

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

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$^{35}\text{Cl}$  NQR measurements revealed two phase transitions at 14.5 K and 70 K in  $\text{NH}_4\text{ICl}_4$ . By deuteration of the ammonium ions, the respective transition temperature increased to 27 K and 74 K. In the lowest-temperature phase of  $\text{NH}_4\text{ICl}_4$ , by the deuteration a remarkable change of the temperature dependence of the  $^{35}\text{Cl}$  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  $\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$ , respectively. The activation energy of the ammonium motion and the fluctuation fraction  $\langle \dot{q} \rangle / q$  of the EFG were determined to be  $0.32 \text{ kJ mol}^{-1}$  and  $1.3 \times 10^{-3}$  for  $\text{NH}_4\text{ICl}_4$ , and  $0.30 \text{ kJ mol}^{-1}$  and  $0.88 \times 10^{-3}$  for  $\text{ND}_4\text{ICl}_4$ . The experimental result suggests that the inter-ionic interaction between the ammonium ion and the  $\text{ICl}_4^-$  complex anion is weakened by the deuteration. However, the frequency shift observed in the lowest-temperature phase is much larger in  $\text{ND}_4\text{ICl}_4$  than in  $\text{NH}_4\text{ICl}_4$ . This suggests that the lattice distortion in  $\text{NH}_4\text{ICl}_4$  is suppressed to a great deal by the tunneling rotation of  $\text{NH}_4^+$  ions. The effective inter-ionic interaction responsible for the lattice distortion, the transition temperature and the enhancement of tunneling of  $\text{NH}_4^+$  as compared with  $\text{ND}_4^+$  is discussed for  $\text{NH}_4\text{ICl}_4$  as well as for previously reported  $\text{NH}_4\text{AuCl}_4$  and  $\alpha\text{-NH}_4\text{HgCl}_3$ .

*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  $\text{NH}_4^+$  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  $\text{NH}_4^+$  and  $\text{ND}_4^+$  motion, that the relaxation mechanism is expected to be the same for the  $\text{NH}_4^+$  and  $\text{ND}_4^+$  compounds.

$^{35}\text{Cl}$  NQR frequencies and spin-lattice relaxation times were measured as functions of temperature for  $\text{NH}_4\text{ICl}_4$ ,  $\text{ND}_4\text{ICl}_4$ , and  $\alpha\text{-ND}_4\text{HgCl}_3$ . By combination with the reported results for  $\alpha\text{-NH}_4\text{HgCl}_3$  [6],  $\text{NH}_4\text{AuCl}_4$  [7], and  $\text{ND}_4\text{AuCl}_4$  [9], the deuteration effect on the ammonium motion and structural phase transition in these compounds will be discussed.

## 2. Experimental

$\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$  were prepared according to the method described in [10, 11]. For the preparation of the deuterated compound,  $\text{ND}_4\text{Cl}$  and  $\text{D}_2\text{O}$

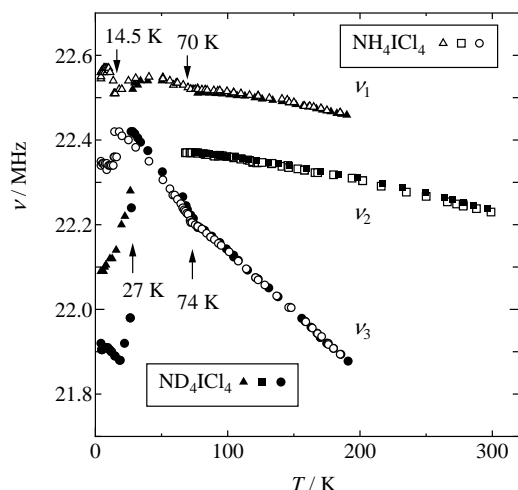


Fig. 1. Temperature dependences of  $^{35}\text{Cl}$  NQR frequencies of  $\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$ , open and solid symbols, respectively.

were used instead of  $\text{NH}_4\text{Cl}$  and  $\text{H}_2\text{O}$ . The very deliquescent golden-yellow crystals obtained from the aqueous solution were dried over  $\text{P}_2\text{O}_5$  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.  $\alpha$ - $\text{ND}_4\text{HgCl}_3$  was prepared by melting an equimolar mixture of  $\text{HgCl}_2$  and  $\text{ND}_4\text{Cl}$  at *ca.* 210 °C [6, 12]. Chemical Analysis: Calcd. for  $\text{NH}_4\text{ICl}_4$ :  $\text{NH}_4$ , 6.3 %;  $\text{Cl/I} = 4.0$ . Found:  $\text{NH}_4$ , 6.2 %;  $\text{Cl/I} = 4.0$ .

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  $\tau_e$  was set at *ca.* 120 - 250  $\mu\text{s}$ . 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  $\pm 0.5$  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  $^{35}\text{Cl}$  NQR frequencies of  $\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$  are shown in Figure 1.

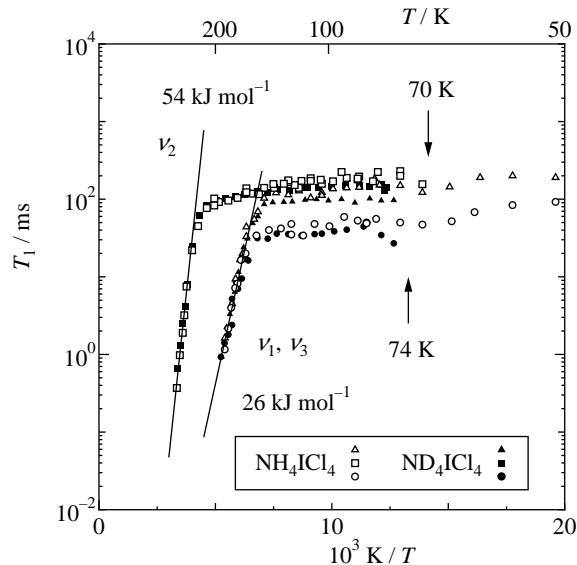


Fig. 2. Temperature dependences of  $^{35}\text{Cl}$  NQR spin-lattice relaxation times  $T_1$  of  $\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$ , open and solid symbols, respectively, in the high-temperature region. For the  $T_1$ -data the same symbols for the respective NQR lines are 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  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  were observed at 22.522, 22.369, and 22.196 MHz for  $\text{NH}_4\text{ICl}_4$ , and at 22.511, 22.370, and 22.194 MHz for  $\text{ND}_4\text{ICl}_4$ . With increasing temperature,  $\nu_1$  and  $\nu_3$  faded out at *ca.* 200 K, while  $\nu_2$  could be detected even at room temperature. At 77.3 K, we have searched for other resonance frequencies for  $\text{ND}_4\text{ICl}_4$  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  $\nu_1$  and  $\nu_3$  frequencies of  $\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$  showed a discontinuity at around 70 K and 74 K, respectively. Below this temperature,  $\nu_2$  could not be observed. An anomalous frequency shift of  $\nu_1$  and  $\nu_3$  was observed at 14.5 K in  $\text{NH}_4\text{ICl}_4$  and at 27 K in  $\text{ND}_4\text{ICl}_4$ . The  $\nu_1$  and  $\nu_3$  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  $\nu_1$  and  $\nu_3$  coincides and shows a rapid decrease with increasing temperature above *ca.* 150 K, while  $T_1$  of  $\nu_2$  begins to decrease similarly for the first time at above *ca.* 250 K. Little anomalies in the temperature

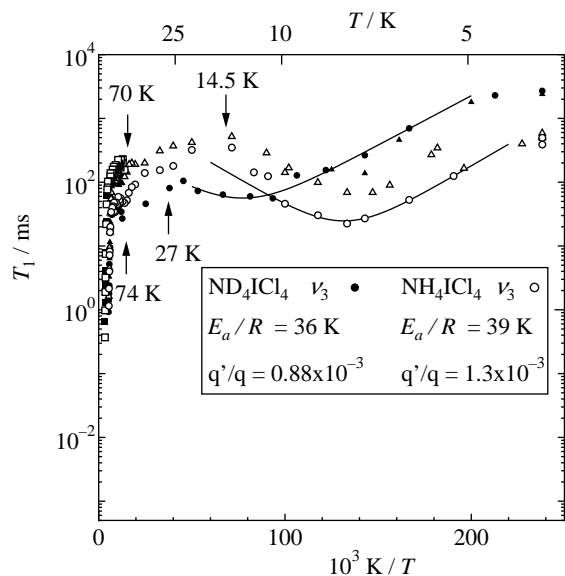


Fig. 3. As Fig. 2, but for the low-temperature region. The solid curves are the least-squares fitting of the  $T_1$ -data of  $\nu_3$  with the assumption of the relaxation mechanism by EFG modulation.

dependence of  $T_1$  were observed where anomalies in the temperature dependences of the resonance frequencies occurred. On the other hand, at very low temperatures a  $T_1$  minimum was observed at *ca.* 7 K in  $\text{NH}_4\text{ICl}_4$  and at *ca.* 11 K in  $\text{ND}_4\text{ICl}_4$ .

### 3.2. Ammonium trichloromercurate(II)

The temperature dependences of the NQR frequency and  $T_1$  of the higher-frequency line of  $\alpha\text{-ND}_4\text{HgCl}_3$  and  $\alpha\text{-NH}_4\text{HgCl}_3$  are shown in Fig. 4 and 5, respectively. These results are very similar to those of  $\alpha\text{-NH}_4\text{HgCl}_3$  reported by Sagisawa *et al.* [6].

## 4. Discussion

### 4.1. Ammonium tetrachloroiodate(III)

#### 4.1.1. Assignment of resonance frequencies and reorientation of $\text{ICl}_4^-$ anions

The  $\nu_2$  frequency of 22.230 MHz at 299 K for  $\text{NH}_4\text{ICl}_4$  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 monohy-

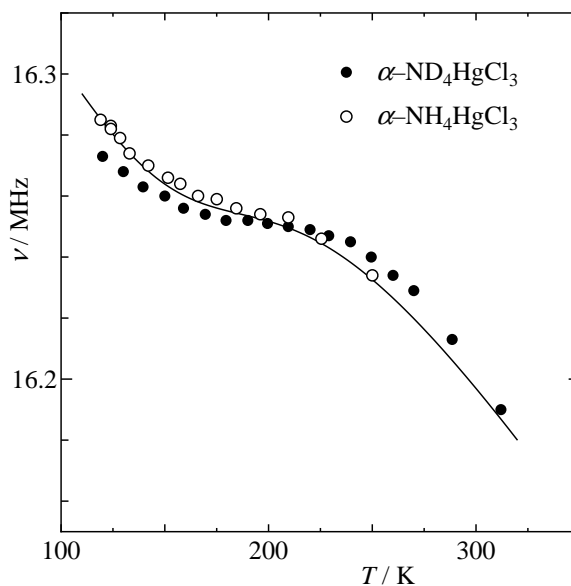


Fig. 4. Temperature dependences of  $^{35}\text{Cl}$  NQR frequencies of the higher-frequency lines of  $\alpha\text{-ND}_4\text{HgCl}_3$  and  $\alpha\text{-NH}_4\text{HgCl}_3$ . The solid curve shows the theoretical curve reported by K. Negita *et al.* [18] for the temperature dependence of  $\alpha\text{-NH}_4\text{HgCl}_3$ .

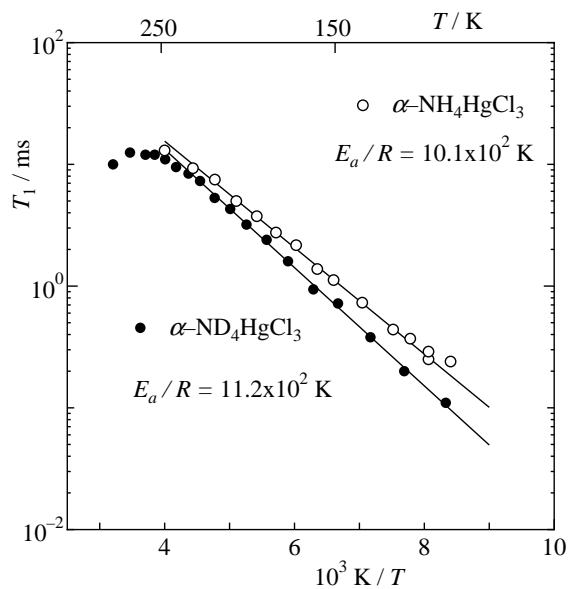


Fig. 5. Temperature dependences of  $^{35}\text{Cl}$  NQR spin-lattice relaxation times  $T_1$  of the higher-frequency lines of  $\alpha\text{-ND}_4\text{HgCl}_3$  and  $\alpha\text{-NH}_4\text{HgCl}_3$ .

drate  $\text{NH}_4\text{ICl}_4 \cdot \text{H}_2\text{O}$  shows three frequencies of 19.98, 24.68, and 27.96 MHz at 296 K. The resonance lines

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  $\text{NH}_4\text{ICl}_4$  crystal above 70 K.

Unfortunately there is no structural information about the present crystal. However, the  $\nu_1$  and  $\nu_3$  frequencies which fade out at *ca.* 200 K, and the  $\nu_2$  frequency which can be detected even at room temperature, may be assigned to crystallographically inequivalent  $\text{ICl}_4^-$  anions. This assignment is supported by the temperature dependence of the  $T_1$  above *ca.* 100 K. Above 150 K,  $\nu_1$  and  $\nu_3$  have the same  $T_1$ -values which decrease with increasing temperature following an Arrhenius relation,

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

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  $90^\circ$  reorientation of  $\text{ICl}_4^-$  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  $\text{ICl}_4^-$  anion are the same, the  $T_1$ -values of these chlorines should coincide. Therefore, the experimental observation of the same  $T_1$ -values between  $\nu_1$  and  $\nu_3$  strongly suggests that they arise from a single kind of  $\text{ICl}_4^-$  anions. The  $T_1$ -value of the  $\nu_2$  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  $\text{ICl}_4^-$  anions to which the  $\nu_2$  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  $\text{ICl}_4^-$  anionic reorientations are obtained as  $26 \text{ kJ mol}^{-1}$  and  $54 \text{ kJ mol}^{-1}$  for the two kinds of  $\text{ICl}_4^-$  anions from  $T_1$  of  $\nu_1$  and  $\nu_3$ , and  $T_1$  of  $\nu_2$ , 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  $\text{NH}_4\text{ICl}_4$ , and at 27 K and 74 K in  $\text{ND}_4\text{ICl}_4$

(cf. Fig. 1) indicate the onset of structural phase transitions. Since  $\nu_1$  and  $\nu_3$  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.  $\nu_2$  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  $\text{NH}_4\text{ICl}_4$  (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:

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

Here,  $e^2 Q q / \hbar$ ,  $\omega_Q$ ,  $q' / q$ , and  $\tau_c$  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  $\eta$  of the EFG is small,

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

then

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

is obtained. Although non-disregardable values of  $\eta = 0.12 - 0.36$  are reported for the  $\text{ICl}_4^-$  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

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

the low-temperature  $T_1$  minimum of  $\nu_3$  depicted in Fig. 3 ( open and solid circles for  $\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$ , 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  $\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$ , 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  $\tau_0$ , and the fluctuation fraction  $q'/q$  of the EFG were chosen as fitting parameters. From the fitting calculations in the temperature range of  $100 \leq 10^3\text{K}/T \leq 200$ ,  $E_a = 0.32 \text{ kJ mol}^{-1}$  (39 K),  $\tau_0 = 4.2 \times 10^{-11} \text{ s}$ , and  $q'/q = 1.3 \times 10^{-3}$  were obtained for the ammonium motion in  $\text{NH}_4\text{ICl}_4$ . For the motion in  $\text{ND}_4\text{ICl}_4$ ,  $E_a = 0.30 \text{ kJ mol}^{-1}$  (36 K),  $\tau_0 = 4.6 \times 10^{-10} \text{ s}$ , 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  $\text{ND}_4^+$  equals that of  $\text{NH}_4^+$ , 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  $\text{NH}_4\text{AuCl}_4$  crystal [9]. In the present compound, however,  $E_a$  was almost the same for the  $\text{NH}_4^+$  and  $\text{ND}_4^+$  reorientation. This suggests that the inter-ionic interaction between the ammonium ion and the  $\text{ICl}_4^-$  anion is affected by the deuteration.

From the  $T_1$  analysis, the inter-ionic interaction in  $\text{NH}_4\text{ICl}_4$  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  $\text{ND}_4\text{ICl}_4$  than in  $\text{NH}_4\text{ICl}_4$ . These two expectations, which seem at first glance to be inconsistent with each other, lead to the idea that the lattice distortion in  $\text{NH}_4\text{ICl}_4$  is suppressed

to a great deal by the tunneling rotation of the  $\text{NH}_4^+$  ions.

#### 4.2. Ammonium trichloromercurate(II)

The temperature dependences of the  $^{35}\text{Cl}$  NQR frequencies and spin-lattice relaxation times of  $\alpha\text{-NH}_4\text{HgCl}_3$  have been ascribed by Sagisawa *et al.* [6] to the motion of the ammonium ions. They assumed a  $90^\circ$ -reorientational motion about the  $S_4$  symmetry axis of the  $\text{NH}_4^+$  ion as a cause of the EFG fluctuation. The activation energy for the  $90^\circ$ -reorientation in  $\alpha\text{-NH}_4\text{HgCl}_3$  is reported to be  $9.4 \text{ kJ mol}^{-1}$  ( $11.3 \times 10^2 \text{ K}$ ) [6]. Almost the same values of  $9.3 \text{ kJ mol}^{-1}$  ( $11.2 \times 10^2 \text{ K}$ ) and  $8.4 \text{ kJ mol}^{-1}$  ( $10.1 \times 10^2 \text{ K}$ ) were obtained for the same motion in  $\alpha\text{-ND}_4\text{HgCl}_3$  and  $\alpha\text{-NH}_4\text{HgCl}_3$ , 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  $^1\text{H}$  NMR spin-lattice relaxation at 55 K, a phase transition was ascribed to the ordering of the  $\text{NH}_4^+$  ions in  $\alpha\text{-NH}_4\text{HgCl}_3$  [6]. Matsuo *et al.* determined the transition temperatures of  $\alpha\text{-NH}_4\text{HgCl}_3$  and  $\alpha\text{-ND}_4\text{HgCl}_3$  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  $\text{NH}_4^+$  ions was taken into account [18 - 22]. The theoretical curve reported for the temperature dependence of  $\alpha\text{-NH}_4\text{HgCl}_3$  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  $\langle J \rangle$  for the lattice distortion will be given as follows:

$$\langle J \rangle = \frac{\tau_r(1 - \alpha)J}{\tau_r + \tau_t}. \quad (6)$$

Here, the transient time  $\tau_t$  is the time for which the ammonium ion exists in a transient state from one orientation to another, the residence time  $\tau_r$  is the time which it spends in a single orientation in a potential well. The parameter  $\alpha$  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

$$T_c = \frac{z \langle J \rangle}{k} \quad (7)$$

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

$$\frac{T_c(\text{H})}{T_c(\text{D})} = \frac{\langle J \rangle_{\text{H}}}{\langle J \rangle_{\text{D}}} = \frac{(1 - \alpha_{\text{H}})J_{\text{H}}}{(1 - \alpha_{\text{D}})J_{\text{D}}} \cdot \frac{1 + (\tau_t/\tau_r)_{\text{D}}}{1 + (\tau_t/\tau_r)_{\text{H}}}. \quad (8)$$

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  $\tau_t/\tau_r$ , (8) becomes

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

$E_a$  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),  $E_a(\text{H})/R = 39$  K,  $T_c(\text{H}) = 14.5$  K,  $E_a(\text{D})/R = 36$  K,  $T_c(\text{D}) = 27$  K were obtained. Using these values in (9), we have

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

In the case of  $\text{NH}_4\text{ICl}_4$ , the inter-ionic interaction is expected to be weakened by deuteration, that is,  $J_{\text{D}}/J_{\text{H}} \leq 1$ . Therefore,

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

or

$$\alpha_{\text{H}} \geq 0.55 + 0.45\alpha_{\text{D}}. \quad (12)$$

This means that a quantum mechanical delocalization by tunneling is highly enhanced in  $\text{NH}_4\text{ICl}_4$  as compared with in  $\text{ND}_4\text{ICl}_4$ , 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  $\text{NH}_4\text{ICl}_4$  as compared with  $\text{ND}_4\text{ICl}_4$  can be ascribed to the enhancement of tunneling motion of  $\text{NH}_4^+$  ions.

Then, how does a tunneling motion of  $\text{NH}_4^+$  ions affect the phase transition temperature in the previously reported case of  $\text{NH}_4\text{AuCl}_4$  [7, 9]? The transition temperature shifts by 5 K from 28.5 K in  $\text{NH}_4\text{AuCl}_4$  to 33.5 K in  $\text{ND}_4\text{AuCl}_4$ . The  $^{35}\text{Cl}$  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,  $E_a(\text{H})/R$  and  $E_a(\text{D})/R$ , were determined to be 96 K and 217 K, respectively. For the ammonium tetrachloroaurate(III), the assumption of the same potential curve for the  $\text{NH}_4^+$  and  $\text{ND}_4^+$  reorientations resulted in quite reasonable values of parameters such like the moment of inertia of  $\text{NH}_4^+$  and the number of potential wells. Hence,  $J_{\text{D}} = J_{\text{H}}$  can be assumed for  $\text{NH}_4\text{AuCl}_4$  and  $\text{ND}_4\text{AuCl}_4$ . From (9),

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

or

$$\alpha_{\text{H}} = 0.12 + 0.88\alpha_{\text{D}} \quad (14)$$

is obtained, which suggests less importance of the tunneling effect as compared with  $\text{NH}_4\text{ICl}_4$ .

The larger the activation energy  $E_a$ , the less important is the tunneling effect. This tendency is clearer if the data for  $\alpha\text{-NH}_4\text{HgCl}_3$  and  $\alpha\text{-ND}_4\text{HgCl}_3$  which have  $T_c(\text{H}) = 55$  K,  $E_a(\text{H})/R = 11.3 \times 10^2$  K, and  $T_c(\text{D}) = 58$  K,  $E_a(\text{D})/R = 11.2 \times 10^2$  K, respectively, are analyzed in a similar way. From (9),

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

or

$$\alpha_{\text{H}} \geq 0.05 + 0.95\alpha_{\text{D}} \quad (16)$$

is obtained for  $\alpha\text{-NH}_4\text{HgCl}_3$  and  $\alpha\text{-ND}_4\text{HgCl}_3$ . A similar analysis by employing the reported values for  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$  [24],  $T_c(\text{H}) = 242.8$  K,

$E_a(\text{H})/R = 21.6 \times 10^2$  K, and  $T_c(\text{D}) = 248.9$  K,  $E_a(\text{D})/R = 17.8 \times 10^2$  K, results in

$$\alpha_{\text{H}} \geq 0.025 + 0.975\alpha_{\text{D}}. \quad (17)$$

In the order of  $\text{NH}_4\text{ICl}_4 < \text{NH}_4\text{AuCl}_4 < \alpha\text{-NH}_4\text{HgCl}_3 < \text{NH}_4\text{Cl}$  the activation energy  $E_a/R$  increases as 39 K, 96 K,  $11.3 \times 10^2$  K, and  $21.6 \times 10^2$  K, while the lower-limit of the tunneling parameter  $\alpha_{\text{H}}$  decreases as 0.55, 0.12, 0.05, and 0.025. Although the type of the ammonium motion which causes the EFG fluctuations in  $\text{NH}_4\text{ICl}_4$  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  $\text{NH}_4\text{ICl}_4$ , in contrast to  $\text{NH}_4\text{AuCl}_4$  [9]. This means that the ordering of the ammonium ions below  $T_c$  does not cause crystallographically inequivalent chlorines in  $\text{NH}_4\text{ICl}_4$ . The ammonium motion in  $\text{NH}_4\text{ICl}_4$  should satisfy this condition.

## 5. Conclusions

(i)  $\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$  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  $\text{NH}_4\text{ICl}_4$ , a remarkable change of the temperature dependence of the  $^{35}\text{Cl}$  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  $\text{NH}_4\text{ICl}_4$  and  $\text{ND}_4\text{ICl}_4$ , respectively.

(iv) The activation energy of the ammonium motion and the fluctuation fraction  $q'/q$  of the EFG were determined to be  $0.32 \text{ kJ mol}^{-1}$  and  $1.3 \times 10^{-3}$  for  $\text{NH}_4\text{ICl}_4$ , and  $0.30 \text{ kJ mol}^{-1}$  and  $0.88 \times 10^{-3}$  for  $\text{ND}_4\text{ICl}_4$ .

(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  $\text{ND}_4\text{ICl}_4$  than in  $\text{NH}_4\text{ICl}_4$ . This suggests that the lattice distortion in  $\text{NH}_4\text{ICl}_4$  is suppressed to a great deal by the tunneling rotation of  $\text{NH}_4^+$  ions.

(vi) In the order of  $\text{NH}_4\text{ICl}_4 < \text{NH}_4\text{AuCl}_4 < \alpha\text{-NH}_4\text{HgCl}_3 < \text{NH}_4\text{Cl}$  the activation energy  $E_a/R$  for an ammonium motion increases as 39 K, 96 K,  $11.3 \times 10^2$  K, and  $21.6 \times 10^2$  K, while the lower-limit of the tunneling parameter  $\alpha_{\text{H}}$  decreases as 0.55, 0.12, 0.05, and 0.025.

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