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Nuclear quadrupole resonance studies on weak exchange interactions between paramagnetic ions in $M(\text{II})(\text{H}_2\text{O})_6\text{SnCl}_6$ ($M(\text{II}) = \text{Mn}, \text{Co}, \text{and Ni}$)

Hiroshi Miyoshi¹, Ryuichi Ikeda¹, Akira Koshio¹ and Keizo Horiuchi^{2,3}

¹ Department of Chemistry, University of Tsukuba, Tsukuba 305-8571, Japan

² Faculty of Science, University of the Ryukyus, Nishihara-cho, Okinawa 903-0213, Japan

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Abstract

The ^{35}Cl NQR spin–lattice relaxation times T_{1Q} in paramagnetic $\text{Mn}(\text{H}_2\text{O})_6\text{SnCl}_6$ and $\text{Co}(\text{H}_2\text{O})_6\text{SnCl}_6$ crystals were measured as a function of temperature. Using the T_{1Q} values observed, the correlation times τ_f of electron-spin flip-flops and exchange parameters J were estimated. The J value in Mn salt was found to be smaller than those found for Co and Ni salts. It is inferred from the J values that the indirect interaction where some chemical bonds (including $\text{OH}\cdots\text{Cl}$ hydrogen bonds) intervene is dominant in the exchange interactions between the paramagnetic ions in $M(\text{II})(\text{H}_2\text{O})_6\text{SnCl}_6$ ($M(\text{II}) = \text{Mn}, \text{Co}$ and Ni).

1. Introduction

Measurements of nuclear spin–lattice relaxation times in paramagnetic insulators can give dynamical information of unpaired electrons through the magnetic hyperfine interactions. When an atom of the resonant nucleus is not directly bonded to any paramagnetic atoms, it is an excellent approximation for nuclear spin relaxation to take into account only magnetic dipole–dipole interactions between the nucleus and unpaired electrons. Since it is easy to estimate magnetic dipolar interactions as long as the exact geometrical information is available, values of electron correlation times obtained from nuclear-relaxation measurements are quite reliable.

In our previous papers [1, 2], we measured the temperature dependence of the ^{35}Cl nuclear quadrupole resonance (NQR) and ^1H nuclear magnetic resonance (NMR) spin–lattice relaxation times in paramagnetic $\text{Ni}(\text{H}_2\text{O})_6\text{SnCl}_6$ crystals, and estimated the correlation time for electron-spin flips and exchange interactions between the paramagnetic ions. These investigations showed that in measuring electron-spin dynamics an NQR method can afford some advantages: a resonance signal can be observed even in nuclei close to paramagnetic

³ Author to whom any correspondence should be addressed.

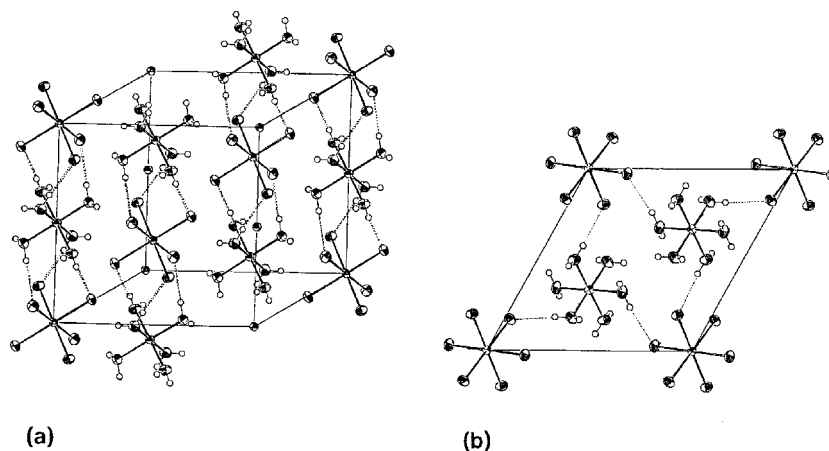


Figure 1. The crystal structure of $\text{Ni}(\text{H}_2\text{O})_6\text{SnCl}_6$ drawn by ORTEP with 50%-probability-displacement ellipsoids [6]. (a) Trigonal unit cell (b) projection of the unit cell onto the ab -plane. Double and single dotted lines indicate $\text{OH}\cdots\text{Cl}$ hydrogen bonds along the c -axis and on the ab -plane, respectively.

atoms, and resonance signals can be one-to-one corresponded to nonequivalent lattice sites in crystals. As a result of these benefits we were able to measure precisely the electron correlation times in paramagnetic crystals. The NQR method has another advantage. A very small exchange parameter of around 10^{-2} K can be estimated without measuring at very low temperatures. In our former studies [1, 2], all relaxation-time measurements were carried out only above 77 K and an exchange parameter of 0.019 K was obtained.

In the present investigation we measure the ^{35}Cl NQR spin-lattice relaxation time T_{1Q} in isomorphous $\text{Mn}(\text{H}_2\text{O})_6\text{SnCl}_6$ and $\text{Co}(\text{H}_2\text{O})_6\text{SnCl}_6$ crystals, and discuss weak exchange interactions in $\text{M}(\text{II})(\text{H}_2\text{O})_6\text{SnCl}_6$ ($\text{M}(\text{II}) = \text{Mn}, \text{Co}$ and Ni).

2. Experimental

The polycrystalline samples were prepared by the same method as described in [1]. The temperature variation of the ^{35}Cl NQR T_{1Q} was measured with a homemade pulsed NQR spectrometer described in [3]. The sample temperature was controlled and determined within ± 1 K. T_{1Q} was measured by a $180^\circ - \tau - 90^\circ - \tau' - 180^\circ$ pulse sequence with a fixed τ' of 110–150 μs through the whole T_{1Q} measurement.

3. Results and analysis

$\text{Mn}(\text{H}_2\text{O})_6\text{SnCl}_6$ and $\text{Co}(\text{H}_2\text{O})_6\text{SnCl}_6$ have been shown to be isomorphous with $\text{Ni}(\text{H}_2\text{O})_6\text{SnCl}_6$ [4], which forms a trigonal crystal with space group $R\bar{3}$ and a slightly distorted CsCl-type structure with $\alpha = 96^\circ 45'$ consisting of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{SnCl}_6]^{2-}$ octahedra [5]. The unit cell of $\text{Ni}(\text{H}_2\text{O})_6\text{SnCl}_6$ is shown in figure 1 [6]. Each chlorine atom is surrounded by five H_2O molecules, while each $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion is in contact with 12 chlorine atoms at 4.2–4.4 Å.

A single ^{35}Cl NQR signal has been detected for the both compounds [7] in agreement with the above crystal structure. The temperature dependences of the ^{35}Cl NQR T_{1Q} in Mn and Co salts are shown in figure 2. We find marked differences in the magnitude and temperature

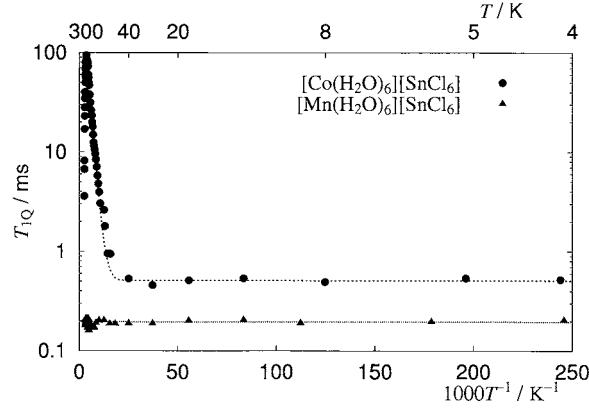


Figure 2. Temperature dependence of ^{35}Cl NQR T_{1Q} in $\text{Mn}(\text{H}_2\text{O})_6\text{SnCl}_6$ and $\text{Co}(\text{H}_2\text{O})_6\text{SnCl}_6$ crystals.

dependence in T_{1Q} between the two salts. That is, T_{1Q} in Mn salt is almost constant over the whole temperature region investigated, whereas in Co salt it increases rapidly on heating. We shall see, however, that both of them are governed by electron-spin dynamics, except for the rapid decrease above room temperature observed in Co salt, which is attributed to electric-field-gradient (EFG) fluctuation at the chlorine sites caused by the $[\text{SnCl}_6]^{2-}$ reorientations with an activation energy of $69 \pm 10 \text{ kJ mol}^{-1}$ [8]. Although the same relaxation mechanism must exist in the Mn salt, it is masked by the paramagnetic relaxation.

When a resonant quadrupolar nucleus with $I = 3/2$ experiences a fluctuation in the magnetic field caused by the motion of electron spins S , T_{1Q} is expressed as [9]

$$T_{1Q}^{-1} = 9\gamma_I^2 g^2 \mu_B^2 S(S+1) \sum_i \Lambda_i \frac{\tau_e}{1 + \omega_Q^2 \tau_e^2}. \quad (1)$$

Here γ_I , g and μ_B indicate the gyromagnetic ratio of ^{35}Cl nucleus, the g factor and the Bohr magneton, respectively. ω_Q and τ_e are the resonance frequency of the NQR line measured and the electron-spin correlation time, respectively. The geometrical factor Λ_i is given by

$$\Lambda_i = \frac{1}{18} |F_i^{(0)}|^2 + |F_i^{(1)}|^2 + \frac{1}{2} |F_i^{(2)}|^2. \quad (2)$$

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

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

Here θ_i represents the angle between the principal axis of EFG at the resonant nucleus and the interspin vector r_i . Since ^{35}Cl NQR frequencies in Mn and Co salts were observed around 16 MHz, the condition $\omega_Q^2 \tau_e^2 \ll 1$ is fulfilled and hence we have

$$T_{1Q}^{-1} = 9\gamma_I^2 g^2 \mu_B^2 S(S+1) \sum_i \Lambda_i \tau_e. \quad (4)$$

We see that the relaxation rate T_{1Q}^{-1} is proportional to τ_e .

The electron-spin correlation time τ_e is given by the electron-spin–lattice relaxation time T_{1e} and the correlation time τ_f of electron-spin flip-flops as follows [10]

$$\tau_e^{-1} = T_{1e}^{-1} + \tau_f^{-1}. \quad (5)$$

Since the electron-spin flips are caused by the exchange interaction between neighbouring 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 [11]:

$$T_{1e}^{-1} = \beta \coth\left(\frac{h\nu_e}{2kT}\right) + \gamma T^n + \frac{\zeta}{\exp(\Delta/kT) - 1}. \quad (6)$$

The first term represents the direct process where ν_e is a Larmor 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.

3.1. $Mn(H_2O)_6SnCl_6$

The T_{1Q} values observed in Mn salt shown in figure 2 were almost temperature-independent, suggesting that T_{1Q} is governed by electron-spin flip-flops. The correlation time τ_f can be evaluated from the observed T_{1Q} value using (4) and (5). Since the effective Bohr magneton value μ_{eff} and detailed data on the crystal structure are unavailable for Mn salt, we used the μ_{eff} value for Mn^{2+} in $(NH_4)_2[Mn(H_2O)_6](SO_4)_2$ for the former [12], the lattice parameters in table 2 [4] and assumed the chlorine positions for the latter to estimate τ_f . We finally obtained $\tau_f = 1.1 \times 10^{-10}$ s by substituting $\mu_{\text{eff}} = 5.88 \mu_B$ and $\sum \Lambda_i = 2.42 \times 10^{44} \text{ cm}^{-6}$, where contributions from the paramagnetic ions within 11^3 primitive cells around the resonant nucleus were summed up.

On the basis of Kubo and Tomita [13], Moriya [14] derived the following equation for the exchange frequency ω_{ex} on the assumption of the nearest-neighbour interaction:

$$\omega_{\text{ex}}^2 = \frac{2}{3} \frac{J^2}{\hbar^2} z S(S+1) \quad (7)$$

where z is the number of nearest neighbours of the paramagnetic ion and J is the exchange parameter that appears in the following Hamiltonian of the isotropic exchange interaction

$$H_{\text{ex}} = \sum_{i < j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (8)$$

Using the relation [13]

$$\omega_{\text{ex}}^2 = \frac{\pi}{2\tau_f^2} \quad (9)$$

the exchange parameter J can be evaluated from τ_f . Moreover, since the paramagnetic Curie temperature Θ is given by

$$\Theta = \frac{z}{3} \frac{J}{k} S(S+1) \quad (10)$$

in the mean-field approximation [15] Θ can also be evaluated from τ_f .

The values of J and Θ obtained from τ_f are listed in table 1. Since J and/or Θ values determined experimentally for Mn salt by no other methods have been reported, the paramagnetic Curie temperature Θ_{obs} determined from the adiabatic magnetization curves observed in the isomorphous complex $Mn(H_2O)_6SiF_6$ is listed for comparison [16].

Table 1. Observed T_{1Q} values, the correlation time τ_f of electron-spin flip-flops, exchange parameter J values between nearest neighbours and the paramagnetic Curie temperature values Θ for $\text{Mn}(\text{H}_2\text{O})_6\text{SnCl}_6$ and $\text{Co}(\text{H}_2\text{O})_6\text{SnCl}_6$.

Compound	T_{1Q} (μs)	τ_f (10^{-10} s)	J (10^{-2} cm^{-1})	Θ (K)	Θ_{obs} (K) ^a
$\text{Mn}(\text{H}_2\text{O})_6\text{SnCl}_6$	196 ± 7	1.1	0.84	0.28	0.11–0.12 ^b
$\text{Co}(\text{H}_2\text{O})_6\text{SnCl}_6$	510 ± 30	0.97	1.6	0.22	0.15–0.19 ^c

^a Θ_{obs} is the absolute value of the paramagnetic Curie temperature determined in the isomorphous $\text{Mn}(\text{H}_2\text{O})_6\text{SiF}_6$ and $\text{Co}(\text{H}_2\text{O})_6\text{SiF}_6$ crystals.

^b $\text{Mn}(\text{H}_2\text{O})_6\text{SiF}_6$ [16].

^c $\text{Co}(\text{H}_2\text{O})_6\text{SiF}_6$ [16].

Table 2. Exchange parameter J values between the nearest neighbours, the lengths of the a - and c -axes of the unit cell [4] and electronegativities [22] for $M(\text{II})(\text{H}_2\text{O})_6\text{SnCl}_6$.

Compound	J (10^{-2} cm^{-1})	a (\AA)	c (\AA)	Electronegativity
$\text{Mn}(\text{H}_2\text{O})_6\text{SnCl}_6$	0.84	9.87	10.25	1.5
$\text{Co}(\text{H}_2\text{O})_6\text{SnCl}_6$	1.6	10.69	10.91	1.8
$\text{Ni}(\text{H}_2\text{O})_6\text{SnCl}_6$	1.3	10.60	10.74	1.8

3.2. $\text{Co}(\text{H}_2\text{O})_6\text{SnCl}_6$

Figure 2 shows that T_{1Q} observed in Co salt below room temperature decreased gradually on cooling and at temperatures below 40 K it became constant as in the Mn salt. This temperature dependence seems to be explained by the fact that τ_c is dominated by T_{1e} below room temperature and by τ_f at lower temperatures. Using the assumption that the Orbach process is most effective in T_{1e} , the best-fit calculation leads to the energy difference $\Delta = 550$ K (350 cm^{-1}) between the ground and the first-excited states of Co^{2+} , with this value being comparable to reported values in several compounds [10, 17–20]. According to [11], the parameter ζ in (6) is estimated to be $10^4 \Delta^3$ in K units for the rare-earth group. Using this value, T_{1e}^{-1} is calculated to be 1.5×10^8 s^{-1} for 50 K, 3.7×10^{10} s^{-1} for 100 K, and 1.5×10^{12} s^{-1} for 300 K, which are very reasonable values compared with the τ_f value given below.

From the temperature-independent part of T_{1Q} , we estimated τ_f using (4) and (5). By substituting $\mu_{\text{eff}} = 4.61\mu_B$ observed for Co^{2+} in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ [12], and $\sum \Lambda_i = 1.57 \times 10^{44}$ cm^{-6} calculated with lattice parameters in table 2 [4] and assuming chlorine positions in the equation, we obtained $\tau_f = 0.97 \times 10^{-10}$ s. The values of J and Θ obtained from τ_f using (7), (9) and (10) are listed in table 1 along with Θ_{obs} determined from the adiabatic magnetization curves in isomorphous complex $\text{Co}(\text{H}_2\text{O})_6\text{SiF}_6$ [16].

4. Discussion and conclusion

The J value decreases in the order of Co, Ni and Mn, as does the unit-cell volume. Since the calculation of the J value includes some approximations and/or hypotheses, it is difficult to discuss the differences in the J values between the Co and Ni salts. However, the J value in Mn salt is certainly smaller than the values in the other two salts. Hence it is concluded that the exchange interaction between the paramagnetic ions in Mn salt is weaker than that in the others and the J value has no correlation with the lattice size in the present system. This suggests that the exchange interactions in the three salts are made indirectly through some chemical bonds in such a path, $\text{M}(\text{II})\text{--OH} \cdot \cdot \text{Cl}\text{--Sn}\text{--Cl} \cdot \cdot \text{HO}\text{--M}(\text{II})$, rather than directly. This path has two $\text{M}(\text{II})\text{--O}$ bonds and two $\text{O}\text{--H} \cdot \cdot \text{Cl}$ hydrogen bonds. The order of J values in the three compounds seems to be explained by differences in these bond characters.

The frequencies of M(II)-O stretching and M(II)-OH₂ wagging vibrations are reported to be 405 and 645 cm⁻¹, respectively in Ni(H₂O)₆SiF₆, while those in Mn(H₂O)₆SiF₆ are 395 and 560 cm⁻¹, respectively [21]. If the Ni-O bond in the present system is stronger than the Mn-O bond, Ni salt can have a larger *J* than Mn salt. Electronegativities of Mn, Co and Ni are listed in table 2 [22]. Since Co and Ni are more electronegative than Mn, the O-H···Cl hydrogen bonds in Co and Ni salts are stronger than those in Mn salt, leading to *J* values in the former being larger than those in the latter. Therefore it is concluded that the direct exchange interactions between the paramagnetic ions have a minor effect compared with the indirect interactions in M(II)(H₂O)₆SnCl₆ (M(II) = Mn, Co and Ni), and the small *J* value in Mn salt can be explained by a relatively weak Mn-O bond and a small Mn electronegativity making the O-H···Cl bonds weak.

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