^{2}H NMR Study of Molecular and Electron Spin Dynamics in Paramagnetic $[Co(H_2O)_6][SiF_6]$

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The temperature dependences of ^{2}H NMR spectra and the spin-lattice relaxation time T_1 were measured for $[Co(H_2O)_6][SiF_6]$. The variation of the spectrum above room temperature can be explained by the reorientation of $[Co(H_2O)_6]^{2+}$ about the C_3 axis. The activation energy E_a and the jumping rate at infinite temperature k_0 for the three site jump of $[Co(H_2O)_6]^{2+}$ were obtained as 82 kJmol^{-1} and 2×10^{17}s^{-1} from the spectral simulation. Below room temperature, the spectral line shape was dominated by the 180° flip of the water molecule. The minimum of T_1 caused by the 180° flip of the water molecule was observed at ca. 260 K. The jumping rate of the 180° flip of the water molecule was estimated from the ^{2}H NMR T_1 and the spectral simulation. E_a = 38 kJmol^{-1} and $k_0 = 6\times10^{15}$s^{-1} for the 180° flip of the water molecule were obtained from T_1.

Key words: Phase Transition; ^{2}H NMR; Nuclear Quadrupole Interaction; Paramagnetic Shift; Molecular Dynamics.

Introduction

It is known that $[Co(H_2O)_6][SiF_6]$ undergoes two successive phase transitions [1 - 8]. The phases are denoted by I, II, and III starting from the high temperature side. The symmetry of this crystal is trigonal with a space group $R\bar{3}$ in phase I and reduced to monoclinic with $P2_1/c$ in phase II [3, 4]. The I - II phase transition temperature of T_{c1} = 264.8 K, which rises by ca. 8 K on deuteration, was determined by the heat capacity measurement [5, 6]. The large hysteresis for the I-II phase transition has been reported from several measurements [3, 7, 8]. This phase transition is considered to be closely related to the motions of the $[Co(H_2O)_6]^{2+}$ and $[SiF_6]^{2-}$, since the orientations of $[Co(H_2O)_6]^{2+}$ and $[SiF_6]^{2-}$ octahedra change in phase II, whereas the deviations of these octahedra from the high temperature forms are small [4] and the equivalency of six water molecules is preserved [1]. The II-III phase transition at T_{c2} = 170 K has been reported from ^{2}H NMR measurements on a single crystal [1, 2]. The equivalency of six water molecules is destroyed in phase III. Therefore, the motion of the water molecule is predicted to take part in this phase transition. In the present work, we measured the ^{2}H NMR spectra and spin-lattice relaxation time T_1 in order to clarify the relation between these phase transitions and the motions of $[Co(H_2O)_6]^{2+}$ and H_2O. The change of ^{2}H NMR spectrum owing to the molecular motions was simulated by considering the quadrupole interaction and the dipole interaction between the ^{2}H nucleus and the Co^{2+} ion. The thermal anomalies of the deuterated and protonated samples were also examined by differential thermal analysis (DTA).

Experimental

The deuterated sample was obtained by repeated recrystallization from heavy water. The ^{2}H NMR spectra were measured by using a CMX-300 spectrometer at 45.825 MHz. A $(\pi/2)_x$-τ/2-$(\pi)_y$-τ/2-$(\pi/2)_y$-τ/2-$(\pi)_y$-τ/2-acq pulse sequence was used which refocuses the dephasing due to the quadrupolar interaction and the paramagnetic shift [9 - 13]. The $\pi/2$ pulse width and τ/2 were 2.0 and 20 μs, respectively. T_1 was

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measured by the inversion recovery method. DTA was performed with a home-made apparatus.

Results and Discussion

DTA

DTA measurements were performed between 100 and 300 K. For the deuterated sample, two heat anomalies were detected at 269 and 169 K on heating and 251 and 134 K on cooling. The anomalies at 269 K on heating and 251 K on cooling were considered to correspond to the phase I-II transition. The anomalies at 169 K on heating and 134 K on cooling were considered to correspond to the phase II-III transition. For the protonated sample, the anomalies of the phase II-III transition were not observed although the heat anomalies due to the phase I-II transition were observed at 261 K on heating and 243 K on cooling.

^{2}H NMR Spectra

Figure 1(a) shows the ^{2}H NMR spectra observed in the temperature range of 303 - 393 K. The spectrum showed the asymmetric line shape due to the paramagnetic shift caused by the dipole interaction between the ^{2}H nuclei and Co^{2+} ions. The change of the line shape can be explained by the reorientation of $[Co(H_2O)_6]^{2+}$ about the C_3 axis. The site frequency ω_i, dominated by the nuclear quadrupole interaction and the dipole interaction between the ^{2}H nuclei and Co^{2+} ions, is written as [10 - 13]

$$\omega_i = \mp\omega_Q - \omega_P. \tag{1}$$

Here, ω_Q and ω_P are the contributions of the quadrupole interaction and the dipolar interaction between the ^{2}H nuclei and Co^{2+} ions and written by the second-order Wigner rotation matrix as [11 - 15]

$$\omega_Q = \sqrt{\frac{3}{2}} \sum_{n,m=-2}^{2} D_{0n}^{(2)*}(\psi,\theta,\phi) D_{nm}^{(2)*}(\alpha,\beta,\gamma) T_{mQ}^{(2)}, \tag{2}$$

$$\omega_P = \sum_{n=-2}^{2} D_{0n}^{(2)*}(\psi,\theta,\phi) D_{n0}^{(2)*}(\alpha',\beta',\gamma') \omega_D, \tag{3}$$

$$T_{0Q}^{(2)} = \sqrt{\frac{3}{8}} e^2Qq/\hbar, \; T_{\pm 2Q}^{(2)} = (\eta/4) e^2Qq/\hbar, \tag{4}$$

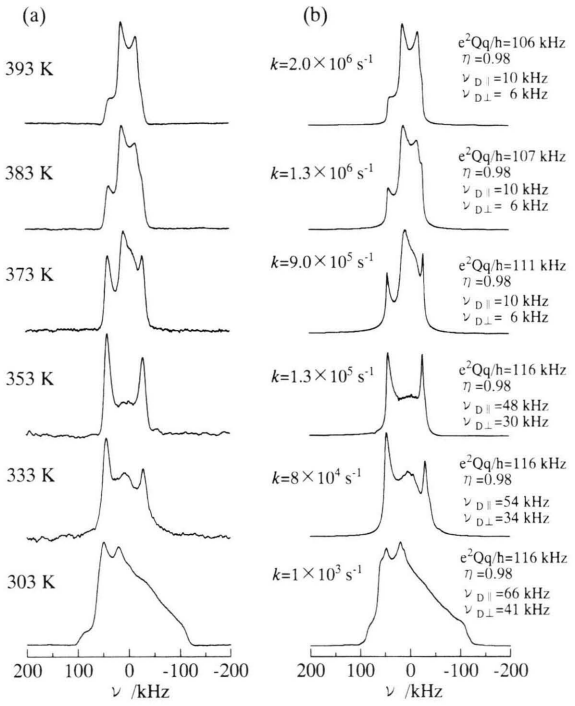

Fig. 1. Temperature dependence of ^{2}H NMR spectra in $[Co(D_2O)_6][SiF_6]$ at high temperatures. (a) and (b) show the observed and the theoretical spectra, respectively.

$$\omega_D = 2\gamma_D g \mu_B \langle \boldsymbol{S}_z \rangle r^{-3}, \tag{5}$$

where (α,β,γ), (ψ,θ,ϕ) and (α',β',γ') represent the Euler angles for the transformation from the molecular axes to the principal axis system of the quadrupolar tensor, from the laboratory axes to the molecular axes and from the molecular axes to the principal axis system of the dipolar tensor between the ^{2}H nuclei and the Co^{2+} ion, respectively. Here, the dipole interaction was confined to the contribution from the nearest Co^{2+} ion. $\langle \boldsymbol{S}_z \rangle$ is the expectation value of $\boldsymbol{S}_z$ of the unpaired electron spin in the Co^{2+} ion. γ_D is the gyromagnetic ratio of the ^{2}H nucleus, μ_B Bohr's magneton and r is the distance between the ^{2}H nucleus and the Co^{2+} ion. For the axial symmetric $\boldsymbol{g}$-tensor, g is given by

$$g = \sqrt{g_\parallel^2 \cos^2\beta'' + g_\perp^2 \sin^2\beta''}, \tag{6}$$

where β'' is an angle between the static magnetic field and the z principal axis of $\boldsymbol{g}$-tensor. In this temperature range, the electric field gradient (EFG) at the ^{2}H nucleus is averaged by the fast 180° flip of the water

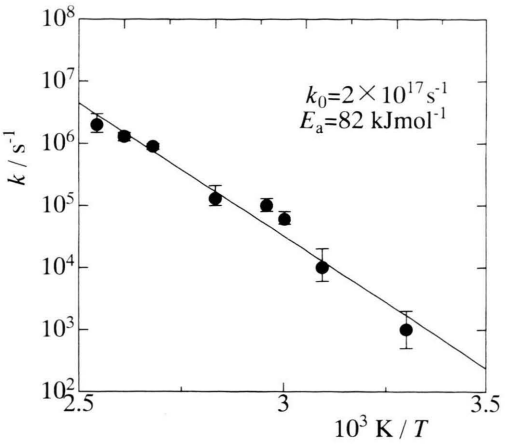

Fig. 2. Temperature dependence of the jumping rate (k) for the reorientation of $[Co(D_2O)_6]^{2+}$. $k_0 = 2 \times 10^{17} s^{-1}$.

molecule. The principal axes system of the averaged EFG tensor (3,2,1) was assigned as follows [16]: the 1 axis is perpendicular to the water molecular plane, the 2 axis lies in the water molecular plane and the 3 axis is parallel to the bisector of D-O-D. Values of β = −84.5° and γ = 42.8° were estimated from the result of the neutron diffraction analysis [3]. β' = 24.0° and γ' = 0° were assumed. The frequencies of the three sites were specified by (α, α') = (0°, 90°), (120°, 210°), and (240°, 330°). β'' is consist with θ, since the z axis of the g-tensor is parallel to the three-fold axis. The simulation of the ^{2}H NMR spectrum was performed by using these angles and the method which was previously described [17]. Figure 1(b) shows the theoretical spectra of the ^{2}H NMR. The jumping rate (k) for the $[Co(H_2O)_6]^{2+}$ ion about the C_3 axis was obtained by the simulation. The temperature dependence of k obtained by the spectral simulation is shown in Figure 2. Assuming an Arrhenius relation, k is given by

$$k = k_0 \exp(-E_a/RT), \tag{7}$$

where k_0 and E_a are the jumping rate at the limit of infinite temperature and the activation energy for the reorientation of $[Co(H_2O)_6]^{2+}$ ion about the C_3 axis. By fitting (7) to the temperature dependence of k, k_0 = 2.0×10^{17} s^{-1} and E_a = 82 kJmol^{-1} were obtained. Figure 3(a) shows the temperature dependence of the ^{2}H NMR spectra observed in the temperature range of 163 - 243 K. The variation of the spectrum was examined by the 180° flip of the water molecule around the bisector of D-O-D. By assuming

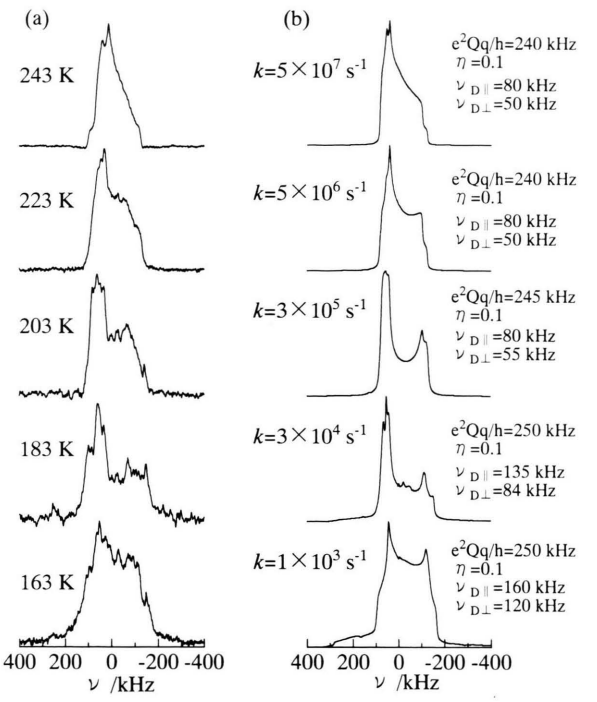

Fig. 3. Temperature dependence of ^{2}H NMR spectra in $[Co(D_2O)_6][SiF_6]$ at low temperatures. (a) and (b) show the observed and the theoretical spectra, respectively.

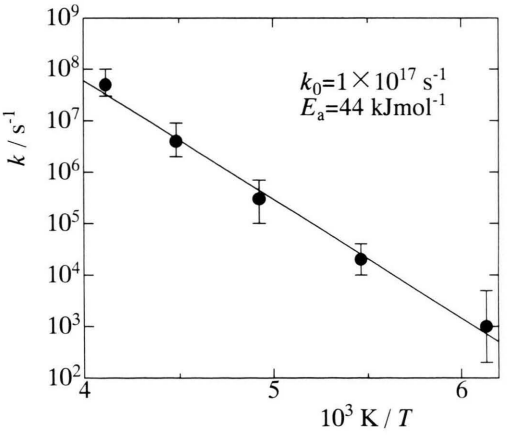

Fig. 4. Temperature dependence of the jumping rate (k) for the 180° flip of the water molecule.

that the direction of Co-O is parallel to the bisector of D-O-D, β = 54.5° and β' = 27.5° were estimated from the result of the neutron diffraction analysis [3]. $\gamma = \gamma'$ = 0° was assumed, and two sites of the ^{2}H nucleus were specified by $\alpha = \alpha'$ = 0° and 180°. Using

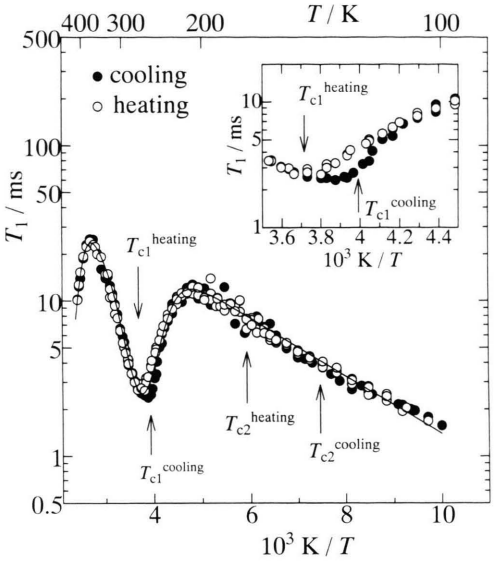

Fig. 5. Temperature dependence of the ^{2}H NMR T_1 in $[Co(D_2O)_6][SiF_6]$. • and ○ show T_1 in cooling and heating processes, respectively. The solid line shows a best-fitted theoretical curve by use of (14).

these angles, the site frequencies of ^{2}H nuclei were calculated from (1) - (6). Figure 3(b) shows the simulated ^{2}H NMR spectra. The temperature dependence of k for the 180° flip of the water molecule obtained by the spectral simulation is shown in Figure 4. k_0 and E_a for the 180° flip of the water molecule were obtained as 1.0×10^{17} s^{-1} and 44 kJmol^{-1} by fitting (7) to the temperature dependence of k.

Figure 5 shows the temperature dependence of ^{2}H NMR T_1. Because of the decomposition of the complex, T_1 could not be observed above ca. 415 K. The hysteresis of T_1 was observed around T_{c1}, whereas the considerable change of T_1 due to the phase transition was not seen around T_{c2}. Above ca. 380 K, T_1 decreased with increasing temperature. In this temperature range, T_1 is considered to be dominated by the reorientation of $[Co(H_2O)_6]^{2+}$. The contribution from the reorientation of $[Co(H_2O)_6]^{2+}$ to T_1 is written as

$$T_{1re}^{-1} = C_{re}\exp(-E_a^{re}/RT). \tag{8}$$

The minimum of T_1 observed at ca. 260 K is considered to be due to the 180° flip of the water molecule. The relaxation rate due to the 180° flip of the water

Table 1. The optimized parameters for the respective contributions to the spin-lattice relaxation rate of ^{2}H NMR of $[Co(D_2O)_6][SiF_6]$.

Reorientation of $[Co(D_2O)_6]^{2+}$	C_{re}/s^{-1}	2.2×10^{12}
	E_a^{re}/kJmol^{-1}	83
180° Flip of D_2O	C_{fl}/s^{-1}	7.1×10^{10}
	E_a^{fl}/kJmol^{-1}	38
	τ_{c0}^{fl}/s	8.0×10^{-17}
Electron spin in Co^{2+}	C_{el}/s^{-1}	10
	Δ/cm^{-1}	300
	τ_{e0}/s	2.5×10^{-13}

molecule is written by assuming $\eta = 0$ as [18 - 20]

$$T_{1fl}^{-1} = C_{fl}\left\{\frac{\tau_c}{1+\omega_D^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_D^2\tau_c^2}\right\}, \tag{9}$$

$$C_{fl} = \frac{1}{10}\left(\frac{3e^2Qq}{4\hbar}\right)^2(\sin 2\beta)^2, \tag{10}$$

where ω_D is the angular NMR frequency of the ^{2}H nucleus. β is the angle between the O-H bond and the flipping axis. The correlation time τ_c is described by Arrhenius relation as

$$\tau_c = \tau_{c0}^{fl}\exp(E_a^{fl}/RT). \tag{11}$$

Below ca. 200 K, T_1 decreased exponentially with decreasing temperature. T_1 is considered to be dominated by the fluctuation of the dipole interaction between the ^{2}H nuclei and Co^{2+} ions caused by the fast electron spin-lattice relaxation of Co^{2+} due to the Orbach process [21, 22]. In this case, the relaxation rate can be written as

$$T_{1el}^{-1} = C_{el}\exp(\Delta/kT), \tag{12}$$

$$C_{el} = \frac{2}{5}\gamma^2g^2\mu_B^2\sum_i r_i^{-6}S(S+1)\tau_{e0}. \tag{13}$$

Here, τ_{e0} is the electron spin correlation time at infinite temperature and Δ the energy difference between the electric ground and first excited states of the Co^{2+} ion. r_i is the distance between the ^{2}H nucleus and i-th Co^{2+} ion. $\sum_i r_i^{-6}$ was obtained from the crystal data of $[Co(H_2O)_6][SiF_6]$ [3], and the contribution from paramagnetic ions with 11^3 primitive cells around the resonant nucleus was calculated. The temperature dependence of T_1 can be explained by the equation

$$T_1^{-1} = T_{1re}^{-1} + T_{1fl}^{-1} + T_{1el}^{-1}. \tag{14}$$

A least-squares fitting calculation was performed using (14) with C_{re}, E_a^{re}, C_{fl}, E_a^{fl}, τ_{c0}^{fl}, C_{el}, and Δ as parameters. The best fit parameters are listed in Table 1. The electron spin correlation time of Co^{2+} was obtained as $\tau_e = 2.5\times10^{-13}\exp(300/kT)$ s from (12) and (13). The reorientation of $[Co(H_2O)_6]^{2+}$ about the C_3 axis is predicted to dominate T_1 at high temperatures, since the activation energy estimated from T_1 is consistent with the result of the spectral simulation. For the 180° flip of the water molecule, k_0 was estimated as $6\times10^{15}s^{-1}$ from T_1 by using the relation $k = (2\tau_c)^{-1}$. The k value estimated from T_1 agreed with the result of the spectral simulation within the limits of accuracy.

Conclusions

The reorientation of $[Co(H_2O)_6]^{2+}$ about the C_3 axis was found to occur most frequently in the reorientations about the C_2, C_3, and C_4 axes at high temperatures. The reorientation of $[Co(H_2O)_6]^{2+}$ becomes very slow near T_{c1}, although the fast 180° flip of the water molecule occurs. The rate of the 180° flip of the water molecule decreases to the order of about 10^3 s^{-1} near T_{c2}. The destruction of the equivalency of six water molecules due to the II-III phase transition may be associated with the change of the hydrogen bonding network owing to the freeze of the 180° flip of the water molecule.

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