Effect of Deuteration on Ammonium Motion and Structural Phase Transition Studied by Nuclear Quadrupole Resonance

Tetsuo Asaji and Tomohiro Ishizaka
Department of Chemistry, College of Humanities and Sciences, Nihon University,
Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan
Reprint requests to Prof. T. A.; E-mail: asaji@chs.nihon-u.ac.jp

Z. Naturforsch. **55 a**, 83–89 (2000); received August 26, 1999

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions, Leipzig, Germany, July 25 - 30, 1999.

^{35}Cl NQR measurements revealed two phase transitions at 14.5 K and 70 K in NH_4ICl_4. By deuteration of the ammonium ions, the respective transition temperature increased to 27 K and 74 K. In the lowest-temperature phase of NH_4ICl_4, by the deuteration a remarkable change of the temperature dependence of the ^{35}Cl NQR frequencies was observed. The NQR spin-lattice relaxation-time minimum, ascribable to the modulation effect of the electric field gradient (EFG) due to a motion of the ammonium ions, was observed at 7 K and 11 K in NH_4ICl_4 and ND_4ICl_4, respectively. The activation energy of the ammonium motion and the fluctuation fraction q'/q of the EFG were determined to be 0.32 kJ mol^{-1} and 1.3×10^{-3} for NH_4ICl_4, and 0.30 kJ mol^{-1} and 0.88×10^{-3} for ND_4ICl_4. The experimental result suggests that the inter-ionic interaction between the ammonium ion and the ICl_4^- complex anion is weakened by the deuteration. However, the frequency shift observed in the lowest-temperature phase is much larger in ND_4ICl_4 than in NH_4ICl_4. This suggests that the lattice distortion in NH_4ICl_4 is suppressed to a great deal by the tunneling rotation of NH_4^+ ions. The effective inter-ionic interaction responsible for the lattice distortion, the transition temperature and the enhancement of tunneling of NH_4^+ as compared with ND_4^+ is discussed for NH_4ICl_4 as well as for previously reported NH_4AuCl_4 and α-NH_4HgCl_3.

Key words: Isotope Effect; Tunneling; Phase Transition; Ammonium; NQR.

1. Introduction

In the ammonium compounds a structural phase transition is often observed, which seems to be caused by the locking of a rotational motion of NH_4^+ ions. When a quantum effect in the reorientational motion of the ions is significant, a remarkable increase of the transition temperature T_c or even a new phase transition is observed by the deuteration [1 - 5].

In order to investigate such a deuteration effect on the ammonium motion and phase transition, we have applied NQR measurements on nearby nuclei. When the spin-lattice relaxation time T_1 is determined by the modulation of the electric field gradient (EFG) due to the motion of ammonium ions in crystals, it is possible to obtain information about the molecular motion of ammonium ions from NQR measurements [6 - 8].

It is an advantage of the NQR method applied to nearby nuclei, as compared with the NMR method applied to the NH_4^+ and ND_4^+ motion, that the relaxation mechanism is expected to be the same for the NH_4^+ and ND_4^+ compounds.

^{35}Cl NQR frequencies and spin-lattice relaxation times were measured as functions of temperature for NH_4ICl_4, ND_4ICl_4, and α-ND_4HgCl_3. By combination with the reported results for α-NH_4HgCl_3 [6], NH_4AuCl_4 [7], and ND_4AuCl_4 [9], the deuteration effect on the ammonium motion and structural phase transition in these compounds will be discussed.

2. Experimental

NH_4ICl_4 and ND_4ICl_4 were prepared according to the method described in [10, 11]. For the preparation of the deuterated compound, ND_4Cl and D_2O

0932–0784 / 00 / 0100–0083 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

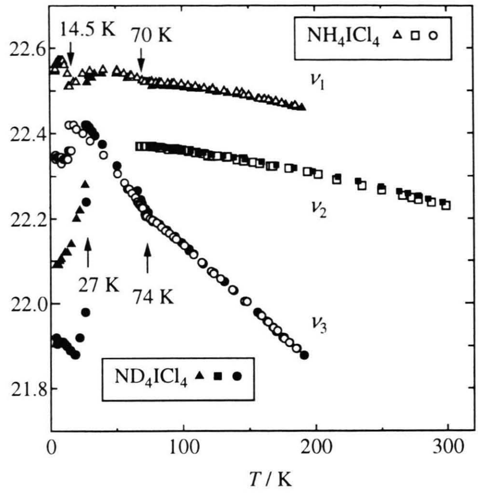

Fig. 1. Temperature dependences of ^{35}Cl NQR frequencies of NH_4ICl_4 and ND_4ICl_4, open and solid symbols, respectively.

were used instead of NH_4Cl and H_2O. The very deliquescent golden-yellow crystals obtained from the aqueous solution were dried over P_2O_5 in a vacuum desiccator for several days in order to remove the possible water of crystallization [11] and then sealed in a glass tube with a heat-exchange helium gas. α-ND_4HgCl_3 was prepared by melting an equimolar mixture of $HgCl_2$ and ND_4Cl at *ca.* 210 °C [6, 12]. Chemical Analysis: Calcd. for NH_4ICl_4: NH_4, 6.3 %; Cl/I = 4. 0. Found: NH_4, 6.2 %; Cl/I = 4.0.

A pulsed spectrometer based on the Matec gated amplifier 515A was used. The resonance frequency was determined by plotting the echo height as a function of the carrier frequency. The spin-lattice relaxation time T_1 was determined by observing the recovery of the echo height, employing the pulse sequence $\pi - \tau - \pi/2 - \tau_e - \pi$, where τ_e was set at *ca.* 120 - 250 μs. The sample temperature was controlled using an electronic controller (Ohkura EC-61A and Oxford DTC 2 for above 77 K and below 77 K, respectively) and measured with an accuracy of ± 0.5 K by use of copper versus constantan and gold + 0.07 % iron versus chromel thermocouples above 77 K and below 77 K, respectively.

3. Results

3.1. *Ammonium tetrachloroiodate(III)*

Temperature dependences of ^{35}Cl NQR frequencies of NH_4ICl_4 and ND_4ICl_4 are shown in Figure 1.

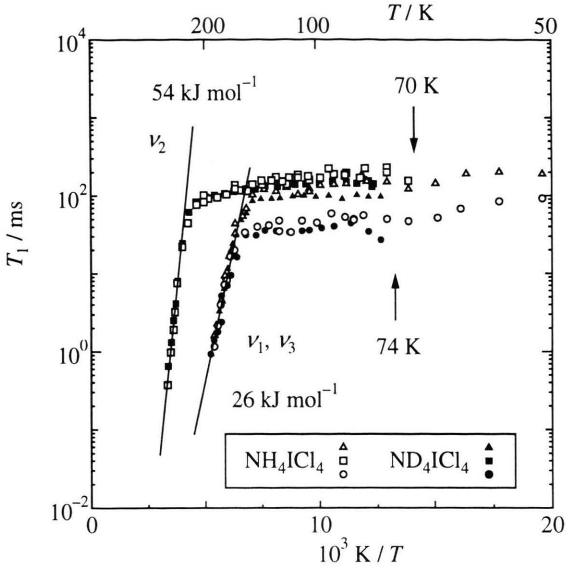

Fig. 2. Temperature dependences of ^{35}Cl NQR spin-lattice relaxation times T_1 of NH_4ICl_4 and ND_4ICl_4, open and solid symbols, respectively, in the high-temperature region. For the T_1-data the same symbols for the respective NQR lines are used as in Figure 1. The solid lines are the least-squares fitting of the T_1-data which show an Arrhenius type temperature dependence.

At 77.3 K, three frequencies ν_1, ν_2, and ν_3 were observed at 22.522, 22.369, and 22.196 MHz for NH_4ICl_4, and at 22.511, 22.370, and 22.194 MHz for ND_4ICl_4. With increasing temperature, ν_1 and ν_3 faded out at *ca.* 200 K, while ν_2 could be detected even at room temperature. At 77.3 K, we have searched for other resonance frequencies for ND_4ICl_4 in the frequency range of 20.4 - 24.4 MHz by employing a super-regenerative spectrometer. However, no additional resonance frequencies could be detected.

The temperature coefficients of the ν_1 and ν_3 frequencies of NH_4ICl_4 and ND_4ICl_4 showed a discontinuity at around 70 K and 74 K, respectively. Below this temperature, ν_2 could not be observed. An anomalous frequency shift of ν_1 and ν_3 was observed at 14.5 K in NH_4ICl_4 and at 27 K in ND_4ICl_4. The ν_1 and ν_3 frequencies showed a remarkable isotope effect below 27 K.

Temperature dependences of the spin-lattice relaxation times T_1 are shown in Figs. 2 and 3. T_1 of ν_1 and ν_3 coincides and shows a rapid decrease with increasing temperature above *ca.* 150 K, while T_1 of ν_2 begins to decrease similarly for the first time at above *ca.* 250 K. Little anomalies in the temperature

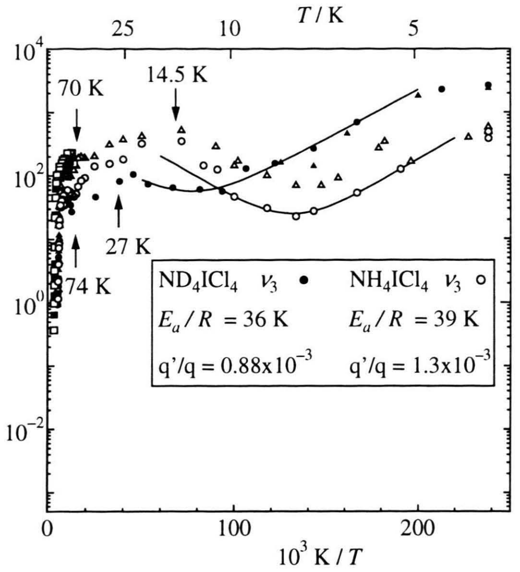

Fig. 3. As Fig. 2, but for the low-temperature region. The solid curves are the least-squares fitting of the T_1-data of ν_3 with the assumption of the relaxation mechanism by EFG modulation.

dependence of T_1 were observed where anomalies in the temperature dependences of the resonance frequencies occured. On the other hand, at very low temperatures a T_1 minimum was observed at *ca.* 7 K in NH_4ICl_4 and at *ca.* 11 K in ND_4ICl_4.

3.2. Ammonium trichloromercurate(II)

The temperature dependences of the NQR frequency and T_1 of the higher-frequency line of α-ND_4HgCl_3 and α-NH_4HgCl_3 are shown in Fig. 4 and 5, respectively. These results are very similar to those of α-NH_4HgCl_3 reported by Sagisawa *et al.* [6].

4. Discussion

4.1. Ammonium tetrachloroiodate(III)

4.1.1. Assignment of resonance frequencies and reorientation of ICl_4^- anions

The ν_2 frequency of 22.230 MHz at 299 K for NH_4ICl_4 agrees well with the reported value of 22.25 MHz at 295 K by Kurita *et al.* [11]. In the range 70–200 K three resonance frequencies were observed. According to Kurita *et al.* [11], the monohydrate $NH_4ICl_4 \cdot H_2O$ shows three frequencies of 19.98, 24.68, and 27.96 MHz at 296 K. The resonance lines

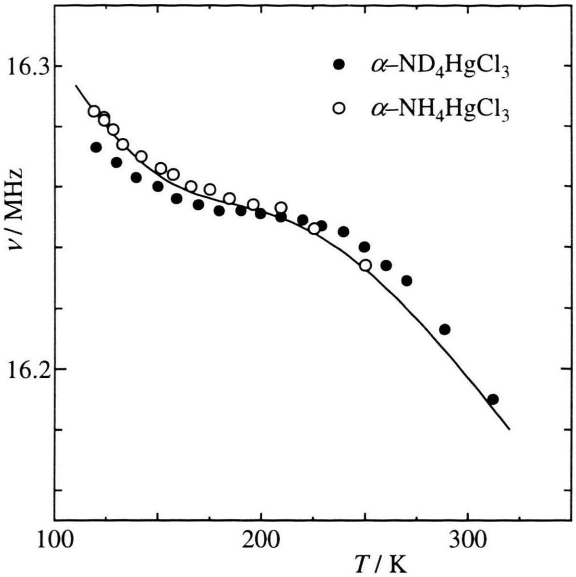

Fig. 4. Temperature dependences of ^{35}Cl NQR frequencies of the higher-frequency lines of α-ND_4HgCl_3 and α-NH_4HgCl_3. The solid curve shows the theoretical curve reported by K. Negita *et al.* [18] for the temperature dependence of α-NH_4HgCl_3.

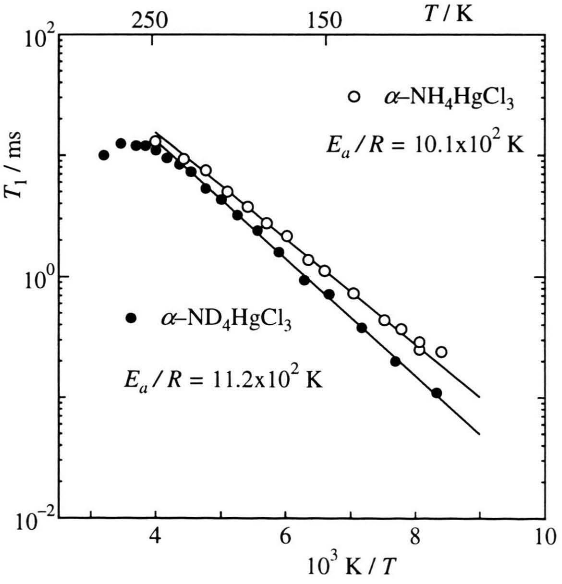

Fig. 5. Temperature dependences of ^{35}Cl NQR spin-lattice relaxation times T_1 of the higher-frequency lines of α-ND_4HgCl_3 and α-NH_4HgCl_3.

observed in the present study cannot be considered to correspond to these values. Hence, it is concluded that there exist three kinds of crystallographically inequivalent chlorines in the NH_4ICl_4 crystal above 70 K.

Unfortunately there is no structural information about the present crystal. However, the ν_1 and ν_3 frequencies which fade out at *ca.* 200 K, and the ν_2 frequency which can be detected even at room temperature, may be assigned to crystallographically inequivalent ICl_4^- anions. This assignment is supported by the temperature dependence of the T_1 above *ca.* 100 K. Above 150 K, ν_1 and ν_3 have the same T_1-values which decrease with increasing temperature following an Arrhenius relation,

$$T_1 \propto \exp\left(\frac{E_a}{RT}\right). \tag{1}$$

This type of temperature dependence of T_1 is usually ascribed to a sudden jump reorientation of an atomic group, for example, in this case to a 90° reorientation of ICl_4^- anions about the pseudo C_4 axis [13]. In this mechanism T_1 is proportional to the residence time in a single molecular orientation or the correlation time of the reorientation. Since the residence times of the chlorines within a single ICl_4^- anion are the same, the T_1-values of these chlorines should coincide. Therefore, the experimental observation of the same T_1-values between ν_1 and ν_3 strongly suggests that they arise from a single kind of ICl_4^- anions. The T_1-value of the ν_2 frequency begins to decrease rapidly with increasing temperature for the first time when the sample is heated above *ca.* 250 K. The second kind of ICl_4^- anions to which the ν_2 frequency is assigned, starts to perform the same kind of reorientation at a higher temperature.

By fitting (1) to the experimental data in the high-temperature region, the activation energies E_a for the ICl_4^- anionic reorientations are obtained as 26 kJ mol^{-1} and 54 kJ mol^{-1} for the two kinds of ICl_4^- anions from T_1 of ν_1 and ν_3, and T_1 of ν_2, respectively (Figure 2). It was revealed that the deuteration of ammonium ions has a negligible influence on the activation energy of the anionic reorientation.

4.1.2. Phase transitions

The anomalies in the temperature dependences of the resonance frequencies observed at 14.5 K and 70 K in NH_4ICl_4, and at 27 K and 74 K in ND_4ICl_4 (cf. Fig. 1) indicate the onset of structural phase transitions. Since ν_1 and ν_3 change continuously through the phase transition temperature at 70 K (or 74 K in the deuterated compound), this phase transition seems to be of second order. ν_2 could not be detected below this temperature. This may be due to a steep and large splitting of the resonance frequency below the transition temperature, although we have not yet succeeded in finding the corresponding frequencies. The phase transition at 14.5 K (or 27 K in the deuterated compound) is also ascribed to be of second order, judging from the order-parameter-like temperature dependence of the frequencies. The low-temperature phase transition shows a remarkable isotope effect. By the deuteration, the phase transition temperature T_c about doubles and below T_c the frequency shifts much more, indicating an increase of the lattice distortion by the deuteration. This isotope effect will be discussed later on.

4.1.3. Ammonium motion at low-temperature

A distinct T_1 minimum was observed at *ca.* 7 K in NH_4ICl_4 (cf. Fig. 3). Such a V-shaped broad T_1 minimum is often detected in the temperature dependence of the NQR T_1 due to the modulation of the EFG caused by the motion of a nearby atomic group [6 - 8]. According to Woessner and Gutowsky [14], the spin-lattice relaxation rate T_1^{-1} due to the modulation effect can be expressed as:

$$T_1^{-1} = \frac{1}{12}\left(\frac{e^2Qq}{\hbar}\right)^2 \left(\frac{q'}{q}\right)^2 \frac{\tau_c}{(1+\omega_Q^2\tau_c^2)}. \tag{2}$$

Here, $e^2Qq/\hbar, \omega_Q, q'/q$, and τ_c denote the quadrupole coupling constant, the nuclear quadrupole angular frequency of chlorine, the fluctuation fraction of the field gradient, and the correlation time of the motion in question. In the present case a motion of nearby ammonium ions must be important. If the asymmetry parameter η of the EFG is small,

$$\omega_Q = \frac{e^2Qq}{2\hbar}\left(1+\frac{\eta^2}{3}\right)^{1/2} \approx \frac{e^2Qq}{2\hbar}, \tag{3}$$

then

$$T_1^{-1} = \frac{1}{3}\omega_Q^2 \left(\frac{q'}{q}\right)^2 \frac{\tau_c}{(1+\omega_Q^2\tau_c^2)} \tag{4}$$

is obtained. Although non-disregardable values of η = 0.12 - 0.36 are reported for the ICl_4^- anions in the crystal [15], (4) was applied in the following discussion since $\eta^2/3 \ll 1$.

Assuming that a reorientational motion of ammonium ions about the axis through the nitrogen atom is responsible for the T_1 minimum, and the corresponding correlation time obeys an Arrhenius relation

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right), \tag{5}$$

the low-temperature T_1 minimum of ν_3 dipicted in Fig. 3 (open and solid circles for NH_4ICl_4 and ND_4ICl_4, respectively) was least-square-fitted by use of (4). In the calculations, $\nu_Q = \omega_Q/2\pi$ was set to be 22.34 MHz and 21.90 MHz for NH_4ICl_4 and ND_4ICl_4, respectively, in the temperature range where the T_1 minimum was observed. The activation energy E_a of the ammonium motion, the correlation time at infinitive temperature τ_0, and the fluctuation fraction q'/q of the EFG were chosen as fitting parameters. From the fitting calculations in the temperature range of $100 \leq 10^3\text{K}/T \leq 200$, E_a = 0.32 kJ mol^{-1} (39 K), $\tau_0 = 4.2 \times 10^{-11}$ s, and $q'/q = 1.3 \times 10^{-3}$ were obtained for the ammonium motion in NH_4ICl_4. For the motion in ND_4ICl_4, E_a = 0.30 kJ mol^{-1} (36 K), $\tau_0 = 4.6 \times 10^{-10}$ s, and $q'/q = 0.88 \times 10^{-3}$ were obtained for $50 \leq 10^3\text{K}/T \leq 180$.

If the potential curve for the motion of ND_4^+ equals that of NH_4^+, the activation energy for the reorientation is expected to increase by the deuteration due to the increase of the moment of inertia or the decrease of the zero-point energy of the rotational vibration. Indeed, this was the case for the previously reported NH_4AuCl_4 crystal [9]. In the present compound, however, E_a was almost the same for the NH_4^+ and ND_4^+ reorientation. This suggests that the inter-ionic interaction between the ammonium ion and the ICl_4^- anion is affected by the deuteration.

From the T_1 analysis, the inter-ionic interaction in NH_4ICl_4 is expected to be weakened by the deuteration. On the other hand, the lattice distortion below the low-temperature transition point is expected to be enhanced by the deuteration, because the frequency shift is much larger in ND_4ICl_4 than in NH_4ICl_4. These two expectations, which seem at first glance to be inconsistent with each other, lead to the idea that the lattice distortion in NH_4ICl_4 is suppressed to a great deal by the tunneling rotation of the NH_4^+ ions.

4.2. Ammonium trichloromercurate(II)

The temperature dependences of the ^{35}Cl NQR frequencies and spin-lattice relaxation times of α-NH_4HgCl_3 have been ascribed by Sagisawa *et al.* [6] to the motion of the ammonium ions. They assumed a 90°-reorientational motion about the S_4 symmetry axis of the NH_4^+ ion as a cause of the EFG fluctuation. The activation energy for the 90°-reorientation in α-NH_4HgCl_3 is reported to be 9.4 kJ mol^{-1} (11.3×10^2 K) [6]. Almost the same values of 9.3 kJ mol^{-1} (11.2×10^2 K) and 8.4 kJ mol^{-1} (10.1×10^2 K) were obtained for the same motion in α-ND_4HgCl_3 and α-NH_4HgCl_3, respectively, from the analysis of the T_1 data of Fig. 5 with the assumption that the relaxation mechanism is due to the EFG modulation. From the marked change in the ^{1}H NMR spin-lattice relaxation at 55 K, a phase transition was ascribed to the ordering of the NH_4^+ ions in α-NH_4HgCl_3 [6]. Matsuo *et al.* determined the transition temperatures of α-NH_4HgCl_3 and α-ND_4HgCl_3 to be 54.97 K and 58.3 K, respectively, by heat capacity measurements [16, 17]. In order to explain the anomalous temperature dependence of the NQR frequency shown in Fig. 4, a model has been proposed by N. Nakamura *et al.* in which the reorientational jumping time of NH_4^+ ions was taken into account [18 - 22]. The theoretical curve reported for the temperature dependence of α-NH_4HgCl_3 is depicted by a solid curve in Figure 4.

4.3. Ammonium Motions and Inter-ionic Interactions

The inter-ionic interaction in the ammonium compounds is expected to depend on the rotational state of the ammonium ions. That is, the effective interactions between the ammonium ions and the complex anions or among the complex anions via the ammonium ions will be different depending on whether the ammonium ions are rotating or not. Let J denote an effective interaction for the lattice distortion associated with a structural phase transition of a fictitious lattice, where all hydrogen-atoms of the ammonium ion are quantum mechanically localized at the stable positions. According to a two-state approximation [18 - 22], the averaged effective interaction $< J >$ for the lattice distortion will be given as follows:

$$< J > = \frac{\tau_r(1-\alpha)J}{\tau_r + \tau_t}. \tag{6}$$

Here, the transient time τ_t is the time for which the ammonium ion exists in a transient state from one orientation to another, the residence time τ_r is the time which it spends in a single orientation in a potential well. The parameter α is introduced in order to take into account a quantum mechanical delocalization by tunneling.

In the molecular field approximation of the Ising model [23], the phase transition temperature T_c is given by

$$T_c = \frac{z < J >}{k} \tag{7}$$

with k the Boltzmann constant and z the number of interactions. Then, we have the following relation for the ratio of the transition temperatures T_c(H) and T_c(D) of normal and deuterated salts:

$$\frac{T_c(\mathrm{H})}{T_c(\mathrm{D})} = \frac{< J >_\mathrm{H}}{< J >_\mathrm{D}} = \frac{(1-\alpha_\mathrm{H})J_\mathrm{H}}{(1-\alpha_\mathrm{D})J_\mathrm{D}} \cdot \frac{1+(\tau_t/\tau_r)_\mathrm{D}}{1+(\tau_t/\tau_r)_\mathrm{H}}. \tag{8}$$

In (8), the subscripts H and D denote parameters of normal and deuterated salts.

Putting a Boltzmann factor exp(-E_a/RT) for the ratio of τ_t/τ_r, (8) becomes

$$\frac{T_c(\mathrm{H})}{T_c(\mathrm{D})} = \frac{(1-\alpha_\mathrm{H})J_\mathrm{H}}{(1-\alpha_\mathrm{D})J_\mathrm{D}} \cdot \frac{1+\exp(-E_a(\mathrm{D})/RT_c(\mathrm{D}))}{1+\exp(-E_a(\mathrm{H})/RT_c(\mathrm{H}))}. \tag{9}$$

E_a is the activation energy of the ammonium motion which is responsible for the phase transition. For the low-temperature phase transition in ammonium tetrachloroiodate(III), E_a(H)/R = 39 K, T_c(H) = 14.5 K, E_a(D)/R = 36 K, T_c(D) = 27 K were obtained. Using these values in (9), we have

$$\frac{(1-\alpha_\mathrm{H})J_\mathrm{H}}{(1-\alpha_\mathrm{D})J_\mathrm{D}} = 0.45. \tag{10}$$

In the case of NH_4ICl_4, the inter-ionic interaction is expected to be weakened by deuteration, that is, $J_\mathrm{D}/J_\mathrm{H} \leq 1$. Therefore,

$$\frac{(1-\alpha_\mathrm{H})}{(1-\alpha_\mathrm{D})} = 0.45\frac{J_\mathrm{D}}{J_\mathrm{H}} \leq 0.45, \tag{11}$$

or

$$\alpha_\mathrm{H} \geq 0.55 + 0.45\alpha_\mathrm{D}. \tag{12}$$

This means that a quantum mechanical delocalization by tunneling is highly enhanced in NH_4ICl_4 as compared with in ND_4ICl_4, as expected from the smaller shift of the NQR frequencies observed below T_c in spite of the larger inter-ionic interaction. The remarkable decrease of T_c of NH_4ICl_4 as compared with ND_4ICl_4 can be ascribed to the enhancement of tunneling motion of NH_4^+ ions.

Then, how does a tunneling motion of NH_4^+ ions affect the phase transition temperature in the previously reported case of NH_4AuCl_4 [7, 9]? The transition temperature shifts by 5 K from 28.5 K in NH_4AuCl_4 to 33.5 K in ND_4AuCl_4. The ^{35}Cl NQR spin-lattice relaxation caused by the modulation of the EFG due to the motion of nearby ammonium ions was observed in the high-temperature phase of each compound. The activation energies of the ammonium motion, E_a(H)/R and E_a(D)/R, were determined to be 96 K and 217 K, respectively. For the ammonium tetrachloroaurate(III), the assumption of the same potential curve for the NH_4^+ and ND_4^+ reorientations resulted in quite reasonable values of parameters such like the moment of inertia of NH_4^+ and the number of potential wells. Hence, $J_\mathrm{D} = J_\mathrm{H}$ can be assumed for NH_4AuCl_4 and ND_4AuCl_4. From (9),

$$\frac{(1-\alpha_\mathrm{H})}{(1-\alpha_\mathrm{D})} = 0.88, \tag{13}$$

or

$$\alpha_\mathrm{H} = 0.12 + 0.88\alpha_\mathrm{D} \tag{14}$$

is obtained, which suggests less importance of the tunneling effect as compared with NH_4ICl_4.

The larger the activation energy E_a, the less important is the tunneling effect. This tendency is clearer if the data for α-NH_4HgCl_3 and α-ND_4HgCl_3 which have T_c(H) = 55 K, E_a(H)/R = 11.3×10^2 K, and T_c(D) = 58 K, E_a(D)/R = 11.2×10^2 K, respectively, are analized in a similar way. From (9),

$$\frac{(1-\alpha_\mathrm{H})}{(1-\alpha_\mathrm{D})} = 0.95\frac{J_\mathrm{D}}{J_\mathrm{H}} \leq 0.95 \tag{15}$$

or

$$\alpha_\mathrm{H} \geq 0.05 + 0.95\alpha_\mathrm{D} \tag{16}$$

is obtained for α-NH_4HgCl_3 and α-ND_4HgCl_3. A similar analysis by employing the reported values for NH_4Cl and ND_4Cl [24], T_c(H) = 242.8 K,

$E_a(\mathrm{H})/R = 21.6\times10^2$ K, and $T_c(\mathrm{D}) = 248.9$ K, $E_a(\mathrm{D})/R = 17.8\times10^2$ K, results in

$$\alpha_\mathrm{H} \geq 0.025 + 0.975\alpha_\mathrm{D}. \tag{17}$$

In the order of NH_4ICl_4 < NH_4AuCl_4 < α-NH_4HgCl_3 < NH_4Cl the activation energy E_a/R increases as 39 K, 96 K, 11.3×10^2 K, and 21.6×10^2 K, while the lower-limit of the tunneling parameter α_H decreases as 0.55, 0.12, 0.05, and 0.025. Although the type of the ammonium motion which causes the EFG fluctuations in NH_4ICl_4 remains unknown, it might be a small angle reorientation because of the very low activation energy for the motion. Across the low-temperature phase transition temperature T_c, the number of NQR lines does not change in NH_4ICl_4, in contrast to NH_4AuCl_4 [9]. This means that the ordering of the ammonium ions below T_c does not cause crystallographically inequivalent chlorines in NH_4ICl_4. The ammonium motion in NH_4ICl_4 should satisfy this condition.

5. Conclusions

(i) NH_4ICl_4 and ND_4ICl_4 undergo two phase transitions at 14.5 K and 70 K, and at 27 K and 74 K, respectively.

(ii) In the lowest-temperature phase of NH_4ICl_4, a remarkable change of the temperature dependence of the ^{35}Cl NQR frequencies was observed upon deuteration.

(iii) An NQR spin-lattice relaxation-time minimum, ascribable to the modulation effect of the EFG due to ammonium motion, was observed at 7 K and 11 K in NH_4ICl_4 and ND_4ICl_4, respectively.

(iv) The activation energy of the ammonium motion and the fluctuation fraction q'/q of the EFG were determined to be 0.32 kJ mol^{-1} and 1.3×10^{-3} for NH_4ICl_4, and 0.30 kJ mol^{-1} and 0.88×10^{-3} for ND_4ICl_4.

(v) The inter-ionic interaction is expected to be weakened by the deuteration. However, the frequency shift observed at the lowest-temperature phase is much larger in ND_4ICl_4 than in NH_4ICl_4. This suggests that the lattice distortion in NH_4ICl_4 is suppressed to a great deal by the tunneling rotation of NH_4^+ ions.

(vi) In the order of NH_4ICl_4 < NH_4AuCl_4 < α-NH_4HgCl_3 < NH_4Cl the activation energy E_a/R for an ammonium motion increases as 39 K, 96 K, 11.3×10^2 K, and 21.6×10^2 K, while the lower-limit of the tunneling parameter α_H decreases as 0.55, 0.12, 0.05, and 0.025.

[1] J. Pelzl and C. Dimitropoulos, Z. Naturforsch. **49a**, 232 (1994).
[2] Y. Kume and T. Asaji, J. Mol. Structure **345**, 145 (1995).
[3] M. Ichikawa and T. Matsuo, J. Mol. Structure **378**, 17 (1996).
[4] T. Asaji, Y. Kume, K. Ohya, and T. Chiba, J. Phys.: Codens. Matter **9**, 2563 (1997).
[5] Y. Kume and T. Asaji, Z. Naturforsch. **53a**, 514 (1998).
[6] K. Sagisawa, H. Kiriyama, and R. Kiriyama, Chem. Lett. **1975**, 1285.
[7] A. Ishikawa, T. Asaji, D. Nakamura, and R. Ikeda, Z. Naturforsch. **45a**, 467 (1990).
[8] T. Asaji, K. Horiuchi, T. Chiba, T. Shimizu, and R. Ikeda, Z. Naturforsch. **53a**, 419 (1998).
[9] T. Asaji, M. Yoza, and T. Ishizaka, J. Phys.: Codens. Matter **11**, 5219 (1999).
[10] Gmelin Handbuch der Anorganischen Chemie, NH4 (23), Verlag Chemie, Berlin 1936, p 237.
[11] Y. Kurita, D. Nakamura, and N. Hayakawa, J. Chem. Soc. Japan, Pure Chem. Sec. **79**, 1093 (1958).
[12] R. M. Barr and M. Goldstein, J. Chem. Soc., Dalton Trans. **1974**, 1180.
[13] A. Ishikawa, T. Asaji, and D. Nakamura, Z. Naturforsch. **44a**, 1226 (1989).
[14] D. E. Woessner and H. S. Gutowsky, J. Chem. Phys. **39**, 440 (1963).
[15] M. Mishima and T. Okuda, J. Mol. Structure **412**, 205 (1997).
[16] T. Matsuo, H. Kitano, and H. Suga, Solid State Commun. **19**, 863 (1976).
[17] H. Suga, J. Mineral. Soc. Japan **14**, 284 (1980).
[18] K. Negita, N. Nakamura, and H. Chihara, Chem. Phys. Lett. **63**, 187 (1979).
[19] H. Chihara, K. Negita, Y. Yoshioka, and N. Nakamura, J. Mol. Structure **58**, 155 (1980).
[20] Y. Yoshioka, N. Nakamura, and H. Chihara, J. Chem. Soc., Faraday Trans. 2, **79**, 497 (1983).
[21] N. Nakamura, Z. Naturforsch. **41a**, 243 (1986).
[22] R. J. C. Brown, Z. Naturforsch. **45a**, 449 (1990).
[23] R. Kubo, Statistical Mechanics, pp. 302-305, North-Holland, Amsterdam, 1965.
[24] K. Morimoto, K. Shimomura, and M. Yoshida, J. Phys. Soc. Japan **52**, 3927 (1983).