4). Large values, such as that of \( v_2 \), have been reported for s-triazine (3.44 and 3.64), which undergoes a second order phase transition from hexagonal to monoclinic at 198.9 K [14].

In pyridinium hexachlorometallates(IV), it has been proposed [3] that the relaxation of the chlorine nuclei.

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**Table 3.** The power index \( n \) of \( T \) in (1) for the low temperature phase resonance lines

<table>
<thead>
<tr>
<th>Lines</th>
<th>( v_1 )</th>
<th>( v_2 )</th>
<th>( v_3 )</th>
<th>( v_4 )</th>
<th>( v_5 )</th>
<th>( v_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>1.6</td>
<td>3.7</td>
<td>1.7</td>
<td>2.2</td>
<td>1.9</td>
<td>1.7</td>
</tr>
</tbody>
</table>

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**Fig. 4.** The \(^{35}\text{Cl} \) \( T_{1Q} \) of \( v_2 \) versus log \( T \). The straight line, obtained by least-squares fitting, yields \( d \log(T_{1Q}/s)/d \log(T/K) = -3.7 \).
is attributable to the fluctuation of the EFG modulated by 60° jumps of the cation around its pseudo C₆ axis. As described above, the chlorines responsible for ν₂ are thought to form H-bonds with the cations. Therefore it is expected that the motions of the (2,6-lutH)⁺ ion modulate the EFG at the chlorine nuclei in question. The motions should not be 60° jumps of the cation. From the fade-out phenomenon of ν₂, a slight disorder of the cations is inferred. Small angle reorientations among the disordered sites could produce the fluctuation of the EFG.

νₒ and T₁ₒ in the High Temperature Phase

In the HTP, T₁ₒ of ν₆ decreased rather steeply with increasing temperature. The linear portion of log T₁ₒ vs. T⁻¹ plots with a steep inclination is solely attributable to the overall reorientational motion of [TeCl₆]²⁻ anions [15]. The activation energy of this motion is about 82 kJ mol⁻¹. The same type of the octahedral complex anionic motion has been observed for pyridinium hexachlorotellurate(IV) [3]. The ³⁵Cl NQR line of this crystal disappeared at ca. 320 K, and the activation energy is estimated to be 55 kJ mol⁻¹. The activation energy for the motion of the complex anion in the present crystal is much larger than that for the anion in pyridinium hexachlorotellurate(IV). This may be due to the steric hindrance of the substituted methyl groups of the present complex.