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NQR and NMR studies on the electron-spin correlation time in paramagnetic insulators

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The ^{35}Cl NQR and ^{1}H NMR spin-lattice relaxation times, T_{1Q} and T_{1M}, respectively, in paramagnetic $\mathrm{Ni(H_2O)_6SnCl_6}$ crystals were measured as a function of temperature. Their temperature variations depend on the correlation time τ_e of the unpaired electron spins in the paramagnetic Ni^{2+} ions, and τ_e was found to be governed mainly by the electronic spin-lattice relaxation originating from the spin-phonon interaction above approximately 250 K and by electron-spin flips caused by the exchange interaction below approximately 150 K. The temperature dependence of T_{1Q} and T_{1M} at high temperatures shows that the electronic spin-lattice relaxation time is determined by the Raman process. The correlation time of the electron flips was evaluated to be 1.8×10^{-10} s from T_{1Q}. The exchange parameter between the nearest electronic spins and the paramagnetic Curie temperature were estimated to be 0.013 cm^{-1} and 0.075 K, respectively. It was shown that reliable information on the electron-spin dynamics can be obtained from T_{1Q} and T_{1M}.

I. INTRODUCTION

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) studies on magnetic substances such as paramagnetic insulators have been carried out extensively since around 1950.[1,2] NMR and NQR studies on paramagnetic insulators can be classified into the following two categories;[1] the resonant nucleus and unpaired electrons are on the same atom in one case and on different atoms in the other case. An example of the former (case 1) is ^{59}Co NMR of CoO.[3] It seems better, however, to classify the latter further into two groups. When an atom including the resonant nucleus is bonded directly to a paramagnetic ion, the transferred hyperfine interaction[4] between the resonant nucleus and the electron that is partly transferred to the resonant atom generally prevails over the direct dipole-dipole interaction between the resonant nucleus and the electron on a paramagnetic ion. Examples of this case (case 2) are ^{19}F NMR of $\mathrm{MnF_2}$ (Ref. 5) and halogen NQR of paramagnetic halides of transition metals.[6] On the other hand, when the resonant atoms are not bonded directly to a paramagnetic ion, the magnetic dipole-dipole interaction is dominant. Examples of this case (case 3) are ^{1}H NMR of $\mathrm{CuSO_4\cdot5H_2O}$ (Ref. 7) and $\mathrm{CuCl_2\cdot2H_2O}$,[8] and ^{35}Cl NQR of M(II)$\mathrm{PtCl_6\cdot6H_2O}$ [M(II)=Mn, Fe, Co, Ni, and Cu].[9]

Measurements of nuclear spin-lattice relaxation times in paramagnetic insulators can give us dynamical information of unpaired electrons. It is relatively easy in the third case to estimate the magnetic hyperfine interaction and hence easy to obtain the electron correlation time. This is because the interaction to be considered in this case is limited only to the magnetic dipole-dipole interaction, and delocalization of unpaired electrons, even if exists, usually has a minor effect on the interaction. The method of obtaining the electron correlation time from nuclear spin-lattice relaxation times is useful especially in case it is difficult to observe electron-paramagnetic-resonance (EPR) spectra owing to the lifetime broadening.

Although many NMR studies on the electron dynamics have been reported,[10] no NQR papers have been found as far as we know except our previous studies.[11,12] In the present investigation we have measured the temperature dependence of the ^{35}Cl NQR and ^{1}H NMR spin-lattice relaxation times in the paramagnetic $\mathrm{Ni(H_2O)_6SnCl_6}$ crystals, which belongs to the third case. These NQR and NMR relaxation-time measurements are expected to give reliable information on the electron-spin dynamics in the third case.

II. EXPERIMENTAL

$\mathrm{Ni(H_2O)_6SnCl_6}$ was prepared by the same method as described in Ref. 13. The crystals obtained were green-colored and hygroscopic. For the NQR measurement, the polycrystalline sample was sealed in a glass tube and annealed at approximately 400 K for 24 h to increase the signal intensity. For the NMR measurement, the sample was powdered and dried in a desicator with silica gel for about one day before sealed in a sample tube.

The temperature variation of the ^{35}Cl NQR spin-lattice relaxation time T_{1Q} was measured with a homemade pulsed NQR spectrometer equipped with a homemade cryostat.[14] The temperature of the specimen was controlled within ±0.5 K, and determined within ±1 K. T_{1Q} was measured by a $180°$-τ-$90°$-τ_e-$180°$ pulse sequence, where τ_e was fixed at 100–200 μs through each T_{1Q} measurement.

The ^1H NMR spin-lattice relaxation time T_{1M} was measured at a Larmor frequency of 60 MHz (the static magnetic field H_0 of 1.4093 T) with a homemade pulsed NMR spectrometer.[15] The sample temperature was controlled and determined within ± 1 K. T_{1M} was measured by the conventional 180°-τ-90° pulse sequence.

The NMR free-induction decay signals under H_0 lower than 1.4 T were observable but too weak to determine T_{1M}. This is probably due to ^1H T_{1M} being very short and also the recovery time of the receiver being prolonged, which time is inversely proportional to H_0.[16] $H_0 \sim 1.4$ T seems to be the lower limit for the T_1 measurement in the present complex.

III. NUCLEAR RELAXATION TIMES IN PARAMAGNETIC INSULATORS

A general treatment of the nuclear magnetic relaxation in magnetic insulators has been given by Moriya based on the Kubo-Tomita theory.[17] Armstrong and co-workers have applied this to the analysis of the ^{35}Cl NQR T_{1Q} and spin-spin relaxation time T_{2Q} in K_2IrCl_6 and K_2ReCl_6 (case 2), where the transferred hyperfine and magnetic dipolar interactions play an important role.[18]

On the other hand, in a similar manner to Bloembergen, Purcell, and Pound, several expressions for the NMR relaxation times due to the magnetic dipole-dipole interactions have been derived for various cases.[1] When the resonant nucleus with $I=\frac{1}{2}$ is placed in the fluctuating local magnetic field caused by flip-flops of unlike spins S, the spin-lattice relaxation time T_{1M} of the nucleus I in a powder sample is expressed as[19]

$$T_{1M}^{-1}=\frac{2\gamma_I^2\gamma_S^2\hbar^2 S(S+1)}{15} \times \sum_i r_1^{-6}\left[\frac{\tau_{2s}}{1+(\omega_I+\omega_S)^2\tau_{2s}^2}+\frac{3\tau_{1s}}{1+\omega_I^2\tau_{1s}^2} + \frac{6\tau_{2s}}{1+(\omega_I-\omega_S)^2\tau_{2s}^2}\right] . \tag{1}$$

where γ, ω, and r_i stand for a gyromagnetic ratio, a Larmor frequency, and a distance between the resonant nucleus and the ith unlike spin, respectively. τ_{1s} and τ_{2s} denote the correlation times, characterizing the time dependence of autocorrelation functions $\langle S_z(t)S_z(0)\rangle$ and $\langle S_+(t)S_-(0)\rangle$, respectively. When the unlike spins are electrons, we can assume $\tau_{1s}=\tau_{2s}=\tau_e$ (the electron-spin correlation time) and also $\omega_I \ll \omega_S$. Thus,

$$T_{1M}^{-1}=\frac{2\alpha}{15}\sum_i r_i^{-6}\left[\frac{3\tau_e}{1+\omega_I^2\tau_e^2}+\frac{7\tau_e}{1+\omega_S^2\tau_e^2}\right] , \tag{2}$$

where

$$\alpha=\gamma_I^2 g^2 \mu_B^2 S(S+1) . \tag{3}$$

Here g and μ_B indicate a g factor and the Bohr magneton, respectively. Since our T_{1M} measurements were carried out at 60 MHz and the magnitude of τ_e can be assumed to be on the order of 10^{-10} s (this assumption will be verified afterward), the conditions, $\omega_S^2\tau_e^2 \gg 1$ and $\omega_I^2\tau_e^2 \ll 1$, are satisfied. Then we finally obtain the following equation:

$$T_{1M}^{-1}=\frac{2}{5}\alpha\sum_i r_i^{-6}\tau_e . \tag{4}$$

A similar expression can be obtained for NQR T_{1Q}.[11,12] When the resonant quadrupolar nucleus with $I=\frac{3}{2}$ experiences the fluctuation of the electronic magnetic field caused by electron-spin flips, T_{1Q} is expressed as

$$T_{1Q}^{-1}=9\alpha\sum_i \Lambda_i\frac{\tau_e}{1+\omega_Q^2\tau_e^2} . \tag{5}$$

Here ω_Q is the resonance frequency of the NQR line measured and the geometrical factor Λ_i is given by

$$\Lambda_i=|F_i^{(1)}|^2+\tfrac{1}{18}|F_i^{(0)}|^2+\tfrac{1}{2}|F_i^{(2)}|^2 . \tag{6}$$

Here $F_i^{(q)}$ $(q=0,1,2)$ are the spatial parts of the dipolar Hamiltonian between the nucleus and the ith electron spin and are given by

$$\left.\begin{aligned} |F_i^{(0)}|^2&=(1-3\cos^2\theta_i)^2/r_i^6 ,\\ |F_i^{(1)}|^2&=\sin^2\theta_i\cos^2\theta_i/r_i^6 ,\\ |F_i^{(2)}|^2&=\sin^4\theta_i/r_i^6 . \end{aligned}\right\} \tag{7}$$

Here θ_i represents the angle between the principal axis of the electric-field gradient (EFG) at the resonant nucleus and the interspin vector $\mathbf{r}_i$. Unlike the NMR case, θ_i does not take random values even for a powder sample. Since the ^{35}Cl NQR frequency of $Ni(H_2O)_6SnCl_6$ is around 16 MHz, the condition, $\omega_Q^2\tau_e^2 \ll 1$, is fulfilled and hence we have

$$T_{1Q}^{-1}=9\alpha\sum_i \Lambda_1\tau_e . \tag{8}$$

Now we see that both spin-lattice relaxation rates T_{1M}^{-1} and T_{1Q}^{-1} are proportional to the electron-spin correlation time τ_e in the present experimental conditions. In the following section, we will analyze the observed ^1H NMR T_{1M} and ^{35}Cl NQR T_{1Q} data in $Ni(H_2O)_6SnCl_6$ using Eqs. (4) and (8).

IV. RESULTS AND DISCUSSION

$Ni(H_2O)_6SnCl_6$ forms a trigonal crystal with the space group $R\bar{3}$ and a slightly distorted CsCl-type structure with $\alpha=96°45'$ consisting of $[Ni(H_2O)_6]^{2+}$ and $[SnCl_6]^{2-}$ octahedra.[20] Both octahedra are slightly distorted from the O_h symmetry and located at $\bar{3}$ sites of the crystal. Each chlorine atom is surrounded by five H_2O molecules, while each $[Ni(H_2O)_6]^{2+}$ ion is in contact with 12 chlorine atoms at 4.2–4.4 Å. A single ^{35}Cl NQR signal has been detected between 4.2 and 437 K, which is in agreement with the above crystal structure, and no phase transition has been observed.[13]

The temperature dependence of the ^{35}Cl NQR T_{1Q} and ^1H NMR T_{1M} in the Ni compound are shown in Fig. 1

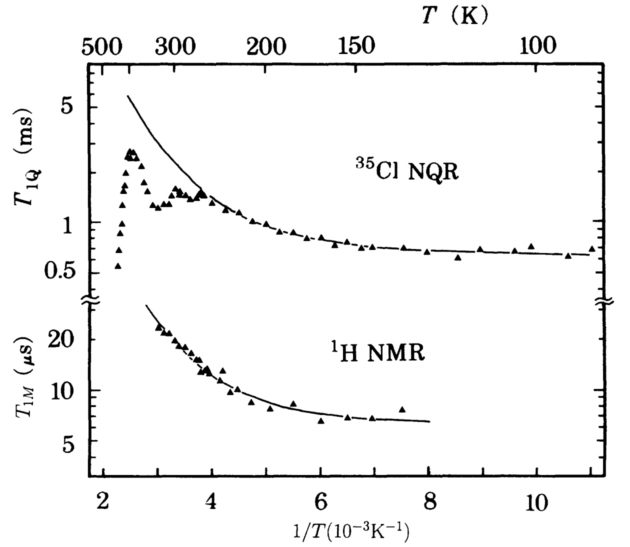

FIG. 1. Temperature dependence of ^{35}Cl NQR spin-lattice relaxation time T_{1Q}(▲) and ^{1}H NMR spin-lattice relaxation time T_{1M}(△) in $\mathrm{Ni(H_2O)_6SnCl_6}$. The solid lines indicate the best-fit curves giving $n=4.0$ in Eqs. (11) and (12).

and the numerical values of the relaxation times determined at several temperatures are listed in Table I. We found marked differences in the magnitude and the temperature dependence between the two relaxation times. Furthermore, we observed a pair of T_{1Q} minima around room temperature and a rapid variation of T_{1Q} above approximately 400 K. We have attributed the T_{1Q} minima to the EFG fluctuation at the chlorine sites caused by thermal motions of the $[\mathrm{Ni(H_2O)_6}]^{2+}$ cations, while the rapid T_{1Q} variation is attributed to the $[\mathrm{SnCl_6}]^{2-}$ reorientations.[21] Below room temperature T_{1Q} behaved similarly to T_{1M}. From now on, we will discuss the T_{1Q} observed only at this temperature region.

The electron-spin correlation time τ_e, which is expected to cause the temperature dependence of T_{1Q} and T_{1M}, is given by the electron spin-lattice relaxation time T_{1e} and the correlation time τ_f for electron-spin slips as follows:[22]

$$\tau_e^{-1}=T_{1e}^{-1}+\tau_f^{-1} . \tag{9}$$

Since the electron-spin flips are caused by the exchange interaction among neighboring electron spins, τ_f is independent of temperature. On the other hand, T_{1e} is ascribed to spin-phonon interactions and depends on temperature T as follows:[23]

$$T_{1e}^{-1}=\beta\coth\left[\frac{h\nu_e}{2kT}\right]+\gamma T^n+\frac{\xi}{\exp(\Delta/kT)-1} . \tag{10}$$

The first term represents the direct process and ν_e is a Larmar frequency of the magnetic ion. The second term corresponds to the Raman process and the exponent n can take numerical values depending on the electronic states of the magnetic ion. The last term describes the Orbach process where transitions between two low-lying states of the magnetic ion occur via an excited state whose energy is less than the maximum phonon energy and also higher by Δ than energies of the two ground states.

TABLE I. ^{35}Cl NQR spin-lattice relaxation times T_{1Q} and ^{1}H NMR spin-lattice relaxation times T_{1M} determined at several temperatures in $\mathrm{Ni(H_2O)_6SnCl_6}$.

Spin-lattice relaxation time	Temperature (K) 100	150	200	250
T_{1Q} (ms)	0.70	0.69	0.96	1.28
T_{1M} (μs)		6.8	7.7	12.4

In the case of NQR, measured with zero applied field, T_{1e} can be interpreted as a time constant for the EPR-signal decay along the local field vector at the paramagnetic ion. In this sense one might conclude that T_{1e} is the same as the NMR dipolar relaxation time T_{1D}.[24] However, the relaxation mechanisms for T_{1e} and T_{1D} are different, that is, T_{1e} is ascribed to the modulation of the crystal electric field or ligand field through motions of the electrically charged ions under the action of lattice vibrations.[23]

Figure 1 shows that both T_{1M} and T_{1Q} are independent of temperature below approximately 200 K, whereas they increase gradually on heating above approximately 200 K. Thus, the temperature dependence above and below approximately 200 K seems to be ascribed to T_{1e} and τ_f, respectively.

A. Electron spin-lattice relaxation time

If the direct process is the most prevailing among the three mechanisms given in Eq. (10), T_{1e}^{-1} is proportional to H_0^2 as long as we can assume $h\nu_e=g\mu_B H_0 \ll kT$.[23] Unfortunately, we could not measure this H_0 dependence, because NMR signals with H_0 lower than 1.4 T were too weak to determine T_{1M}. However, since T_{1Q} showed a temperature variation similar to T_{1M}, the contribution from the direct process seems to be negligible. This is because, since the instantaneous local field at the Ni^{2+} ion site is estimated to be approximately 0.06 T, much less than 1.4 T, T_{1e} would be much longer than τ_f and hence T_{1Q} would be independent of temperature if the direct process were dominant in T_{1e}.

The exponent n in Eq. (10) has been shown to be 7 in case $T \ll \theta_D$ (Debye temperature) and 2 in case $T \gg \theta_D$.[23] Therefore, if T_{1e} is determined by the Raman process, T_{1M} and T_{1Q} are supposed to alter as T^2 or T^7. However, the least-squares fit of the equations

$$T_{1M}=\frac{5}{2\alpha\sum r_i^{-6}}[\gamma T^n+\tau_f^{-1}] , \tag{11}$$

$$T_{1Q}=\frac{1}{9\alpha\sum \Lambda_i}[\gamma T^n+\tau_f^{-1}] , \tag{12}$$

to the experimental data shows that the observed T_{1M} and T_{1Q} are better fitted to a T^4 dependence, which is depicted in Fig. 1 by solid curves. This can be explained by assuming that the high-temperature approximation does not well hold over the whole temperature region investigated. In fact, T_{1M} above approximately 270 K is well fitted to T^2, and θ_D of $Ni(H_2O)_6SiF_6$, isomorphous with the present complex,[20] has been reported as 107 K.[25] Thus, T_{1e} seems to be explained in terms of the Raman process.

Incidentally, the Orbach process can well explain the experimental results, too. The best-fit curves of the equations, obtained by substituting the last term of Eq. (10) for γT^n in Eqs. (11) and (12), are almost the same as those of T^4. The obtained Δ value was about 820 cm^{-1} (1200 K), which is a reasonable magnitude in view of the values of 530 and 900 K reported for $[Co(H_2O)_6]^{2+}$ ions.[12,22] However, we cannot definitely conclude solely from this result that the excited state exists surely in the $[Ni(H_2O)_6]^{2+}$ ion.

B. Correlation time for electron-spin flips

The correlation time τ_f for electron-spin flips can be evaluated from T_{1M} and T_{1Q} values using Eqs. (11) and (12). Since the lattice coordinates of the protons are unknown, we estimated τ_f by the least squares fit of Eq. (12) to the T_{1Q} data. We finally obtained $\tau_f = 1.8 \times 10^{-10}$ s by substituting the g value of 2.24, reported for $Ni(H_2O)_6SiF_6$,[26] and $\sum \Lambda_i = 1.63 \times 10^{44}$ cm^{-6}, where contributions from the paramagnetic ions within 11^3 primitive cells around the resonant nucleus were summed up into Eq. (12).

Electron-spin flips results from the exchange interaction of the form,

$$\mathcal{H}_{\text{ex}} = \sum_{i<j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \ , \tag{13}$$

where the interaction is assumed to be isotropic for simplicity and J_{ij} is the exchange parameter or coupling constant, which is twice the exchange integral. Using the general expression given by Kubo and Tomita[27] for the exchange frequency ω_{ex}, characterizing the time dependence of spin autocorrelation functions $\langle S_{iq}(t) S_{iq}(0) \rangle$ $(q = x, y, z)$ in the same way as τ_e,[28] Moriya has derived the following equation on the assumption of the nearest-neighbor interaction:

$$\omega_{\text{ex}}^2 = \frac{2}{3} \frac{J^2}{\hbar^2} z S(S+1) \ , \tag{14}$$

where z is the number of nearest neighbors of the paramagnetic ion.[17] Thus, the exchange parameter J can be evaluated from the relation $\omega_{\text{ex}}^2 = \pi/(2\tau_f^2)$.[27] Moreover, the paramagnetic Curie temperature Θ, which appears in the Curie-Weiss law for magnetic susceptibility, is given by,

$$\Theta = \frac{z}{3} \frac{J}{k} S(S+1) \ , \tag{15}$$

in the mean-field approximation.[29] Therefore, the paramagnetic Curie temperature is related to τ_f through the exchange parameter.

TABLE II. Correlation times τ_f of electron-spin-flip flops obtained from NQR T_{1Q}, exchange parameter J between the nearest neighbors, and paramagnetic Curie temperature Θ in the paramagnetic insulators $M(II)(H_2O)_6M(IV)Cl_6$. Θ_{obs} is the absolute value of paramagnetic Curie temperature determined in the isomorphous $M(II)(H_2O)_6SiF_6$ crystals.

Compound	τ_f (10^{-10} s)	J (cm^{-1})	Θ (K)	Θ_{obs} (K)
$Ni(H_2O)_6SnCl_6$	1.8	0.013	0.075	0.08–0.15[d]
$Mn(H_2O)_6PtCl_6$	1.8[a]	0.0062	0.16	0.11–0.12[e]
$Co(H_2O)_6PtCl_6$	0.9[b]	0.019	0.21	0.15–0.19[f]
$Cu(H_2O)_6PtCl_6$	6.4[c]	0.0060	0.013	0.05–0.08[g]

[a] Reference 30.

[b] Reference 12.

[c] Reference 11.

[d] $Ni(H_2O)_6SiF_6$ (ferromagnet) in Ref. 31.

[e] $Mn(H_2O)_6SiF_6$ (antiferromagnet) in Ref. 32.

[f] $Co(H_2O)_6SiF_6$ (antiferromagnet) in Ref. 32.

[g] $Cu(H_2O)_6SiF_6$ (ferromagnet) in Ref. 31.

The values of J and Θ obtained from τ_f are listed in Table II along with those derived in the same way from T_{1Q} for $M(II)(H_2O)_6PtCl_6$ [M(II)=Mn, Co, and Cu].[11,12,30] Since J and/or Θ values determined experimentally for the present complex and $M(II)(H_2O)_6PtCl_6$ are unavailable, the paramagnetic Curie temperatures Θ_{obs} determined from the adiabatic magnetization curves for the isomorphous complexes $M(II)(H_2O)_6SiF_6$ are listed for comparison.[31,32] The Θ values obtained from T_{1Q} are consistent with Θ_{obs} of the fluorosilicates. The values of τ_f obtained from T_{1Q} are, therefore, considered to be reasonable. Incidentally, the value of $\Theta = 0.11$ K, which agrees well with Θ_{obs}, has been reported for $Ni(H_2O)_6SiF_6$ using τ_f of 0.9×10^{-10} s obtained from ^{19}F NMR T_1.[22]

V. CONCLUSIONS

When an atom containing the NMR or NQR nucleus is not bonded directly to a paramagnetic ion, it is an excellent approximation for the nuclear spin relaxation to take into account only the magnetic dipole-dipole interaction between the nucleus and unpaired electrons. Since it is easy to estimate the magnetic dipolar interaction as long as the exact geometrical information is available, the electron-spin-flip correlation times τ_f can be obtained from the nuclear relaxation times using Eqs. (2) and (8). The τ_f values obtained from both NMR and NQR relaxation times can be expected to be reasonable as well as reliable, although only a few NMR works have been reported for τ_f.[22,33]

It seems difficult to conclusively determine the mechanism responsible for the electron spin-lattice relaxation time T_{1e} solely from the nuclear relaxation-time measurements. However, reliable values of the energy gap Δ can be obtained from NMR (Refs. 10, 22, 33, and 34) and NQR,[11,12] in case there is an excited state whose energy is less than the maximum phonon energy.

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