Chlorine Nuclear Quadrupole Relaxation Studies on Ionic Dynamics and Phase Transition in NH_4AuCl_4 *

Atsushi Ishikawa, Tetsuo Asaji, and Daiyu Nakamura
Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01, Japan

Ryuichi Ikeda
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Z. Naturforsch. **45a**, 467–471 (1990); received August 25, 1989

Chlorine NQR frequencies, and NQR spin-lattice and spin-spin relaxation times (T_{1Q} and T_{2Q}) were measured for NH_4AuCl_4 crystals at various temperatures between 4.2 and 337 K. Each of the two resonance lines observed at room temperature is split into a doublet below $T_c = 29$ K, indicating a phase transition. A rapid decrease of T_{1Q} above ca. 290 K is attributable to 90° reorientational jumps of the complex anion about its pseudo C_4 axis. An activation energy of 80 kJ mol^{-1} was obtained for this motion. ^{35}Cl T_{1Q} exhibits a minimum at T_c. The T_{1Q} isotope ratio $T_{1Q}(^{37}Cl)/T_{1Q}(^{35}Cl)$ becomes 1.6 and 1.0 on the high- and low-temperature sides of this minimum, respectively. These results were explained by fluctuations of the electric field gradient produced at the chlorine nuclei by the reorientational jumps of the NH_4^+ ions. The motion of the cations is much faster and much slower than the resonance frequencies on the high- and low-temperature sides, respectively. This suggests that the phase transition is of the order-disorder type relating to the orientation of the NH_4^+ ion.

Introduction

Recently, the dynamics of pyridinium ions (pyH^+) in crystals have been studied in $(pyH)_2MCl_6$ (M: Sn, Te, Pb), $(pyH)AuCl_4$, and $(pyH)ICl_4$ by measuring chlorine NQR and ^1H NMR relaxation times [1–6]. It has been shown that reorientation of the cations about the pseudohexad axis causes fluctuations of the electric field gradient (EFG) at nearby chlorine nuclei and becomes a dominant mechanism of spin-lattice relaxation of the chlorine nuclei. The experimental results were explained by reorientational jumps of the cations with a finite electric dipole moment, taking place among nonequivalent potential wells.

Also NH_4^+ cations, although having a higher symmetry than pyH^+, can be expected to produce fluctuations of the EFG at the resonant chlorine nuclei in the respective complexes, dynamically disordered orientations of NH_4^+ ions having been observed in many ammonium compounds [7]. However, owing to its small size and highly symmetrical charge distribution, the hindrance barrier for reorientation is expected to be lower for NH_4^+ than for pyH^+ [2, 5, 8, 9], suggesting that relaxation associated with this process becomes effective at lower temperatures than for pyH^+.

^{35}Cl NQR frequencies in NH_4AuCl_4 crystals have been reported at temperatures above 77 K [10], where the NH_4^+ reorientation is so rapid that it cannot become an effective relaxation mechanism. In this work, measurements have been carried out at lower temperatures where the NH_4^+ motions are slower and expected to contribute to the relaxation.

Experimental

The chlorine NQR spin-lattice relaxation time T_{1Q} and spin-spin relaxation time T_{2Q} were measured with a homemade pulsed NQR spectrometer described elsewhere [11]. Values of T_{1Q} and T_{2Q} were determined from the height of echo signals observed after the pulse sequences, $\pi/2$-τ-$\pi/2$-τ_e-π and $\pi/2$-τ-π, respectively, where the echo height was observed at various interpulse spacing times τ changed up to about twice of each relaxation time, while τ_e was set constant (100 μs) throughout the measurements. Exponential decay of the echo amplitude against τ was observed in the whole temperature range studied for T_{1Q} and T_{2Q}.

---

* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Takayama, Japan, August 22–26, 1989.

Reprint requests to Prof. D. Nakamura, Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01, Japan

0932-0784 / 90 / 0300-0467 $ 01.30/0. – Please order a reprint rather than making your own copy

For 4.2–50 K, a homemade cryostat with liquid helium [12] was employed. Temperatures between 50 and 77 K were obtained by pumping off the ambient gas above liquid nitrogen and regulating the gas pressure with a homemade manostat. Above 77 K, another liquid nitrogen cryostat [11] was employed. The sample temperature was controlled within ±0.5 K and determined by a gold (0.07% Fe) vs. chromel thermocouple between 4.2 and 77 K, and a copper vs. constantan thermocouple above 77 K. The determined temperatures are estimated to be accurate within ±1 K.

$NH_4AuCl_4 \cdot \frac{2}{3} H_2O$ crystals were prepared by the method described in [10, 13]. The water of crystallization was completely removed by keeping the sample in a vacuum at ca. 100 °C for 10 h. Powdered NH_4AuCl_4 thus obtained was identified by observing the ^{35}Cl NQR signals at the frequencies reported [10].

Results

Temperature Dependence of Chlorine NQR Frequencies

The observed temperature dependence of the ^{35}Cl NQR frequencies of NH_4AuCl_4 is plotted in Fig. 1 and listed in Table 1. The frequencies observed above 77 K have equal intensity and are in good agreement with those reported by Sasane et al. [10]. They are hereafter called as ν_H and ν_L (high- and low-frequency).

Table 1. ^{35}Cl NQR frequencies ν, and spin-lattice and spin-spin relaxation times (T_{1Q} and T_{2Q}) observed at several temperatures for NH_4AuCl_4 crystals.

T/K	ν/MHz	T_{1Q}/ms	T_{2Q}/ms
4.2	28.44	–	–
4.2	27.99	–	–
4.2	27.70	–	–
4.2	26.98	–	–
22	28.01	640	–
22	27.70	360	0.37
22	26.99	370	0.37
*22	21.29	400	–
37	28.20	100	0.35
41	27.33	21	0.31
*41	21.55	38	–
129	28.08	170	0.49
129	27.27	110	0.32
332	27.72	0.58	0.22
332	26.90	0.60	0.20

* The data for ^{37}Cl.

With decreasing temperature, at ca. 29 K the lines split into two lines each, indicating a phase transition. To determine T_c accurately, frequency dependences of the echo height for ν_H and ν_L near T_c were measured. The curves obtained at several temperatures are shown in Figure 2. With decreasing temperature, the peaks of both ν_H and ν_L suddenly broadened at 29 K, and below 29 K two peaks with equal height appeared. From these data we determined $T_c = 29$ K. Below T_c, ν_H and ν_L were almost symmetrically split into ν_{H1} and ν_{H2}, and ν_{L1} and ν_{L2}, respectively. $\nu_{H1} - \nu_{H2}$ and $\nu_{L1} - \nu_{L2}$ became almost temperature independent below ca. 15 K and gave ca. 450 kHz and ca. 700 kHz, respectively.

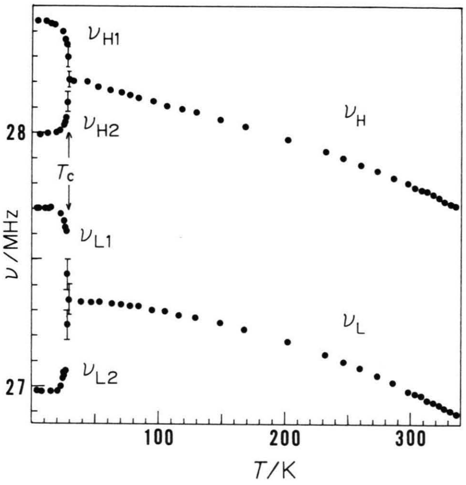

Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies, ν_H and ν_L above the phase transition temperature, $T_c = 29$ K, and ν_{H1}, ν_{H2}, ν_{L1}, and ν_{L2} below T_c.

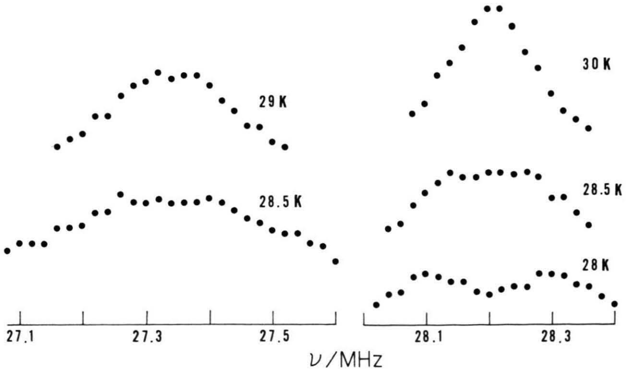

Fig. 2. Frequency dependences of the heights of ^{35}Cl NQR echo signals corresponding to ν_H (right) and ν_L (left) observed near T_c.

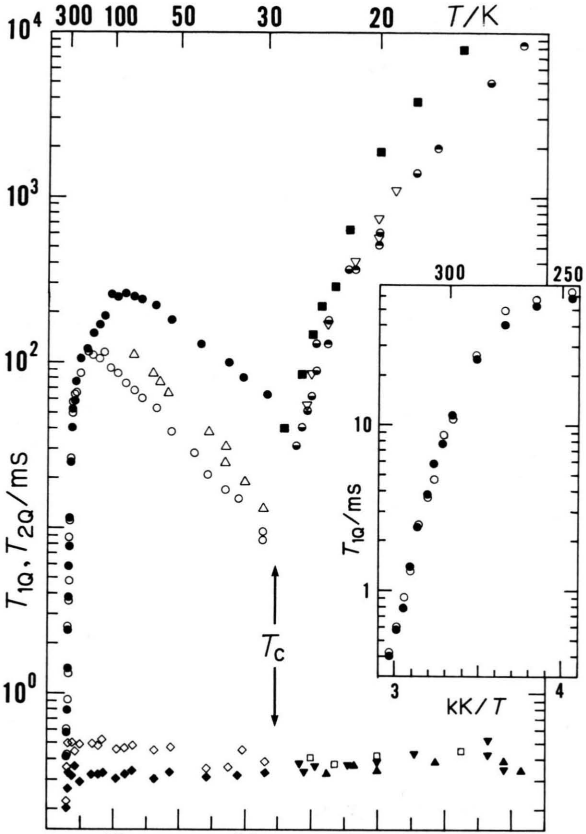

Fig. 3. Temperature dependences of ^{35}Cl and ^{37}Cl NQR spin-lattice relaxation time T_{1Q}, and ^{35}Cl NQR spin-spin relaxation time T_{2Q}. For ^{35}Cl T_{1Q}, ●: ν_H ○: ν_L ◒: ν_{L1} ◓: ν_{L2} ■: ν_{H2}; for ^{37}Cl T_{1Q}, △: ν_L ▽: ν_{L2}; for ^{35}Cl T_{2Q}, ◇: ν_H ◆: ν_L □: ν_{H2} ▲: ν_{L1} ▼: ν_{L2}.

Chlorine NQR Relaxation Times T_{1Q} and T_{2Q}

Figure 3 shows the temperature dependences of T_{1Q} and T_{2Q} for ^{35}Cl nuclei in NH_4AuCl_4 crystals observed between 14 and 337 K. Numerical values are given in Table 1.

With increasing the temperature from 15 K to T_c, ^{35}Cl T_{1Q} for ν_{H2}, ν_{L1}, and ν_{L2} decreased rapidly and reached a minimum at T_c. Above T_c, T_{1Q} of both ν_H and ν_L increased almost linearly with T^{-1} and showed a T_{1Q} maximum around 80 and 120 K for ν_H and ν_L, respectively. With further increasing temperature, T_{1Q} for both lines became the same above ca. 290 K and decreased rapidly down to ca. 400 μs at 337 K. Above this temperature, no T_{1Q} could be determined because the echo signals weakened.

^{37}Cl T_{1Q} was determined in the range 19–77 K for ν_{L2} or ν_L. They showed analogous temperature dependences to those of the corresponding ^{35}Cl line. The T_{1Q} isotope ratio

$$R = T_{1Q}(^{37}\text{Cl})/T_{1Q}(^{35}\text{Cl}) \tag{1}$$

became 1.0±0.2 and 1.6±0.2 for the temperature ranges 19–25 and 31–77 K, respectively.

Discussion

High-Temperature Range ($T > 290$ K)

Above ca. 290 K, log T_{1Q} depended linearly on T^{-1} for both ν_H and ν_L. A quite similar ^{35}Cl T_{1Q} behavior was observed for $RbAuCl_4$ and $CsAuCl_4$ [14], whose crystal structures are isomorphous with that of the present complex around room temperature [15–17]. The temperature dependence of T_{1Q} in the rubidium and cesium salts has been explained by sudden and infrequent 90° jumps of the square planar $[AuCl_4]^-$ ions about the pseudo C_4 axis. Applying the same analysis to the present T_{1Q} data, we determined the activation energy of the in-plane 90° reorientational jumps of $[AuCl_4]^-$ ions as 80 ± 5 kJ mol^{-1} above 290 K. This activation energy is slightly larger than that of $RbAuCl_4$ and much larger than that of $CsAuCl_4$, and may be due to the effect of crystal packing.

Intermediate-Temperature Range ($T_c < T < 100$ K)

With decreasing temperature, T_{1Q} for both ν_H and ν_L decreased over a wide temperature range, namely, from ca. 80 K to T_c for ν_H, and from ca. 120 K to T_c for ν_L. This temperature dependence is unusual because in general the relaxation mechanism mainly contributing to T_{1Q} in this temperature range is librations of the complex anions which usually reduce T_{1Q} with increasing temperature. One could consider softening of some librational modes in crystals as one of the causes for this anomalous T_{1Q} behavior. This, however, is no possible explanation for reason given in the following section.

The most probable mechanism we can propose is the motion of the counter cations, which fluctuate the EFG produced at the chlorine nuclei (cf. the Introduction).

T_{1Q} of chlorine nuclei with spin $I = 3/2$, as determined by the motion of the counter ions, can be expressed as [18]

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

Here, e^2qQ, q'/q, ω_Q, and τ_c denote the quadrupole coupling constant, the EFG fluctuation fraction related to the matrix elements of the EFG tensor, the angular NQR frequency, and the correlation time of the cationic motion, respectively. In (2), T_{1Q}^{-1} is proportional to Q^2 and τ_c under the condition of $(\omega_Q\,\tau_c)^2 \ll 1$. In this case

$$R = [Q(^{35}\mathrm{Cl})/Q(^{37}\mathrm{Cl})]^2 = 1.61. \qquad (3)$$

This agrees very well with the experimental data observed between 77 and 31 K given by

$$T_{1Q}(^{37}\mathrm{Cl}\ \nu_L)/T_{1Q}(^{35}\mathrm{Cl}\ \nu_L) = 1.6 \pm 0.2. \qquad (4)$$

Assuming the Arrhenius relationship for τ_c, we can write T_{1Q} as

$$T_{1Q} \propto \exp(-E_a/R\,T), \qquad (5)$$

where E_a is the activation energy for the cationic motion. By fitting (5) to the observed temperature dependence of T_{1Q} for ν_H and ν_L, E_a values of 0.63 and 0.83 kJ mol^{-1}, respectively, are obtained. These activation energies are assumed to be the same because they are believed to originate from the same cationic motion. In the derivation of these activation energies, no correction was made for the contribution to T_{1Q} from lattice vibrations, which increases with increasing temperature. Since $T_{1Q}(\nu_H)$, which is longer than $T_{1Q}(\nu_L)$, is thought to be affected by lattice vibrations more strongly than $T_{1Q}(\nu_L)$, the smaller E_a for ν_H is understandable in view of this lattice effect.

Some kind of reorientation of the NH_4^+ ions is acceptable as the cationic motion responsible for this T_{1Q} decrease. The activation energy of less than 1.0 kJ mol^{-1} is small as compared with those reported for analogous compounds, such as $(NH_4)_2SnCl_6$, $(NH_4)_2PdCl_6$, and $(NH_4)_2PtCl_6$, having E_a of 5.0 [19], 1.75 [20], and 1.6 kJ mol^{-1} [20], respectively, for the NH_4^+ reorientation. This comparison suggests the possibility that the jump angle of the expected cationic reorientation is smaller than 120° or 90°.

Low Temperature Range ($T < T_c$)

Below T_c, the T_{1Q} isotope ratio R for ν_{L2} became 1.0 ± 0.2 in the range 19–25 K. This can also be explained by the above cationic motion. By assuming $(\omega_Q\,\tau_c)^2 \gg 1$ in (2) for the present temperature range, T_{1Q} becomes proportional to τ_c but independent of Q. This T_{1Q} gives $R = 1.0$, in good agreement with the observation. Accordingly, the relaxation process below T_c is attributable to the classical reorientation of NH_4^+ ions with a slower rate than the NQR frequencies.

In this temperature range it is also possible that quantum mechanical tunneling of the NH_4^+ ion contributes to T_{1Q} through magnetic dipolar coupling between chlorine nuclei and protons. It has been reported that a ^{35}Cl T_{1Q} minimum observed in $(NH_4)_2SnCl_6$ at ca. 55 K can be explained by this mechanism [21]. In the present complex, however, the T_{1Q} minimum was observed just at T_c, and $R = 1.0$ was observed below T_c. However, R usually differs from 1.0 for T_{1Q} governed by the tunneling assisted mechanism. For these reasons, the main relaxation mechanism in this temperature range is attributable to the fluctuation of chlorine EFG caused by the NH_4^+ reorientation in the neighborhood of T_c.

Mechanism of Phase Transition

In the present complex, the R values were determined as 1.6 and 1.0 on the high- and low-temperature sides of T_c, respectively. These values cannot be explained by attributing the relaxation mechanism near T_c to the softening of the lattice vibrations which is expected to give $R = 1.6$ if it works as the main process of the relaxation [11, 22].

In the foregoing analysis of T_{1Q}, the classical reorientation of NH_4^+ ions has been accepted as the origin of relaxation where the NH_4^+ ions are assumed to reorient much more rapidly and slowly than ω_Q in the high- and low-temperature phases, respectively. From this cationic motion around T_c, we can propose a model of order-disorder type phase transition as for the orientation of the NH_4^+ ion in the present complex. The splittings of ν_H and ν_L observed at T_c and the gradual shift of the split lines with temperature below T_c seem to be attributable to a small deformation of the crystalline lattice occurring at the phase transition. Probably, the order-disorder of the NH_4^+ orientations and the lattice deformation take place correlatively at T_c.

[1] Y. Tai, A. Ishikawa, K. Horiuchi, T. Asaji, D. Nakamura, and R. Ikeda, Z. Naturforsch. **43a,** 1002 (1988).

[2] Y. Tai, T. Asaji, D. Nakamura, and R. Ikeda, Z. Naturforsch. **45a,** 477 (1990).

[3] Y. Tai, T. Asaji, R. Ikeda, and D. Nakamura, Z. Naturforsch. **44a,** 300 (1989).

[4] A. Ishikawa, Y. Ito, K. Horiuchi, T. Asaji, and D. Nakamura, J. Mol. Struct. **192,** 221 (1989).

[5] Y. Ito, T. Asaji, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **92,** 885 (1988).

[6] A. Ishikawa, T. Asaji, and D. Nakamura, Z. Naturforsch. **44a,** 1226 (1989).

[7] N. G. Parsonage and L. A. K. Staveley, Disorder in Crystals, Clarendon Press, Oxford 1978, p. 311.

[8] J. A. Ripmeester, J. Chem. Phys. **85,** 747 (1986).

[9] J. A. Ripmeester, Can. J. Chem. **54,** 3454 (1976).

[10] A. Sasane, T. Matuo, D. Nakamura, and M. Kubo, J. Magn. Reson. **4,** 257 (1971).

[11] K. Horiuchi, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **91,** 1351 (1987).

[12] H. Ishida, R. Ikeda, and D. Nakamura, Bull. Chem. Soc. Japan **60,** 467 (1987).

[13] J. W. Mellor, A. Comprehensive Treatise on Inorganic and Theoretical Chemistry **Vol. III,** Longmans, London 1960, p. 593.

[14] A. Ishikawa, T. Asaji, D. Nakamura, and R. Ikeda, Z. Naturforsch. **44a,** 125 (1989).

[15] G. Sleater, H. Barnighansen, and G. Braner, Z. Anorg. Allg. Chem. **372,** 9 (1970).

[16] J. Strähle and H. Barnighansen, Z. Naturforsch. **25b,** 1186 (1970).

[17] J. Strähle, J. Gelinek, and M. Kolmel, Z. Anorg. Allg. Chem. **456,** 241 (1979).

[18] D. E. Woessner and H. S. Gutowsky, J. Chem. Phys. **39,** 440 (1963).

[19] J. H. Strange and M. Terenzi, J. Phys. Chem. Solids **33,** 923 (1972).

[20] M. Bonori and M. Terenzi, Chem. Phys. Lett. **27,** 281 (1974).

[21] J. J. van der Klink and C. Dimitropoulos, J. Phys. C; Solid State Phys. **15,** 3381 (1982).

[22] A. Ishikawa, K. Horiuchi, R. Ikeda, and D. Nakamura, J. Mol. Struct. **192,** 237 (1989).