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NMR study of ^{1}H and ^{205}Tl in ammonium and thallium perchlorates in the rotating frame: Indirect measurement of the relaxation time of rare-spin ^{17}O

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The spin-lattice relaxation times T_1 and $T_{1\rho}$ of ^{1}H and ^{205}Tl were measured in ammonium and thallium perchlorates (NH_4ClO_4 and $TlClO_4$). The temperature dependence of $T_{1\rho}$ of ^{1}H and ^{205}Tl in the rotating frame shows three minimum values (1–3 sec), which are attributable to the interactions between ^{1}H(^{205}Tl) and ^{17}O spins of natural abundance (0.037%); one of the minima is due to the modulation of the dipole-dipole interactions between ^{1}H(^{205}Tl) and ^{17}O spins by the reorientation of the ClO_4 ion, and the other two minima are due to cross relaxation between ^{1}H(^{205}Tl) and ^{17}O spins. The spin-lattice relaxation time T_{1S} of ^{17}O spins was determined from the experimental T_1 and $T_{1\rho}$ data of ^{1}H(^{205}Tl). An expression for T_{1S} of ^{17}O was derived for the reorientation of the ClO_4 ion. The value of the quadrupole coupling constant, $e^2qQ/h \simeq 10$ MHz, of ^{17}O was obtained.

I. INTRODUCTION

The NMR study of a nuclear spin with such a small natural abundance as ^{17}O (0.037% of natural abundance) is not easy, owing to the poor signal-to-noise ratio, in spite of the possibilities of wide applications in physics and chemistry. The NQR signals of ^{17}O in solids are detected in many cases by using double-resonance techniques.[1–5] Isotopically enriched ^{17}O compounds were used for determining the quadrupole coupling constant, e^2qQ/h, of ^{17}O in KH_2PO_4,[3] the spin-lattice relaxation time T_{1S} of ^{17}O in CO (Ref. 6) and the dynamical motions of $SO_4{}^{-2}$ ions in $(NH_4)_2SO_4$.[7] Generally, high levels of chemical and electrolytic techniques are necessary to prepare ^{17}O-enriched compounds.

It was reported that the natural abundance of ^{17}O affects the spin-spin relaxation time T_2 of ^{1}H in water.[8] The low-field spin-lattice relaxation time $T_{1\rho}$ (Refs. 9 and 10) in the rotating frame is a powerful tool for investigating slow-motion atoms and molecules in solids,[11] the diffusion of spins with small gyromagnetic ratios,[12] very short relaxation times which cannot be measured directly,[13] and the small tunneling frequency of the $NH_4{}^+$ ion.[14] The measurement of $T_{1\rho}$ is also useful for studying the dynamic motions of rare-atom spins.

Recently it was found that the natural abundance of ^{17}O spins affects the $T_{1\rho}$ of protons in some solids.[15,16] Remarkable minimum values of $T_{1\rho}$ (1–3 s) appeared near room temperature. At first, the origin of these minimum values of $T_{1\rho}$ was attributed to the modulation of the dipolar interaction between ^{1}H and ^{17}O by the reorientation of anions containing oxygen atoms (^{17}O). This enabled us to investigate the dynamic motions of the oxygen atoms. But later it was revealed that another mechanism of cross relaxation between ^{1}H(^{205}Tl) and ^{17}O also plays an important role in $T_{1\rho}$ for ^{1}H(^{205}Tl) in NH_4ClO_4,$TlClO_4$ (Ref. 17) and $CH_3NH_3ClO_4$. Due to the cross relaxation, we may determine the values of T_{1S}. Chiba and Miyajima[7] obtained a similar result in ^{17}O-enriched $(NH_4)_2SO_4$ to that in Ref. 17. In the present study, the temperature dependences of $T_{1\rho}$ of ^{1}H and ^{205}Tl were measured as functions of the static magnetic field $\mathbf{H}_0$ and the rf fields $\mathbf{H}_1$ in NH_4ClO_4 and $TlClO_4$. It was found that the temperature dependence of $T_{1\rho}$ for ^{1}H(^{205}Tl) shows three minimum values due to the interaction between the ^{1}H(^{205}Tl) and ^{17}O spins; one minimum due to the modulation of the dipolar interaction between the ^{1}H(^{205}Tl) and ^{17}O spins by the reorientation of the ClO_4 ion, and two minima due to the cross relaxation between the ^{1}H(^{205}Tl) and ^{17}O spins. An expression for T_{1S} was derived for the reorientation of the ClO_4 ion. The values of e^2qQ/h of ^{17}O were determined by using the expression for T_{1S} and the experimental data on $T_{1\rho}$.

II. THEORY

We consider the perfect tetrahedron of the ClO_4 ion in a crystalline lattice subjected to a strong magnetic field H_0. The coordinate system of the ClO_4 ion is shown in Fig. 1, where Θ and Φ are the polar and azimuthal angles of the vector H_0 with respect to the $(\mathbf{X},\mathbf{Y},\mathbf{Z})$ axes, which are fixed in space. The Hamiltonian H for the ^{17}O spin is assumed to consist of the Zeeman term H_z and the quadrupole interaction $H_Q(t)$:

$$H = H_z + H_Q(t) , \tag{1}$$

where $H_z = -\hbar\gamma_S H_0 S_z$ and γ_S is the gyromagnetic ratio of the ^{17}O spin ($S=\frac{5}{2}$). The electric field gradient (EFG) tensor $\{V_{\alpha\beta}\}$[18] at the site of ^{17}O is determined by the chemical bonds within the ClO_4 ion and also by the electric charges surrounding the ClO_4 ion. We neglect the latter contribution to the EFG at the site of ^{17}O. $H_Q(t)$ in Eq. (1) is given by

$$H_Q(t) = \frac{eQ}{4S(2S-1)}[V_0(3S_z{}^2 - S^2) + V_{\mp 1}(S_\pm S_z + S_z S_\pm) + V_{\mp 2}(S_\pm)^2] , \tag{2}$$

$$V_0 = \tfrac{1}{2}eq(3\cos^2\theta - 1) , \tag{3a}$$

$$V_{\mp 1} = \tfrac{3}{2}eq\sin\theta\cos\theta e^{\mp i\phi} , \tag{3b}$$

$$V_{\mp 2}=\tfrac{3}{4}eq\sin^{2}\theta e^{\mp i2\phi} \; . \tag{3c}$$

Since we consider the ClO_4 ion as forming a perfect tetrahedron, the terms containing the asymmetry parameter $\eta=(V_{XX}-V_{YY})/V_{ZZ}$ are neglected in Eq. (2). The parameters V_{XX}, V_{YY}, and V_{ZZ} represent the EFG tensor components for the principal axes and $eq=V_{ZZ}$. Generally, three Euler angles[19] θ, ϕ, and ψ are necessary to represent the principal axes with respect to the (x,y,z) coordinate system where the direction of H_0 is parallel to the z direction. But the parameter ψ is physically irrelevant because of the 3-fold symmetry at the ^{17}O site.

The first term in Eq. (2) gives the energy shift due to the quadrupole interaction, and the second and third terms cause the spin-lattice relaxation of ^{17}O spins. We will first derive an expression for T_{1S} of the ^{17}O spin for the reorientation of the ClO_4 ion. We assume that the ClO_4 ion reorients about the four threefold axes and three twofold axes at the rates k_3 and k_2, respectively, for changing the position of ^{17}O. Since an ^{17}O atom occupies randomly the four sites 1—4 in Fig. 1, the first term in Eq. (2) is averaged to zero within the relaxation time T_{1S} and does not contribute to the energy levels of the ^{17}O spin. The transition rate per unit time $W_{m\text{-}n}$ between the $|m\rangle$ and $|n\rangle$ states of the ^{17}O spin is given by first-order perturbation theory:

$$W_{m\text{-}n}=2\hbar^{-2}\mathrm{Re}\int_0^{\infty}\overline{\langle m\,|H_Q(0)|\,n\rangle\langle n\,|H_Q(\tau)|\,m\rangle}\times\exp[-i(E_m-E_n)\tau/\hbar]d\tau \; , \tag{4}$$

where the long overbar denotes an ensemble average, and E_m and E_n are the Zeeman energies of the $|m\rangle$ and $|n\rangle$ states, respectively. Equation (4) has the following form:

$$W_{m-n}=A\,\mathrm{Re}\int_0^{\infty}G_n(\tau)\exp(-in\omega_o\tau)d\tau \; . \tag{5}$$

Here, $G_n(\tau)$ ($n=1$ and 2) is the so-called autocorrelation function and is given by

$$G_n(\tau)=\overline{V_{-n}(0)V_n(\tau)} \; . \tag{6}$$

The expression for $G_n(\tau)$ depends on the type of reorientation of the ClO_4 ion. We consider the probability $P_{ij}(\tau)$ that $V_n(\tau)(n=\pm 1,\pm 2)$ in Eqs. (3b) and (3c) takes the values $V_n^{(i)}$ and $V_n^{(j)}$ at the time $t=0$ and τ, respectively. $V_n^{(k)}$ is the value of $V_n(\theta,\phi)$ when the ^{17}O atom occupies the kth position ($k=1$—4, see Fig. 1). We find, for example,

$$\begin{aligned} P_{11}&=\tfrac{3}{4}e^{-4\alpha\tau}+1/4 \; ,\\ P_{12}=P_{13}=P_{14}&=-\tfrac{1}{4}e^{-4\alpha\tau}+1/4 \; , \end{aligned} \tag{7}$$

where $4\alpha=4(k_2+2k_3)$. Then Eq. (6) is represented by the following form:

$$G_n(\tau)=(V_n^{(1)*}V_n^{(2)*}V_n^{(3)*}V_n^{(4)*})\begin{bmatrix} p_1 & 0 & 0 & 0\\ 0 & p_2 & 0 & 0\\ 0 & 0 & p_3 & 0\\ 0 & 0 & 0 & p_4\end{bmatrix}\begin{bmatrix} P_{11} & P_{12} & P_{13} & P_{14}\\ P_{21} & P_{22} & P_{23} & P_{24}\\ P_{31} & P_{32} & P_{33} & P_{34}\\ P_{41} & P_{42} & P_{43} & P_{44}\end{bmatrix}\begin{bmatrix} V_n^{(1)}\\ V_n^{(2)}\\ V_n^{(3)}\\ V_n^{(4)}\end{bmatrix} \; , \tag{8}$$

where $p_i=\frac{1}{4}$ $(i=1$—$4)$ is the probability that the ^{17}O atom occupies the ith position and the asterisk represents the complex conjugate. We obtain

$$\begin{aligned} G_1(\tau)&=\tfrac{1}{2}(eq)^2(1-2f)e^{-4\alpha\tau} \; ,\\ G_2(\tau)&=\tfrac{1}{4}(eq)^2(1+f)e^{-4\alpha\tau} \; . \end{aligned} \tag{9}$$

All the transition probabilities $W_{m\text{-}n}$ in Eq. (4) are given by

$$\begin{aligned} W_{\pm 5/2\mp 3/2}&=\tfrac{1}{20}(1-2f)(e^2qQ/\hbar)^2f_L(\omega_S,\tau_a) \; ,\\ W_{\pm 3/2\mp 1/2}&=\tfrac{1}{50}(1-2f)(e^2qQ/\hbar)^2f_L(\omega_S,\tau_a) \; ,\\ W_{1/2+1/2}&=0 \; ,\\ W_{\pm 5/2\mp 1/2}&=\tfrac{1}{80}(1+f)(e^2qQ/\hbar)^2f_L(2\omega_S,\tau_a) \; ,\\ W_{\pm 3/2\pm 1/2}&=\tfrac{9}{400}(1+f)(e^2qQ/\hbar)^2f_L(2\omega_S,\tau_a) \; , \end{aligned} \tag{10}$$

where

$$f=\sin^2\Theta-\tfrac{7}{8}\sin^4\Theta-\tfrac{1}{8}\sin^4\Theta\cos(4\Phi) \; , \tag{11}$$

$f_L(\omega,\tau)=\tau/(1+\omega^2\tau^2)$, $\tau_a=1/[4(k_2+2k_3)]$, and $\omega_S=\gamma_S H_0$ is the Larmor frequency of the ^{17}O spins. τ_a is the correlation time for the reorientation of the ClO_4 ion and is usually written as $\tau_a=\tau_\infty\exp(E_a/RT)$, where τ_∞ is

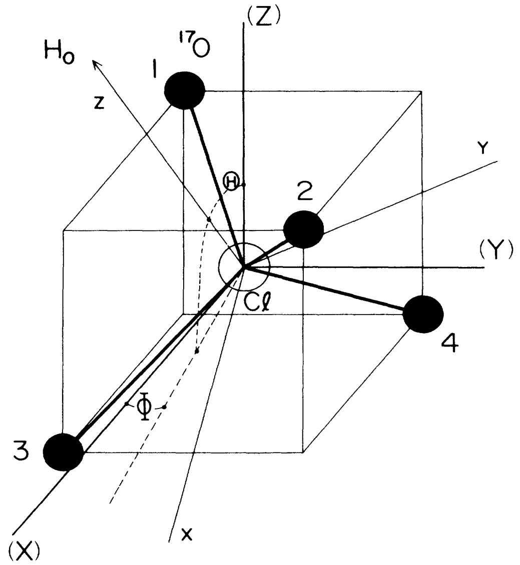

FIG. 1. Coordinate system of the ClO_4 ion. Direction of H_0 is defined by the polar angles (Θ and Φ) with respect to the $(\mathbf{X},\mathbf{Y},\mathbf{Z})$ coordinates. The numbers 1—4 represent the sites of oxygen atoms. (x,y,z) is the coordinate system with the Euler angles (Θ,Φ) and $\Psi=0)$ with respect to the $(\mathbf{X},\mathbf{Y},\mathbf{Z})$ coordinates.

the preexponential factor and E_a is the activation energy. However, τ_a should be written as

$$\tau_a^{-1}=\tau_2^{-1}+\tau_3^{-1}\ , \tag{12a}$$

$$\tau_2=\tau_{2\infty}\exp(E_2/RT)\ , \tag{12b}$$

$$\tau_3=\tau_{3\infty}\exp(E_3/RT)\ , \tag{12c}$$

where τ_i ($i=2$ and 3) is the correlation time, $\tau_{i\infty}$ is the preexponential factor, and E_i is the activation energy for reorientation about i-fold axes. Assuming a common spin temperature of the ^{17}O spins [this assumption is plausible because the first term in Eq. (2) does not contribute to the spin energy of ^{17}O], we obtain an expression for T_{1S} by using the formula for T_1 by Gorter,[20]

$$T_1{}^{-1}=\sum_{m>n} W_{m\text{-}n}(E_m\text{-}E_n)^2/\sum_n E_n^2\ . \tag{13}$$

Inserting Eq. (9) into Eq. (13) we have

$$T_{1S}^{-1}=\tfrac{1}{125}(e^2qQ/\hbar)^2[(1-2f)f_L(\omega_S,\tau_a)$$
$$+2(1+f)f_L(2\omega_S,\tau_a)]\ . \tag{14}$$

Equation (14) shows that T_{1S} depends on the direction of H_0 for $\omega_S\tau_a \gg 1$. Averaging over the space sphere, Eq. (14) yields ($\bar{f}=\frac{1}{5}$)

$$T_{1S}^{-1}=\tfrac{3}{625}(e^2qQ/\hbar)^2[f_L(\omega_S,\tau_a)+4f_L(2\omega_S,\tau_a)]\ . \tag{15}$$

Equation (15) agrees with Eq. (9) and with $\eta=0$ in Ref. (6). This was derived by assuming that τ_a is short enough to average V_0 in Eq. (3a) to zero at high temperatures. But as τ_a becomes longer at low temperatures, the first term in Eq. (2) contributes to the energy levels of the ^{17}O spin, and Eq. (15) fails. The energy-level schemes of the ^{17}O spin for high (I) and low (II) temperatures are shown in Fig. 2.

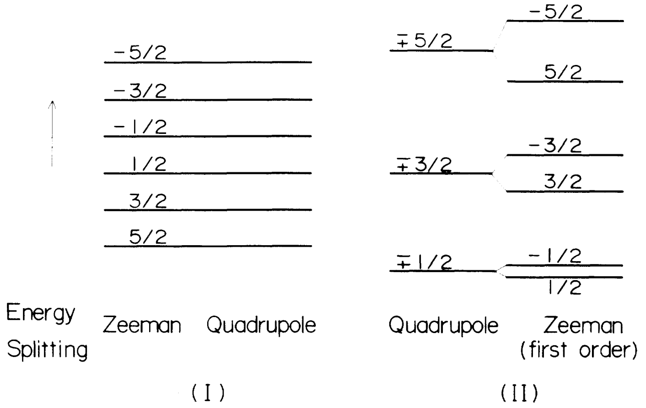

FIG. 2. The energy-level schemes of ^{17}O spin of the ClO$_4$ ion subjected to the magnetic field H_0 for (I) high temperature and (II) low temperature where $\gamma_S H_0 \ll e^2qQ/\hbar$ is assumed.

It will be of interest to compare T_{1S} is Eq. (14) with the relation for T_1 of protons in the tetrahedral NH$_4{}^+$ ion which reorients about the four three-fold axes and three twofold axes.[21,22] The dipolar interaction between protons is changed at the rates k_2 and k_3 by the reorientation of the NH$_4{}^+$ ion with respect to the twofold and threefold axes, respectively, and causes the spin-lattice relaxation. Punkkinen[21] derived the following relation for T_1 of the protons:

$$T_1{}^{-1}=\tfrac{9}{8}\hbar^{-2}\gamma^4 r^{-6}\{f f_L(\omega_0,1/12k_3)+(1-2f)f_L[\omega_0,1/(8k_3+4k_2)]$$
$$+(1-f)f_L(2\omega_0,1/12k_3)+2(1+f)f_L[2\omega_0,1/(8k_3+4k_2)]\}\ , \tag{16}$$

where $\omega_0=\gamma H_0$ is the Larmor frequency of the proton spin and r($\cong$1.65 Å) the distance between protons. Equation (16) predicts that, when $k_2 \gg k_3$, the temperature dependence of T_1 shows two minimum values, while only a single minimum appears in the temperature dependence of T_{1S} in Eq. (14). It will be convenient to modify Eq. (16) to a simpler form here. When $k_3=k_2$ and f is averaged over the space sphere, Eq. (16) yields

$$(T_1)_{\rm HH}^{-1}=\tfrac{9}{10}\hbar^2\gamma^4 r^{-6}[f_L(\omega_0,\tau_{\rm H})+4f_L(2\omega_0,\tau_{\rm H})]\ , \tag{17}$$

$$\tau_{\rm H}=1/12k_3=\tau_{{\rm H}\infty}\exp(E/RT)\ , \tag{18}$$

where $\tau_{\rm H}$ is the correlation time, $\tau_{{\rm H}\infty}$ is the preexponential factor and E is the activation energy for the reorientation of NH$_4{}^+$ ion. Correspondingly, the expression of $(T_1\rho)_{\rm HH}$, the spin-lattice relaxation time of ^{1}H due to the reorientation of NH$_4{}^+$ ion in the rotating frame, is given by[15]

$$(T_{1\rho})_{\rm HH}^{-1}=\tfrac{9}{10}\hbar^2\gamma^4 r^{-6}[\tfrac{3}{2}f_L(2\omega_1,\tau_{\rm H})+\tfrac{5}{2}f_L(\omega_0,\tau_{\rm H})$$
$$+f_L(2\omega_0,\tau_{\rm H})]\ , \tag{19}$$

where $\omega_1=\gamma{\rm H}_1$ is the Larmor frequency of ^{1}H in the rotating frame.

Next we consider the effect of the reorientation of the ClO$_4$ ion on T$_{1\rho}$ of ^{1}H and ^{205}Tl. The reorientation of the ClO$_4$ ion affects $T_{1\rho}$ in two different ways; interaction A: the dipole-dipole interaction between the ^{1}H(^{205}Tl) and ^{17}O spins modulated by the reorientation of the ClO$_4$ ion, and interaction B: cross relaxation between the ^{1}H(^{205}Tl) and ^{17}O spins. An expression for $T_{1\rho}^{\rm RE}$ due to the former effect and its detailed derivation have already been shown to be[15]

$$(T_{1\rho}^{\rm RE})^{-1}=0.000\,37\sum_i^n N(T_{1\rho}^{\rm RE})_i^{-1}=A_1 f_L(\omega_1,\tau_a)\ , \tag{20}$$

where 0.000 37 is the ratio of the natural abundance of ^{17}O, N $(=4)$ is the number of oxygen atoms in the ClO$_4$ ion when the natural abundance of ^{17}O is assumed to be 100%, i represents the ith ClO$_4$ ion in the neighborhood of ^{1}H(^{205}Tl), $N(T_{1\rho}^{\mathrm{RE}})_i^{-1}$ is the relaxation rate due to the reorientation of the ith ClO$_4$ ion, and $\omega_1=\gamma_1 H_1$ the Larmor frequency of the ^{1}H(^{205}Tl) spin in the rotating frame. We have

$$(T_{1\rho}^{\mathrm{RE}})_i^{-1}=(\tfrac{19}{4}\pi)\rightarrow\tfrac{14}{9}\pi\hbar^2\gamma_I^2\gamma_S^2\bar{r}_i^{-6}f_L(\omega_1,\tau_a)\ , \qquad (21)$$

where γ_I is the gyromagnetic ratio of the ^{1}H(^{205}Tl) spin and $\bar{r}_i$ the average length between the ^{1}H(^{205}Tl) and oxygen atoms in the ith ClO$_4$ ion.

The mechanism of the cross relaxation, which is dominant in weak magnetic fields, was first observed in cesium halides by Bloembergen and Sorokin.[23] When T_{1S} of the ^{17}O spin (S spin) is much shorter than T_1 of the ^{1}H(^{205}Tl) spin (I spin), it is reasonable to consider the S spin as a part of the lattice, so that the I spins are subjected to the random time-dependent perturbation with correlation frequency equal to T_{1S}^{-1}. Assuming that the natural abundance of the ^{17}O spin is 100%, the ^{1}H(^{205}Tl) spin in the neighborhood of the ith ^{17}O spin has the following relaxation rate:

$$(T_{1\rho}^{\mathrm{CR}})_i^{-1}=C_i f_L(\omega_1,T_{1S})\ , \qquad (22)$$

$$C_i=\tfrac{1}{3}\hbar^2\gamma_I^2\gamma_S^2 S(S+1)\langle(1-3\cos^2\theta_i)^2\rangle_{\mathrm{av}}r_i^{-6}\ , \qquad (23)$$

where r_i is the distance between I and S spins, θ_i is the angle between the magnetic field H_0 and a vector joining I and S spins and $\langle\ \rangle_{\mathrm{av}}$ represents the powder average. We have

$$\langle(1-3\cos^2\theta_i)^2\rangle_{\mathrm{av}}=\tfrac{4}{5}\ .$$

Since the natural abundance of ^{17}O is 0.037%, the effective relaxation rate $(T_{1\rho}^{\mathrm{CR}})^{-1}$ of ^{1}H(^{205}Tl) in the crystal is given by

$$(T_{1\rho}^{\mathrm{CR}})^{-1}=0.000\,37\sum_i^n(T_{1\rho}^{\mathrm{CR}})_i^{-1}=A_2 f_L(\omega_1,T_{1S})\ . \qquad (24)$$

According to Eq. (15), T_{1S} has a minimum value $(T_{1S})_{\min}$ for $\omega_S\tau_a\cong 1$. If $(T_{1S})_{\min}<\omega_1^{-1}$, $T_{1\rho}^{\mathrm{CR}}$ in Eq. (24) has two minimum values on the high- and low-temperature sides of the position of $(T_{1S})_{\min}$, where the relation $\omega_1 T_{1S}=1$ is satisfied.

The total relaxation rate $(T_{1\rho})_t^{-1}$ of ^{1}H(^{205}Tl) due to the interactions between the ^{1}H(^{205}Tl) and ^{17}O spins is given by

$$\begin{aligned}(T_{1\rho})_t^{-1}&=(T_{1\rho}^{\mathrm{RE}})^{-1}+(T_{1\rho}^{\mathrm{CR}})^{-1}\\&=A_1 f_L(\omega_1,\tau_a)+A_2 f_L(\omega_1,T_{1S})\ .\end{aligned} \qquad (25)$$

The temperature dependence of $(T_{1\rho})_t$ for ^{1}H in Eq. (25) and that of T_{1S} in Eq. (15) were calculated as function of H_1 and $\omega_I=\gamma_I H_0$ for the following three examples: (a) $H_1=2.1$ G, $\omega_I/2\pi=16$ MHz, (b) $H_1=4.2$ G, and $\omega_I/2\pi=16$ MHz, and (c) $H_1=2.1$ G and $\omega_I/2\pi=48$ MHz. Other parameters were chosen as, assuming $\tau_3\ll\tau_2$ in Eq. (12a), $E_3=10.0$ kcal/mol, $\tau_{3\infty}=4.0\times10^{-13}$ s, $e^2qQ/h=12$ MHz in Eq. (15) and $A_1=A_2=1.0\times10^5$ s^{-2} in Eq. (25). The results are summarized in Fig. 3. Essentially three minima of $(T_{1\rho})_t$ appear; minimum 1′ due to interaction A and minima 2′ and 3′ due to interaction B as shown in Fig. 3. In example (a) the positions of the minimum of $T_{1\rho}^{\mathrm{RE}}$ in Eq. (17) and $T_{1\rho}^{\mathrm{CR}}$ in Eq. (24) lie in close proximity, at 288 K ($10^3/T=3.50$) and 303 K ($10^3/T=3.30$), respectively, and only one minimum 21 of $(T_{1\rho})_t$ appears at about 294 K ($10^3/T=3.40$) for $H_1=2.1$ G. While in example (c), one minimum of $(T_{1\rho})_t$ at about 294 K in example (a) is separated into two minima; minimum 1′ at about 288 K ($10^3/T=3.50$) due to interaction A and minimum 2′ at 357 K ($10^3/T=2.80$) due to interaction B. Then, we may distinguish the minimum due to interaction A from that due to B by the measurement of $T_{1\rho}$ with different ω_I and the same values of H_1. Two minima 3 and 3′ of $T_{1\rho}$ due to interaction B appear at the same temperature 714 K ($10^3/T=1.4$) for $H_1=2.1$ G and $\omega_I/2\pi=16$ and 48 MHz.

It is necessary to refer to the role of ^{35}Cl and ^{37}Cl spins on $T_{1\rho}$ of ^{1}H(^{205}Tl). The reorientation of the ClO$_4$ ion about the threefold and twofold axes does not change the EFG tensor at the site of Cl atoms and therefore does not contribute to the spin-lattice relaxation time $T_{1\mathrm{Cl}}$ of Cl spins. It is reported that the lattice vibration affects $T_{1\mathrm{Cl}}$ in ionic crystals.[24] We tried to measure $T_{1\mathrm{Cl}}$ of ^{35}Cl spins, but could not find any signal of ^{35}Cl spins, probably because of a small lattice strain. Since we consider that the

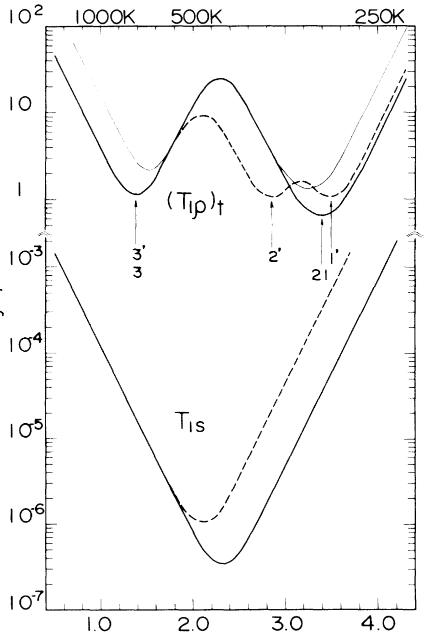

FIG. 3. Temperature dependences of T_{1S} and $(T_{1\rho})_t$ of ^{1}H which are calculated by using Eqs. (15) and (25), respectively. (a) The solid line and dashed line represent T_{1S} of ^{17}O for $H_0=3760$ ($\omega_I/2\pi=16$ MHz) and 11280 G (48 MHz), respectively. (b) The thick solid line and thin solid line represent $(T_{1\rho})_t$ for $H_1=2.1$ and 4.2 G at 16 MHz, respectively, and the dashed line $(T_{1\rho})_t$ for $H_1=2.1$ G at 48 MHz.

ClO_4 ion is a nearly perfect tetrahedron, e^2qQ/h for Cl nuclei at the center of the tetrahedron would be small, and T_{1Cl} in NH_4ClO_4 and $TlClO_4$ might be comparable with that in NaCl (5.2 s at 298 K[24]).

We may evaluate the relaxation time $(T_{1\rho})_{\text{H-Cl}}^{-1}$ of ^{1}H spin due to the interaction between ^{1}H and Cl spins. $(T_{1\rho})_{\text{H-Cl}}^{-1}$ consists of two contributions, one $(T_{1\rho}^{\text{RE}})_{i\text{-Cl}}^{-1}$ due to the modulation of the dipolar interaction between ^{1}H and Cl spins in the ith neighboring ClO_4 ion by the reorientation of $NH_4{}^+$ ion, and the other $(T_{1\rho}^{\text{CR}})_{i\text{-Cl}}^{-1}$ due to the cross relaxation between the ^{1}H and Cl spins. Assuming that the abundance of ^{35}Cl spins is 100% for simplicity, we have the following relations for $(T_{1\rho})_{\text{H-Cl}}$, $(T_{1\rho}^{\text{RE}})_{i\text{-Cl}}$,[15] and $(T_{1\rho}^{\text{CR}})_{i\text{-Cl}}$, respectively:

$$(T_{1\rho})_{\text{H-Cl}}^{-1}=\sum_{i}^{n}\{(T_{1\rho}^{\text{RE}})_{i\text{-Cl}}^{-1}+(T_{1\rho}^{\text{CR}})_{i\text{-Cl}}^{-1}\}\ , \tag{26}$$

$$\begin{aligned}(T_{1\rho}^{\text{RE}})_{i\text{-Cl}}{}^{-1}=\hbar^2\gamma_I^2\gamma_{S'}^2\bar{r}_i{}'^{-6}\pi[\tfrac{14}{9}f_L(\omega_1,\tau_H)+\tfrac{7}{3}f_L(\omega_I,\tau_H)\\ +\tfrac{7}{6}f_L(\omega_{S'},\tau_{\text{H}})+\tfrac{7}{18}f_L(\omega_I+\omega_{S'},\tau_{\text{H}})+\tfrac{7}{3}f_L(\omega_I-\omega_{S'},\tau_{\text{H}})]\ ,\end{aligned} \tag{27}$$

$$(T_{1\rho}^{\text{CR}})_{i\text{-Cl}}^{-1}=\tfrac{1}{3}\hbar^2\gamma_I^2\gamma_{S'}^2S'(S'+1)\langle(1-3\cos^2\theta_i')^2\rangle_{\text{av}}\bar{r}_i{}'^{-6}f_L(\omega_1,T_{1\text{Cl}})\ , \tag{28}$$

where n is the number of ClO_4 ions in the neighborhood of the $NH_4{}^+$ ion, $\omega_I=\gamma_I H_0$ and $\omega_{S'}=\gamma_{S'}H_0$ are the Larmor frequencies of ^{1}H and ^{35}Cl spin in the laboratory frame, respectively, $\bar{r}_i'$ is the average distance between ^{1}H and ^{35}Cl in the neighborhood of $NH_4{}^+$ ion, τ_H is given by Eq. (18), $S'(\frac{3}{2})$ is the spin of ^{35}Cl, and θ_i' is the angle between the magnetic field H_0 and a vector joining I spin and S' spin in the ith ClO_4 ion. Neglecting the effect of the quantum tunneling of $NH_4{}^+$ ion,[25–27] we may evaluate the value τ_H in Eq. (27) by using a relation obtained by Ikeda *et al.*[28] $(T_1)_{\text{HH}}{}^{-1}=1.11\times10^{-11}\tau_{\text{H}}$ for $\omega_0\tau_{\text{H}}\ll1$. Since it is expected that $(T_1)_{\text{HH}}=60$ s at 225 K ($10^3/T=4.0$),[28] we have $\tau_{\text{H}}=1.5\times10^{-13}$ s at this temperature. Assuming that ^{1}H atom is at the site of nitrogen, we adopt $\bar{r}_i'=4.5$ Å in NH_4ClO_4. By using these values τ_{H}, $\bar{r}_i'$, $n=7$, $H_1=2.1$ G, $\langle(1-3\cos^2\theta_i')^2\rangle_{\text{av}}=\frac{4}{5}$, and $T_{1\text{Cl}}=5.2$ s, we have $(T_{1\rho})_{\text{H-Cl}}=3.24\times10^3$ s in Eq. (26). We will find in Sec. IV A that the contribution of $(T_{1\rho})_{\text{H-Cl}}^{-1}$ in Eq. (26) to the observed value of $(T_{1\rho})^{-1}$ is negligible compared with $(T_{1\rho})_t{}^{-1}$ in Eq. (25).

In the case of $TlClO_4$, $(T_{1\rho})_{\text{Tl-Cl}}^{-1}$, the relaxation rate of ^{205}Tl spins due to the interaction between ^{205}Tl and Cl spins, is caused only by the cross relaxation since the lattice constants in $TlClO_4$ are very similar to those in NH_4ClO_4, we adopt $\bar{r}_i'=4.5$ Å as the average distance between ^{205}Tl and Cl spins. By using the same values for n, $\bar{r}_i'$, H_1, $\langle(1-3\cos^2\theta_i')^2\rangle_{\text{av}}$, and $T_{1\text{Cl}}$ as those in NH_4ClO_4, we have $(T_{1\rho})_{\text{Tl-Cl}}=3.57\times10^3$ s. Thus, we find the contribution of Cl spins to $T_{1\rho}$ of ^{205}Tl is also negligible compared with that of ^{17}O spins as shown in Sec. IV B.

III. EXPERIMENTAL PROCEDURE

The relaxation times T_1 and $T_{1\rho}$ were measured using a home-made NMR spectrometer. T_1 was measured with a $\pi/2$-τ_0-$\pi/2$-τ-$\pi/2$-τ_0-$\pi/2$ pulse sequence in order to saturate the magnetization of the ^{1}H(^{205}Tl) spins completely just after the second $\pi/2$ pulse, where τ_0 was chosen to be 300 μs—1 ms. The usual spin-locking method[29] was used in the measurement of $T_{1\rho}$. The locking time reached about 20 s at maximum. Then, in order to reduce the heating of the samples by the rf field, the strength of the rf field H_1 was set at low values within the condition $H_1>H_L$, where H_L is the local dipolar field at the ^{1}H(^{205}Tl) spins. The reduction of the value H_1 during the locking time was less than about 5%. A distortion of the FID signal which prevents accurate measurement was observed after a long-locking rf pulse. This distortion is probably due to the heating up of the phase sensitive detector by the prolonged exposure to high rf level. So, in order to cut off the rf field, a gate circuit constructed by using a double balanced mixer was inserted between the rf receiver and the phase sensitive detector, and no distorted FID signal was observed.

The samples of NH_4ClO_4 (guaranteed grade, assay minimum 96.0%) and $TlClO_4$ (guaranteed grade, assay minimum 99%) were taken from Kanto Chemical Corp., and Mitsuwa Chemical Medicine Corp., respectively. Purification of both samples was done once by solidification from aqueous solutions. The samples were pumped for 24 h and sealed in Pyrex ampoules under helium exchange gas. The sealed ampoule of NH_4ClO_4 exploded above the phase-transition temperature $T_C=512$ K, which is probably caused by ammonia gas from NH_4ClO_4 decomposing partially above T_c.[31] The measurement in NH_4ClO_4 above T_c was then done with an unsealed ampoule.

The temperature of the samples was varied below room temperature by boiling off liquid nitrogen in the storage dewar and passing the cold nitrogen gas over the samples. For the measurements above room temperature, preheated air was passed over the samples. The temperature of the samples was measured by copper-constantan thermocouple calibrated by using the NQR frequency of ^{35}Cl and $KClO_3$.[31] The thermocouple was contacted with the rf coil containing the samples.

In order to avoid the heating of samples by the rf field, it will be useful to measure T_{1D}, the spin-lattice relaxation time of the dipolar energy of ^{1}H(^{205}Tl) spins, by using the technique of adiabatic demagnetization[29] or $\pi/2$-τ_0-$\pi/4$-τ-π4 pulse sequence developed by Jeener and Broekaert.[32]

But the quantitative analysis of T_{1D} data is much more complicated[33–35] than that of $T_{1\rho}$. In order to estimate the increase in temperature of samples by exposure to the rf field, we buried the point of contact of the thermocouple into another sample of NH_4ClO_4. The increase of temperature due to the rf field, $H_1=4.2$ and 2.1 G, was about 1.3 and 0.33 K, respectively, for a locking time of 20 s at room temperature. Since the measurement of $T_{1\rho}$ was done with an interval of about 9 K, and the locking time is less than about 20 s, the increase of temperature due to the rf field may be negligible for $H_1=2.1$ and also 4.2 G.

IV. EXPERIMENTAL RESULTS AND THEIR INTERPRETATIONS

NH_4ClO_4 and $TlClO_4$ belong to the group $MClO_4$ ($M=$Na,NH_4K,Rb,Cs,Ag,Tl). This group of compounds transforms from their orthorhombic low-temperature phase to a cubic high-temperature one at temperatures of 400–600 K.[36,37] NH_4ClO_4 is known to have an extremely low barrier for the rotation of the $NH_4{}^+$ ion, and the reorientation and quantum tunneling of the $NH_4{}^+$ ion have been investigated by a series of x-ray,[38] heat-capacity,[39] neutron scattering[40–43] and NMR[25–27] studies. Metz and Hinton[44] measured the chemical shift of ^{205}Tl spins in $TlClO_4$. Both NH_4ClO_4 and $TlClO_4$ exist in an orthorhombic form, space group D_{2h}[41,44] below the phase transition temperatures T_c.

A. T_1 and $T_{1\rho}$ in ammonium perchlorate, NH_4ClO_4

The temperature dependence of T_1 at 16 and 30 MHz and $T_{1\rho}$ for $H_1=4.2$ and 2.1 G in NH_4ClO_4 are shown in Fig. 4. The values of T_1 at 30 MHz agree with those at 16 MHz below $T_c=512$ K ($10^3/T=1.95$), and T_1 increases with increasing temperature above 125 K ($10^3/T=8.0$). The values of T_1 are determined by the random modulation of the dipole-dipole interaction between protons by the reorientation of the $NH_4{}^+$ ion, the activation energy of which is extremely low (700 cal/mol). T_1 decreases with increasing temperature above 250 K ($10^3/T=4.0$), where Ikeda and McDowell[28] proposed spin-rotational relaxation of ^{1}H. T_1 does not change abruptly at T_c.

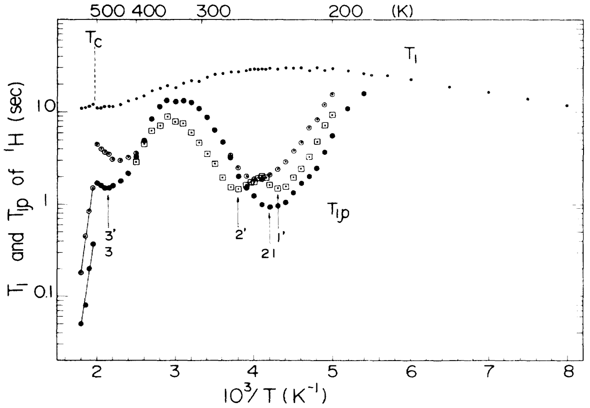

FIG. 4. Temperature dependence of T_1 and $T_{1\rho}$ of ^{1}H in NH_4ClO_4. • represents the data points of T_1 at 16 and 30 MHz; • and ⊙ represent $T_{1\rho}$ for $H_1=2.1$ and 4.2 G, respectively, at 16 MHz. ⊡ represents $T_{1\rho}$ for $H_1=2.1$ G and 30 MHz.

As shown in Fig. 4, $T_{1\rho}$ decreases sharply with increasing temperature above T_c, probably due to the translational diffusion of the $NH_4{}^+$ ion. The activation energy E_d of this diffusion is 28.1 kcal/mol.

With increasing temperature above 192 K ($10^3/T=5.2$), $T_{1\rho}$ at 16 MHz decreases and has a minimum (designated by 21), whose value is 0.94 s at 238 K ($10^3/T=4.20$) for $H_1=2.1$ G, and 1.9 s at 250 K ($10^3/T=4.0$) for $H_1=4.2$ G. In this case the position of the T_1 minimum shifts to the high-temperature side as H_1 increases. T_1 increases with increasing temperature above 263 K ($10^3/T=3.8$) and has a maximum at about 333 K ($10^3/T=3.0$). In the temperature range between 278 K ($10^3/T=3.6$) and 385 K ($10^3/T=2.6$), the values of $T_{1\rho}$ were independent of H_1. $T_{1\rho}$ has a further minimum (designated by 3) with the value of 1.5 s at about 465 ($10^3/T=2.15$) for $H_1=2.1$ G and 3.0 s at 435 K ($10^3/T=2.3$) for $H_1=4.2$ G. Note that the additional $T_{1\rho}$ minimum for $H_1=4.2$ G appears at a lower temperature than that for $H_1=2.1$ G. Thus the temperature dependence of $T_{1\rho}$ at 16 MHz shows two kinds of minima. When $NH_4{}^+$ ion reorients about four threefold and three twofold axes, $(T_{1\rho})_{HH}$ of ^{1}H in Eq. (19) has a minimum value of about 10 μs for $H_1=2.1$ G.[15] Then, the value of minimum 3 at 465 K is about 2×10^5 times longer than that of the minimum of $(T_{1\rho})_{HH}$.

The temperature dependence of $T_{1\rho}$ was also measured for $H_1=2.1$ G at 30 MHz. In contrast to the results at 16 MHz, there appear three minima in the temperature dependence of $T_{1\rho}$; minimum 1′ with a value of 1.5 s at about 233 K ($10^3/T=4.30$), minimum 2′ with 1.45 s at 263 K ($10^3/T=3.80$) and minimum 3′ with 1.5 s at 465 K ($10^3/T=2.15$). Above 417 K ($10^3/T=2.4$), the values of $T_{1\rho}$ at 30 MHz agreed with those at 16 MHz, and then the position and value of the minimum 3′ at 30 MHz agree with those of minimum 3 at 16 MHz. Note that the values of minimum 2′ and minimum 3′ for $H_1=2.1$ G at 30 MHz are longer than that of minimum 21 for $H_1=2.1$ G at 16 MHz.

The origins of the $T_{1\rho}$ minima are attributable to the effect of the natural abundance of ^{17}O which affects $T_{1\rho}$ of ^{1}H through two different interactions A and B as shown in Sec. II; interaction A is the dipole-dipole interaction between the ^{1}H and ^{17}O spins modulated by the reorientation of ClO_4 ions, and interaction B is the cross relaxation between the ^{1}H and ^{17}O spins. We may explain these $T_{1\rho}$ minima by using Eqs. (15), (20), and (24). Minimum 21 at 238 K ($10^3/T=4.20$) for $H_1=2.1$ G and the minimum at 250 K ($10^3/T=4.0$) for $H_1=4.2$ G at 16 MHz ($H_0=3758$ G) are attributed to interactions A and B, respectively. The positions of the minima of $T_{1\rho}^{\mathrm{RE}}$ in Eq. (20) and $T_{1\rho}^{\mathrm{CR}}$ in Eq. (24) lie in close proximity so that only one minimum is observed. The minimum due to $T_{1\rho}^{\mathrm{RE}}$ appears with the condition $\omega_1\tau_a=1$, while that due to $T_{1\rho}^{\mathrm{CR}}$ with $\omega_1 T_{1S}=1$ and $\omega_S\tau_a\gg1$, where τ_a and T_{1S}

are given by Eqs. (12a) and (15), respectively. The minimum 3 at 465 K ($10^3/T=2.15$) for $H_1=2.1$ G and the $T_{1\rho}$ minimum at 435 K ($10^3/T=2.3$) for $H_1=4.2$ G at 16 MHz are due to interaction B. Minimum 3 appears when the conditions $\omega_1 T_{1S}=1$ and $\omega_S \tau_a \ll 1$ are satisfied.

We may evaluate the minimum values of $T_{1\rho}^{\mathrm{RE}}$ in Eq. (20) and $T_{1\rho}^{\mathrm{CR}}$ in Eq. (24) in NH_4ClO_4. The crystal structure of NH_4ClO_4, which is reproduced from the figure by Smith and Levy,[40] is shown in Fig. 5. According to Choi *et al.*,[41] an $NH_4{}^+$ ion is surrounded by seven ClO_4 ions [$n=7$ in Eq. (20)] with short N-O distances ranging from 2.9 to 3.25 Å. Then we adopt $\bar{r}+1.45$ Å as the distance N-Cl, where $\bar{r}=\frac{1}{2}(2.9+3.25)$ Å and 1.45 Å is the Cl-O distance. The average length $\bar{r}_i$ in Eq. (21) is calculated assuming that ^1H and ^{17}O are distributed on spherical surfaces of radii 1.05 Å (^1H-N distance) and 1.45 Å (Cl-O distance), respectively. We obtain $\bar{r}_i=4.72$ Å. The minimum value of $T_{1\rho}^{\mathrm{RE}}$ calculated from Eq. (20) is 1.79 s for $H_1=2.1$ G, which is in good agreement with the observed value 0.94 s of minimum 21 at 238 K ($10^3/T=4.20$). Since minimum 21 consists of the two minima due to $T_{1\rho}^{\mathrm{RE}}$ and $T_{1\rho}^{\mathrm{CR}}$, the observed minimum of $T_{1\rho}$ might be taken to be $0.94\times 2=1.88$ s, which is in better agreement with the calculated one.

According to Choi *et al.*[41] and $NH_4{}^+$ ion is surrounded by ten oxygen atoms at distances ranging from 2.9 to 3.25 Å. Then we take $n=10$ in Eq. (24). Assuming that ^1H is at the site of ^{14}N, we have the minimum value of 1.06 s for $H_1=2.1$ G in Eq. (24). This value is in good agreement with that of minimum 21 of 0.94 s observed at 238 K ($10^3/T=4.2$) and that of minimum 3 of 1.5 s at 465 K ($10^3/T=2.3$).

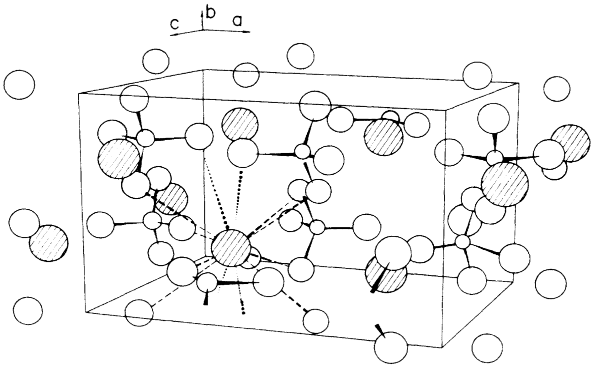

FIG. 5. The crystal structure of NH_4ClO_4. This figure is reproduced from that by Smith and Levy (Ref. 40). The largest sphere shows the rotating $NH_4{}^+$ ion, the next largest, the oxygen atom and the smallest, the chlorine atom.

The measurement of $T_{1\rho}$ for $H_1=2.1$ G at 30 MHz ($H_0=7046$ G) confirms the above statements. As shown in Fig. 4, minimum 21 for $H_1=2.1$ G at 30 MHz is split into two minima; minimum 1′ 233 K ($10^3/T=4.3$) and minimum 2′ at 263 K ($10^3/T=3.8$). Minimum 1′ may be attributable to interaction A because this minimum appears (at 233 K) almost at the same temperature as minimum 21 (at 238 K). This explanation is consistent with the prediction of Eq. (20); the position of the minimum value of $T_{1\rho}^{\mathrm{RE}}$ in Eq. (20) is independent of $\omega_I=\gamma_I H_0$. While minimum 2′, whose position shifts to the high-temperature side of minimum 21, is due to interaction B and is explained by Eqs. (15) and (24) with $\omega_1 T_{1S}=1$ and $\omega_S \tau_a \gg 1$. The value of T_{1S} for $\omega_S \tau_a \gg 1$ is proportional to H_0^2. Then the position that satisfies the condition $\omega_1 T_{1S}=1$ shifts to higher temperature as the value $\omega_I=\gamma_I H_0$ increases, which is consistent with the observed position of the minimum 21 at 238 K ($10^3/T=4.2$) at 16 MHz and that of minimum 2′ at 263 K ($10^3/T=3.80$) at 30 MHz. The position 465 K ($10^3/T=2.3$) and the value 1.5 s of the minimum 3′ for $H_1=2.1$ G at 30 MHz agree with those (465 K, 1.5 s) of minimum 3 for $H_1=2.1$ G at 16 MHz. This confirms the explanation that minimum 3 at 16 MHz is due to interaction B and appears under the condition $\omega_1 T_{1S}=1$ and $\omega_S \tau_a \ll 1$; T_{1S} is independent of $\omega_I=\gamma_I H_0$.

We may determine the relaxation time T_{1S} of ^{17}O spins from T_1 and $T_{1\rho}$ data. Ikeda and McDowell[28] suggested that the observed value $(T_1)_{\mathrm{ob}}$ of ^1H in NH_4ClO_4 below $T_c=512$ K can be expressed as

$$(T_1)_{\mathrm{ob}}^{-1}=(T_1)_{\mathrm{HH}}^{-1}+(T_1)_{\mathrm{SR}}^{-1}\ , \tag{29}$$

where $(T_1)_{\mathrm{HH}}$ is given by Eq. (17) and $(T_1)_{\mathrm{SR}}$ is the relaxation time due to the spin-rotational interaction[45] of $NH_4{}^+$ ion. We assume that the observed value $(T_{1\rho})_{\mathrm{ob}}$ of ^1H below T_c is given by

$$(T_{1\rho})_{\mathrm{ob}}^{-1}=(T_{1\rho})_t^{-1}+(T_{1\rho})_{\mathrm{HH}}^{-1}+(T_{1\rho})_{\mathrm{SR}}^{-1}\ , \tag{30}$$

where $(T_{1\rho})_t$ and $(T_{1\rho})_{\mathrm{HH}}$ are given by Eqs. (25) and (19), respectively. $(T_{1\rho})_{\mathrm{SR}}$ is the spin-lattice relaxation time in the rotating frame due to the spin-rotational interaction of $NH_4{}^+$ ion and may be derived in the same manner as $(T_2)_{\mathrm{SR}}$ in Eq. (4.16) in Ref. (45):

$$(T_{1\rho})_{\mathrm{SR}}^{-1}=(I_M kT/9\hbar^2)[2(C_\perp+C_\parallel)^2 f_L(\omega_1,\tau_1)+2(C_\perp-C_\parallel)^2 f_L(\omega_1,\tau_1)+2(C_\perp+C_\parallel)^2 f_L(\omega_0,\tau_{12})+2(C_\perp-C_\parallel)^2 f_L(\omega_0,\tau_{12})]\ , \tag{31}$$

where I_M is the moment of inertia of $NH_4{}^+$ ion, $C_\perp$ and $C_\parallel$ are the principal components of the spin-rotational tensor, τ_1 is the correlation time relating to the angular velocity and τ_{12} is that relating to the angular velocity and the reorientation of $NH_4{}^+$ ion. Note that Eq. (31) has the same form as $(T_2)_{\mathrm{SR}}^{-1}=J_1(0)+J_1(\omega_0)$ in Eq. (4.16) in Ref. (45) when $J_1(0)$ is replaced by $J_1(\omega_1)$. When $\omega_0 \tau_H \ll 1$, we have $(T_{1\rho})_{\mathrm{HH}}=(T_1)_{\mathrm{HH}}$ in Eqs. (19) and (17). Since $\tau_1 \tau_H=I_M/6kT$,[45] the conditions $\omega_0 \tau_1 \ll 1$ and $\omega_0 \tau_{12} \ll 1$ are satisfied in Eq. (31) in the temperature that concerns

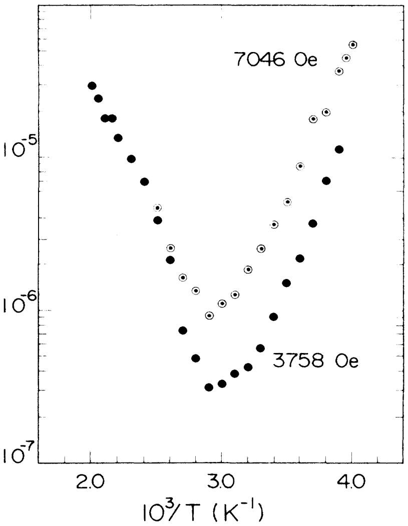

FIG. 6. The temperature dependence of T_{1S} of ^{17}O spins in NH$_4$ClO$_4$. ⊙ represents T_{1S} for $H_0=7046$ G and ● that for 3758 G. Above 417 K ($10^3/T=2.4$) ⊙ agrees with ●.

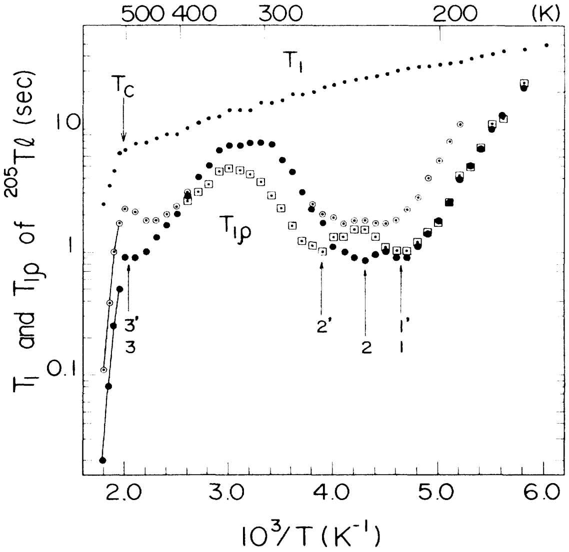

FIG. 7. The temperature dependence of T_1 and $T_{1\rho}$ of ^{205}Tl in TlClO$_4$. • represents the data points of T_1 at 16 and 30 MHz; ● and ⊙ represent $T_{1\rho}$ for $H_1=2.1$ and 4.2 G, respectively, at 16 MHz. ⊡ represents $T_{1\rho}$ for $H_1=2.1$ G at 30 MHz.

us here. Then we also have $(T_{1\rho})_{\rm SR}=(T_1)_{\rm SR}$. The explicit form of $(T_1)_{\rm SR}$ is given by Eq. (4.10) in Ref. (45). From the above considerations and Eqs. (29) and (30), we may write

$$(T_{1\rho})_{\rm ob}^{-1}=(T_{1\rho})_t^{-1}+(T_1)_{\rm ob}^{-1} . \tag{32}$$

Subtracting the contribution of $(T_1)_{\rm ob}^{-1}$ from $(T_{1\rho})_{\rm ob}^{-1}$, we have $(T_{1\rho})_t$. In order to determine $T_{1\rho}^{\rm CR}$, we must further subtract the contribution of $(T_{1\rho}^{\rm RE})^{-1}$ from $(T_{1\rho})_t$. This procedure was done as follows in the case of $T_{1\rho}^{\rm CR}$ for $H_1=2.1$ G at 16 MHz. Assuming that $\tau_3 \ll \tau_2$ in Eq. (12a), we obtained the parameters E_3, $\tau_{3\infty}$, e^2qQ/h, A_1, and A_2 (assuming $A_1=A_2$) by using Powell's nonlinear least-squares method with the data for $(T_{1\rho})_t$ between $10^3/T=3.6$ (278 K) and $10^3/T=5.40$ (185 K) and Eq. (25). We obtain $E_3=8.67$ kcal/mol, $\tau_{3\infty}=6.77\times10^{-14}$ s and $A_1=7.46\times10^4$ s^{-2} with $\chi^2=7.6\times10^{-3}$. Then we have numerical values of $T_{1\rho}^{\rm RE}$ above 278 K with these parameters. Thus the values of $T_{1\rho}^{\rm CR}$ were determined by subtracting the contribution $(T_{1\rho}^{\rm RE})^{-1}$ from $(T_{1\rho})_t^{-1}$. Of course there exists the possibility that the values E_3 and $\tau_{3\infty}$ which are determined between 278 and 185 K may be different above 278 K. But we could not find another appropriate method to subtract the contribution $(T_{1\rho}^{\rm RE})^{-1}$ from $(T_{1\rho})_t^{-1}$. The values of T_{1S} of ^{17}O were obtained from the $T_{1\rho}^{\rm CR}$ values by using Eq. (24) and are summarized in Fig. 6. The values of T_{1S} for $H_1=2.1$ G at 30 MHz were also determined in the same manner as that at 16 MHz. The results are plotted in Fig. 6. As shown in the figure, the field and temperature dependences of T_{1S} may be well explained by using Eq. (15); the ratio of the determined minimum values for $H_0=7046$ and 3758 G is about 2.9 which is in good agreement with the predicted value 1.9 s by Eq. (15). Below the positions of the minima of T_{1S}, the ratio of T_{1S} for $H_0=7046$ and 3758 G is about 3.33 at 286 K ($10^3/T=3.5$), which is also in good agreement with 3.52 predicted by Eq. (15). The parameters E_3, $\tau_{3\infty}$, and e^2qQ/h are determined by using Powell's method with the values of T_{1S} between $10^3/T=2.4$ (417 K) and $10^3/T=4.0$ (250 K) and Eq. (15). The results are summarized in Table I with the χ^2 values.

B. T_1 and $T_{1\rho}$ in thallium perchlorate, TlClO$_4$

The temperature dependences of T_1 at 16 and 30 MHz and $T_{1\rho}$ for $H_1=2.1$ and 4.2 G of ^{205}Tl in TlClO$_4$ are shown in Fig. 7. With increasing temperature, the values

TABLE I. The collected parameters of the activation energy E_3, preexponential factor $\tau_{3\infty}$ and quadrupole coupling constant e^2qQ/h in NH$_4$ClO$_4$ and TlClO$_4$.

	H_0 (G)	e^2qQ/h (MHz)	E_3 (Kcal/mol)	$\tau_{3\infty}$ ($\times10^{-14}$ s)	χ^2
NH$_4$ClO$_4$	3758	12.0	9.49	2.55	0.05
	7046	9.54	9.20	2.70	0.01
TlClO$_4$	6512	10.3	8.19	6.09	0.01
	12210	8.79	7.50	17.9	0.03

of T_1 at 16 MHz decrease gradually in the orthorhombic phase and rather sharply in the cubic phase (above $T_c=505$ K). T_1 at 30 MHz agreed with that at 16 MHz below T_C. $T_{1\rho}$ for ^{105}Tl decreases sharply with increasing temperature above T_c, being probably due to the translational diffusion of thallium atoms. The activation energy E_d is estimated as 39.7 kcal/mol, which is much larger than 28.1 kcal/mol for the $NH_4{}^+$ ion in NH_4ClO_4.

With increasing temperature above 172 K ($10^3/T=5.8$), $T_{1\rho}$ for ^{205}Tl at 16 MHz ($H_0=6512$ G) decreases and has double minima; minimum 1 with the value of 0.9 s at about 215 K ($10^3/T=4.65$) and minimum 2, with 0.85 s at 215 K ($10^3/T=4.65$) for $H_1=2.1$ G. The temperature dependence of $T_{1\rho}$ for $H_1=4.2$ G at 16 MHz also shows double minima of 1.7 s at about 225 K ($10^3/T=4.45$) and 1.7 s at 244 K ($10^3/T=4.1$), though these minima are not well resolved. The values of $T_{1\rho}$ for $H_1=2.1$ and 4.2 G at 16 MHz agree with each other in the temperature range between 270 K ($10^3/T=3.7$) and 307 K ($10^3/T=2.7$). With increasing the temperature above 307 K, $T_{1\rho}$ shows minimum 3 with the value of 0.9 s at about 488 K ($10^3/T=2.05$) for $H_1=2.1$ G and 1.8 s at 444 K ($10^3/T=2.25$) for $H_1=4.2$ G. After all there exist three minima of $T_{1\rho}$ for $H_1=2.1$ G at 16 MHz in $TlClO_4$. This is different from the case of NH_4ClO_4, where two minima of $T_{1\rho}$ for $H_1=2.1$ G at 16 MHz appear. The origins of the three minimum of $T_{1\rho}$ for ^{205}Tl are also attributable to the ^{17}O spins of natural abundance. The minimum 1 at 215 K ($10^3/T=4.65$) is due to interaction A random modulation of dipolar interaction between the ^{205}Tl and ^{17}O spins and is explained by Eq. (20). Minimum 2 at 233 K ($10^3/T=4.3$) and minimum 3 at 488 K ($10^3/T=2.03$) are attributed to the interaction-B cross relaxation between the ^{205}Tl and ^{17}O spins and are explained by Eqs. (15) and (21). Minimum 2 appears with the conditions of $\omega_1 T_{1S}=1$ and $\omega_S\tau_a \gg 1$, and minimum 3 $\omega_1 T_{1S}=1$ and $\omega_S\tau_a \ll 1$.

It is possible to estimate the minimum values of $T_{1\rho}^{\mathrm{RE}}$ in Eq. (20) and $T_{1\rho}^{\mathrm{CR}}$ in Eq. (24) in $TlClO_4$. There are no available data on the precise positions of thallium atoms and ClO_4 ions in $TlClO_4$. But the lattice constants of $TlClO_4$ are very similar to those of NH_4ClO_4, and it might be permissible to use the values n In Eq. (20), $\bar{r}_i$ in Eq. (21), r_i in Eq. (23) and n in Eq. (24) in NH_4-ClO_4 for those in $TlClO_4$. The calculated minimum value of $T_{1\rho}^{\mathrm{Re}}$ is 2.61 s for $H_1=2.1$ G, which is in good agreement with the observed value of 0.9 s minimum 1 at 215 K ($10^3/T=4.56$). We calculated the minimum value of 1.47 s for $T_{1\rho}^{\mathrm{CR}}$ in Eq. (24) with $H_1=2.1$ G, which is also in good agreement with the value of 0.85 s of minimum 2 at 233 K ($10^3/T=4.3$) and that of minimum 3 of 0.9 s at 488 K ($10^3/T=2.03$).

The above explanations in $TlClO_4$ may be confirmed, as in the case of NH_4ClO_4, by the measurement of $T_{1\rho}$ for $H_1=2.1$ G at 30 MHz ($H_0=12\,210$ G). As is shown in Fig. 7, the values of ^{205}Tl for $H_1=2.1$ G at 30 MHz agree with the experimental error with those at 16 MHz between 172 K ($10^3/T=5.8$) and 222 K ($10^3/T=4.5$); the positions and values of minimum 1 at 16 MHz and minimum 1′ at 30 MHz agree with each other. This fact supports the explanation that minimum 1 (for $H_1=2.1$ G at 16 MHz) is due to interaction A; $T_{1\rho}^{\mathrm{RE}}$ in Eq. (20) is independent of H_0. As is shown in Fig. 7, the position of minimum 2′ for $H_1=2.1$ G at 30 MHz appears at a higher temperature than that of minimum 2 for $H_1=2.1$ G at 16 MHz, this is consistent with the prediction of Eqs. (15) and (24) with $\omega_1 T_{1S}=1$ and $\omega_S\tau_a \gg 1$. The position 488 K ($10^3/T=2.05$) and the value 0.9 s of minimum 3′ for $H_1=2.1$ G at 30 MHz agree with those of minimum 3 at 16 MHz, which is also consistent with the predictions of Eqs. (15) and (24) with $\omega_1 T_{1S}=1$ and $\omega_S\tau_a \ll 1$.

The observed value of $(T_{1\rho})_{\mathrm{ob}}$ of ^{205}Tl may be written by

$$(T_{1\rho})_{\mathrm{ob}}^{-1}=(T_{1\rho})_t^{-1}+(T_{1\rho})_{\mathrm{Tl}}^{-1}\,, \tag{33}$$

where $(T_{1\rho})_t$ is given by Eq. (25). We could not clarify the origins of $(T_{1\rho})_{\mathrm{Tl}}$ in Eq. (30) and the observed value $(T_1)_{\mathrm{ob}}$ of ^{205}Tl. Below 150 K ($10^3/T=6.4$), where the first term may be negligible, the values of $(T_{1\rho})_{\mathrm{ob}}$ for $H_1=2.1$ G agreed with those of $(T_1)_{\mathrm{ob}}$ [the T_1 and $T_{1\rho}$ data below 167 K ($10^3/T=6.0$) are not shown in Fig. 7]. Therefore, it is natural to assume that $(T_{1\rho})_{\mathrm{Tl}}=(T_1)_{\mathrm{ob}}$ in Eq. (30). We have the same relation for $(T_{1\rho})_{\mathrm{ob}}$ of ^{205}Tl in $TlClO_4$ as that of Eq. (32). The values of T_{1S} in $TlClO_4$ were determined in the same manner as that in NH_4ClO_4. The results which are summarized in Fig. 8 show that the temperature and magnetic field dependences of T_{1S} are explained by using Eq. (15). The ratio of the minimum values of T_{1S} for $H_0=12\,210$ and 6512 G is 2.5, which is in good agreement with that of 1.9 predicted by Eq. (15). For the condition of $\omega_S\tau_a \gg 1$, the ratio of T_{1S} for $H_0=12\,210$ and 6512 G is about 3.6 at 270 K ($10^3/T=3.7$), which is also in agreement with the value of 3.5 predicted by Eq. (15).

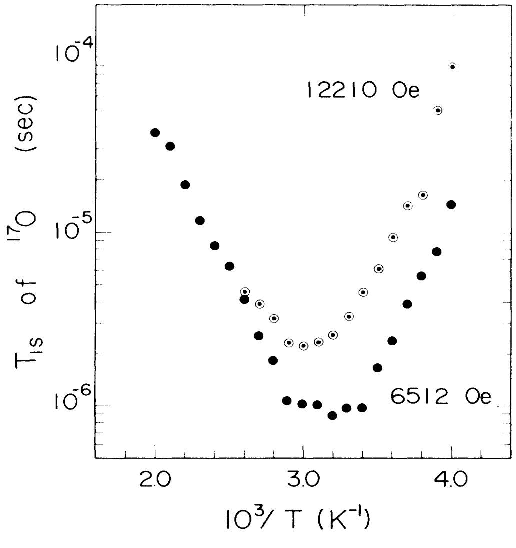

FIG. 8. The temperature dependence of T_{1S} of ^{17}O spins in $TlClO_4$. ⊙ represents T_{1S} for $H_0=12210$ G and ● that for 6512 G. Above 400 K ($10^3/T=2.5$) ⊙ agrees with ●.

The parameters E_3, $\tau_{3\infty}$, and e^2qQ/h are determined by Powell's method, in which the values of T_{1S} between 500 K ($10^3/T=2.0$) and 250 K ($10^3/T=4.0$) and Eq. (15) are used. The results are summarized in Table I.

C. Comparison of the experimental results between NH_4ClO_4 and $TlClO_4$

We will compare the parameters E_3 and e^2qQ/h in NH_4ClO_4 with those in $TlClO_4$ in Table I. We pick up the parameters for $\chi^2=0.01$. The activation energy $E_3=9.20$ kcal/mol in NH_4ClO_4 is larger than 8.19 kcal/mol in $TlClO_4$. The difference between these two compounds is probably due to the presence of the hydrogen bond in NH_4ClO_4. The quadrupole coupling constant $e^2/qQ/h$ at the ^{17}O site is determined by the covalent and ionic bonds within the ClO_4 ion and also by those between the ClO_4 ion and surrounding NH_4^+ ions or thallium ions. The value of $e^2qQ/h=9.50$ MHz in NH_4ClO_4 is almost equal to that of 10.3 MHz in $TlClO_4$, showing that e^2qQ/h is determined mainly by the chemical bonds within the ClO_4 ion. The values of $e^2qQ/h=10$ MHz in NH_4ClO_4 and $TlClO_4$ are compared with that of 5.96 MHz for ^{17}O in ^{17}O enriched KH_2PO_4 which was determined by using double resonance technique by Blinc *et al.*[3]

V. CONCLUDING REMARKS AND DISCUSSION

It was found that the natural abundance of the rare ^{17}O spins has a pronounced effect on $T_{1\rho}$ of ^{1}H(^{205}Tl) through two kinds of interactions A and B: (A) random modulation of the dipolar interaction between the ^{17}O and ^{1}H(^{205}Tl) spins and (B) cross relaxation between the ^{17}O and ^{1}H(^{205}Tl) spins. In both the interactions, the rare ^{17}O spins play the role of strong relaxation centers of ^{1}H(^{205}Tl) spins in the rotating frame. Due to interaction B, we may determine the relaxation time T_{1S} of the ^{17}O spin and evaluate the quadrupole coupling constant e^2qQ/h at the ^{17}O site. The value of e^2qQ/h would be delicately affected by the hydrogen bonds. It will be of interest to determine the resonance frequencies and e^2qQ/h for ^{17}O precisely by using the double resonance technique and to compare them with the present results. The double resonance should be done at low temperatures where the first term in Eq. (2) (and also the second and third terms) contributes to the spin energy of ^{17}O spins as shown in Fig. 2(II).

The minimum of $T_{1\rho}$ of ^{1}H(^{205}Tl) in Eq. (24) takes the value of 1–2 s for $H_1=2.1$ G. In some compounds in which T_1 of ^{1}H(^{205}Tl) is longer than a few seconds, the measurement of $T_{1\rho}$ might make it possible to determine T_{1S} and e^2qQ/h for ^{17}O.

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