Change in Electronic Structure of the ICl\ce{^2} Anion in NH\ce{^4}ICl\ce{^2} Crystals due to an Excitation of Reorientational Motion of the Ammonium Ion

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Two $^{35}$Cl NQR frequencies, $\nu_\alpha = 9.148$ and $\nu_\beta = 28.286$ MHz, were observed at 77.3 K in NH\ce{^4}ICl\ce{^2}. $\nu_\alpha$ and $\nu_\beta$ showed a strong temperature dependence with positive and negative temperature coefficient, respectively. This anomalous temperature dependence is explained by a temperature dependence of the mole fraction of the hydrogen-bonded ICl\ce{^2} ion. The energy difference, $\Delta E_{\text{anion}}$, of the anion between the hydrogen-bonded and the non-bonded states was derived as $\Delta E_{\text{anion}} \approx 700$ K (5.8 kJ mol\(^{-1}\)) and as $\Delta E_{\text{anion}} \approx 640$ K (5.3 kJ mol\(^{-1}\)) for NH\ce{^4}ICl\ce{^2} and ND\ce{^4}ICl\ce{^2}, respectively. The temperature dependence of the spin-lattice relaxation time $T_1$ showed a clear minimum in the ln $T_1$ vs. $10^3$/T plots, which can be interpreted as due to EFG modulation by the reorientational motion of the ammonium ion. The reorientation of the ammonium ion among stable and meta-stable orientations is expected to be responsible to the temperature variation of electronic structure of the ICl\ce{^2} anion.

Key words: Hydrogen Bond; Electronic Structure; Ammonium Ion; Reorientation; NQR.

1. Introduction

A single $^{35}$Cl NQR frequency of 26.14 MHz has been reported for NH\ce{^4}ICl\ce{^2} at 294 K by Y. Kurita et al. [1]. The frequency is exceptionally high as compared with those (17.6 - 19.9 MHz at room temperature) of the other ICl\ce{^2} salts [1], suggesting a strong interionic interaction operative between the ammonium ion and the anion. Presently we have re-investigated the $^{35}$Cl NQR of NH\ce{^4}ICl\ce{^2} as an extension of a series of studies [2 - 4] on the effect of deuteration on ammonium motion in crystals and found an additional NQR line in the low-frequency range. The average of the previously reported frequency and the newly found one lies in the normal frequency range of the ICl\ce{^2} ion. The appearance of the two resonance frequencies, which are largely separated, could be explained by hydrogen bonding as in the case of NH\ce{^3}I\ce{^3} [5]. In the present paper, the temperature dependence of the NQR frequencies both in NH\ce{^4}ICl\ce{^2} and ND\ce{^4}ICl\ce{^2}, and a change in electronic structure of the ICl\ce{^2} anion due to an excitation of reorientational motion of the ammonium ion will be discussed in accordance with the simple theory proposed by Yoshioka, Nakamura, and Chihara [5], which relates the reorientation of the ammonium ion to a concerted change in the relative weights of the resonance structures of the I\ce{^3} anion through formation and scission of the hydrogen bond. The temperature dependence of the spin-lattice relaxation time of $^{35}$Cl NQR is also discussed in connection with the type of reorientational motion of the ammonium ion.

2. Experimental

NH\ce{^4}ICl\ce{^2} was prepared by adding ICl to the NH\ce{^4}Cl solution dissolved in 6N HCl [1, 6]. For the preparation of the deuterated compound ND\ce{^4}Cl, DCI and D\ce{^2}O were used instead of NH\ce{^4}Cl, HCl, and H\ce{^2}O. The crystals of the sample were obtained by slow-evaporation of the aqueous solution in a vacuum desiccator using P\ce{^2}O\ce{^5} as desiccant. Since the freshly prepared crystals are very hygroscopic, they were handled in a dry bag under nitrogen gas. The sample for the NQR
measurements were sealed in a glass tube with a heat-exchange helium gas.

The X-ray powder diffraction patterns for Cu Kα radiation were recorded by use of Rigaku RINT 2100S. Silicon powder was used as an internal standard of the diffraction angle. The powdered crystals were covered by a thin film (parafilm, American National Can), although the completely dried crystals could be measured in open air.

For the NQR measurements, a pulsed spectrometer based on the Matec gated amplifier 515A was used. The spin-lattice relaxation time \( T_1 \) was determined by observing the recovery of the echo height, employing the pulse sequence \( \pi \rightarrow \tau \rightarrow \pi/2 \rightarrow \tau_c \rightarrow \pi \), where \( \tau_c \) was set typically at about 150 \( \mu \)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 vs. constantan and gold + 0.07% iron vs. chromel thermocouples above 77 K and below 77 K, respectively.

3. Results and Discussion

3.1. X-Ray Powder Diffraction

Assuming that the crystal of \( \text{NH}_4\text{ICl}_2 \) is isomorphous with \( \text{NH}_4\text{I}_3 \), which has an orthorhombic cell with the space group Pnma (\( D_{16}^h \)) [7, 8], the powder pattern can be interpreted reasonably well with

![Fig. 1. Temperature dependences of the \( ^{35}\text{Cl} \) NQR frequency \( \nu_a \) of ammonium dichloroiodate. \( \alpha = 10.15, b = 6.146, \) and \( c = 8.404 \) Å as shown in Table 1.](image)

### Table 1. X-Ray powder diffraction angles \( 2\theta \) of \( \text{NH}_4\text{ICl}_2 \) for Cu Kα radiation. Theoretical values \( 2\theta_{\text{calc}} \) were calculated by assuming space group Pnma with \( a = 10.15, b = 6.146, \) and \( c = 8.404 \) Å.

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Figures 1 and 2 show, respectively, the temperature dependence of the \( ^{35}\text{Cl} \) NQR frequencies \( \nu_a \) and \( \nu_b \) of \( \text{NH}_4\text{ICl}_2 \) and its deuterated analogue. The \( \nu_b \) frequency of 26.121 MHz at 297 K for \( \text{NH}_4\text{ICl}_2 \) agrees well with the previously reported frequency of 26.14 MHz at 294 K [1], by which fact the sample was identified as \( \text{NH}_4\text{ICl}_2 \). The strong positive and negative temperature coefficients observed in the \( \nu_a \) and \( \nu_b \) frequencies, respectively, suggest a change in electronic structure of the anion via the temperature dependence of hydrogen bonding, as in the case of \( \text{NH}_4\text{I}_3 \) which has been explained by Yoshioka et al. [5]. Since it has been found that \( \text{NH}_4\text{I}_3 \) and \( \text{NH}_4\text{I}_3 \) are isomorphous, this is very likely.

According to Yoshioka et al., the following three resonance structures

\[ \text{A: } (\text{Cl}^-_\alpha \cdot \text{I-Cl}_b), \text{ B: } (\text{Cl}^-_\alpha \cdot \text{I-Cl}^-_b), \text{ and C: } (\text{Cl}^-_\alpha \cdot \text{I}^- \cdot \text{Cl}^-_b) \]

of the \( \text{ICl}_2^- \) anion are considered.

The weight of the resonance structures A, B, and C are assumed as \( \alpha, \beta, \) and \( 1 - 2\alpha \), respectively, in
the state without hydrogen bonding to the ammonium ion, while \( \alpha + \beta, \alpha - \beta, \) and \( 1 - 2\alpha, \) respectively, in the hydrogen-bonded state. The parameter \( \beta \) accounts for non-equivalence of the structures A and B when the N-H...Cl_\text{a} hydrogen bonding is formed. Let us denote the mole fraction of the hydrogen bonded ICl\(^2^-\) ion by \( \beta. \) In the present discussion the problem is treated as simply as possible. The state without hydrogen bonding may correspond really the state with very weak interactions. The simple Townes-Dailey theory [9] correlates these parameters with the observed NQR frequencies as follows, under the assumption of rapid conversion between the hydrogen bonded and the non-bonded states:

\[
\begin{align*}
  f_a &= \alpha (\alpha - \beta) + (1 - \beta) \alpha = \alpha - \epsilon \beta, \\
  f_b &= \alpha (\alpha + \beta) + (1 - \beta) \alpha = \alpha + \epsilon \beta.
\end{align*}
\]

Here \( f_x \) is a reduced frequency defined by \( f_x = \nu_x / \nu_{\text{atom}}, \) where \( \nu_x (x = a, b) \) is the \(^{35}\text{Cl} \) NQR frequency and \( \nu_{\text{atom}} = 54.96 \text{ MHz} \) is an expected frequency for atomic \(^{35}\text{Cl} \) with \( \eta = 0.1 \) [9, 10]. This value of \( \eta \) was assumed by taking into account the fact that the \( \eta \) value of the terminal \(^{127}\text{I} \) of the \( \text{I}^\text{3}^- \) anion in NH\(_4\)I\(_3\) is approximately about 0.1 [11].

The values of \( \alpha \) and \( \epsilon \beta \) were calculated at each temperature from (1) and (2). An almost temperature independent value of \( \alpha = 0.34 \) was obtained both for NH\(_4\)ICl\(_2\) and ND\(_4\)ICl\(_2\). The smaller \( \alpha \) value compared with \( \alpha = 0.48 \) of the \( \text{I}^\text{3}^- \) anion [5] suggests the more importance of the ionic structure \( \text{C} \) in the ICl\(^2^-\) anion. This is very likely since chlorine is more electronegative than iodine. The temperature dependence of \( \epsilon \beta \) is shown in Figs. 3 and 4 for NH\(_4\)ICl\(_2\) and ND\(_4\)ICl\(_2\),
Fig. 5. The frequency $\nu_a$ plotted against $(1 - c)$, where $c$ denotes the mole fraction of the hydrogen bonded ICl$_2$ anion.

respectively. If the energy difference of the anion between the hydrogen bonded and the non-bonded states is denoted by $\Delta E_{\text{anion}}$, and the ratio of the number of the non-bonded states to that of the bonded states by $N$, a Boltzmann distribution

$$\frac{1 - c}{c} = N \exp(-\Delta E_{\text{anion}}/kT)$$  \hspace{1cm} (3)

will hold. At $T = 0$ K, $c = 1$ is expected. Hence, from the extrapolation of the $c\beta$ value at $T = 0$ K, the value of $\beta$ can be determined as $\beta = 0.175$ and 0.176 at $T = 0$ K for NH$_4$ICl$_2$ and ND$_4$ICl$_2$, respectively. If the value of $\beta$ is assumed to be temperature independent, the temperature dependence of the $c\beta$ value is given by

$$c\beta = \frac{0.175 \text{ or } 0.176}{1 + N \exp(-\Delta E_{\text{anion}}/kT)}.$$  \hspace{1cm} (4)

Equation (4) is fitted to the experimental results of Figs. 3 or 4 using $N$ and $\Delta E_{\text{anion}}$ as fitting parameters. The fitting calculations resulted in $\Delta E_{\text{anion}}/k = 704$ K and $N = 2.87$ for NH$_4$ICl$_2$, and $\Delta E_{\text{anion}}/k = 639$ K and $N = 2.42$ for ND$_4$ICl$_2$. The fitting results are shown by solid curves in Figs. 3 and 4. $\Delta E_{\text{anion}}$ showed a small decrease by the deuteration.

Fig. 6. The frequency $\nu_b$ plotted against $(1 - c)$, where $c$ denotes the mole fraction of the hydrogen bonded ICl$_2$ ion.

From (1) or (2), the resonance frequency should be a linear function of the mole fraction of the non-bonded ICl$_2$ ion, $(1 - c)$, if the parameters $\alpha$ and $\beta$ are constant independently of temperature. In Figs. 5 and 6, the resonance frequencies are plotted against $(1 - c)$ obtained under the assumption of constant $\alpha$ and $\beta$. The straight lines, which were obtained by the least-squares method, are shown in the figures. These plots indicate the validity of the assumptions.

3.3. Temperature Dependence of Spin-Lattice Relaxation Time

Temperature dependence of the $^{35}$Cl NQR spin-lattice relaxation time, $T_1$ of $\nu_a$ and $\nu_b$ frequencies is shown in Figs. 7 and 8, respectively. At around 80 K in NH$_4$ICl$_2$ or at around 100 K in ND$_4$ICl$_2$, a clear minimum was observed in the ln$T_1$ vs. $10^3$ K/T plots of $\nu_a$ and $\nu_b$. This is attributable to the quadrupolar relaxation through an electric field gradient (EFG) modulation due to the reorientational motion of the ammonium ions [2 - 4]. The shift of the $T_1$ minimum to the high-temperature side by the deuteration shows the slowing down of the ammonium motion.

In the previous section, a rapid conversion between the hydrogen bonded and the non-bonded states of the ICl$_2^-$ anion and a change of the weight of these states with temperature were considered as a cause of
the anomalous temperature dependence of the NQR frequencies. The conversion of the states is expected to be synchronized with the reorientational motion of the ammonium ion, because the NH\textsubscript{4}\ldots Cl hydrogen bond must be broken for the ammonium ion to reorient. The appearance of a clear $T_1$ minimum suggests that a considerable fluctuation of the EFG is produced by the reorientational motion. If we suppose that the periods of the bonded and the non-bonded states correspond, respectively, to those where the ammonium ion stays at a stable orientation and is in a transient state from one orientation to another, the life-times of the two states of cation, the transition between which is a cause of the EFG fluctuation, will be very different. Then, the situation is similar to the EFG modulation due to the motion of the nearby ion in a very unequal potential well with two minima. It is known that the relaxation due to the modulation is very inefficient when the potential well is highly asymmetric, and only the bent instead of the minimum could be observed in the ln$T_1$ vs. $T^{-1}$ plot [12]. The transient state from one orientation to another is the state with maximum energy. Therefore, no activation energy can be defined for the transition from the transient state to the state in a stable orientation. In this situation, even a bent could not be observed in the ln$T_1$ vs. $T^{-1}$ plot. The experimental results, however, showed a clear $T_1$ minimum in the plot, as shown in Figs. 7 and 8. This fact suggests that the cationic state, where no hydrogen bonding is formed between the ammonium ion and the ICl\textsuperscript{2-} anion, corresponds not to the transient but to a meta-stable orientation. Even if the potential is unequal, it is known that an almost symmetric $T_1$ minimum could be observed when the potential consists of more than three minima [13]. If we look at Figs. 7 and 8 carefully, a very shallow minimum can be recognized at around 200 - 300 K besides the clear minimum observed below 150 K. This is consistent with the assumption of a potential with several meta-stable minima. Having several meta-stable orientations of the ammonium ion, it may be explained that the ratio, $N$, of the number of the non-bonded states to that of the bonded states of the ICl\textsuperscript{2-} anion was obtained as $N > 1$.

3.4. Concluding Remarks

The strong temperature dependence with positive and negative temperature coefficients, respectively, of $^{35}$Cl NQR frequencies $\nu_0$ and $\nu_b$ of NH\textsubscript{4}ICl\textsubscript{2} has been explained by assuming a change in the relative weights of the resonance structures of the ICl\textsuperscript{2-} anion with temperature which is induced through formation and scission of the N-H\textsubscript{4}\ldots Cl hydrogen bond. It is suggested that the ammonium ion has a stable ori-
orientation and several meta-stable orientations where
the hydrogen bond can be and can not be formed,
respectively.

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(2000).
[6] Gmelins Handbuch der Anorganischen Chemie,
NH₄(23), Verlag Chemie, Berlin 1936, p237.
B26, 904 (1970).
[9] T. P. Das and E. L. Hahn, Nuclear Quadrupole Resonance
Chem. 71, 3249 (1967).
forsch. 45a, 477 (1990).