Studies of Successive Phase Transitions and Molecular Motions in $[Mg(H_2O)_6][SiF_6]$ by $^{1,2}H$ and ^{19}F NMR*

Junko Kimura, Takeshi Fukase, Motohiro Mizuno, and Masahiko Suhara
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920-1192, Japan.

Z. Naturforsch. **53 a,** 453–458 (1998); received December 31, 1997

The successive phase transitions of $[Mg(H_2O)_6][SiF_6]$ were studied by measuring ^2H NMR spectra. The quadrupole coupling constant e^2Qq/h and asymmetry parameter η changed drastically at each transition temperature. $^{1,2}H$ and ^{19}F NMR T_1 were measured for this compound to study the relation between the molecular motions and the successive phase transitions. The activation energy E_a and the pre-exponential factor τ_0 for the reorientation of $[SiF_6]^{2-}$ were estimated as 28 kJmol^{-1} and 6.0×10^{-14} s, and those of the 180° flip of H_2O as 33 kJmol^{-1} and 4.0×10^{-14} s. These two motions occur rapidly even in phase V. For the reorientation of $[Mg(H_2O)_6]^{2+}$, E_a = 62 kJmol^{-1} and $\tau_0 = 1.1\times10^{-16}$ s were obtained from the simulation of ^2H NMR spectra. The jump rate of this motion is of the order of 10^4 - 10^6 s^{-1} in phase II. These results suggest that the successive phase transitions are closely related to the motion of $[Mg(H_2O)_6]^{2+}$.

Introduction

For most of the $[M(H_2O)_6][SiF_6]$ type crystals, the structural phase transitions have been reported. Although these phase transitions are considered to be due to the order-disorder of $[M(H_2O)_6]^{2+}$ and $[SiF_6]^{2-}$ [1], a systematic interpretation was not obtained. Especially, $[Mg(H_2O)_6][SiF_6]$ is known to have five stable phases [2]. Phase II is the incommensurate phase. The modulated structure in phase II has been studied by use of ESR spectroscopy, and a drastic change in the modulation amplitude at 343 K has been reported [2 - 4]. Although the investigations have been performed with the diffraction methods, a detailed analysis of the modulated structure in the incommensurate phase has not been done [5 - 8]. These phase transitions can be considered to be related to the motions of H_2O, $[Mg(H_2O)_6]^{2+}$ and $[SiF_6]^{2-}$. Studies about the motions of $[Mg(H_2O)_6]^{2+}$ and $[SiF_6]^{2-}$ have been carried out by means of ^1H and ^{19}F NMR [2, 9, 10]. Because of the cross relaxation between ^1H and ^{19}F, information about the motion of H_2O has not been obtained from ^1H NMR. In the present work, in each phase ^2H NMR spectra and T_1 have been measured. For $[Mg(H_2O)_6]^{2+}$, the reorientations about C_2, C_3 and C_4 axes are considered. We clarified, which motional mode occurs most frequently and estimated the jumping rate in the incommensurate phase from the spectral simulation. From ^2H NMR T_1, the 180° flip of H_2O and the reorientation of $[Mg(H_2O)_6]^{2+}$ were investigated. By measuring ^1H and ^{19}F NMR T_1, the differences in the motion of $[Mg(H_2O)_6]^{2+}$ and $[SiF_6]^{2-}$ between the protonated and the deuterated compounds were studied.

* Presented at the XIVth International Symposium on Nuclear Quadrupole Interactions, Pisa, Italy, July 20–25, 1997.

Reprint requests to Dr. M. Mizuno; E-mail: mizuno@wriron1.s.kanazawa-u.ac.jp.

Experimental

$[Mg(D_2O)_6][SiF_6]$ was prepared by the recrystallization from heavy water. ^2H NMR was measured by a CMX-300 spectrometer with a 10 mmø glass sample tube at 45.825 MHz. For ^2H NMR spectra, the $(\pi/2)_x - \tau - (\pi/2)_y - \tau$-acq pulse sequence was used. The $\pi/2$ pulse width and τ were set at 2.0 µs and 40 µs, respectively. ^1H and ^{19}F NMR were measured by a home-made pulse NMR spectrometer at 25.000 MHz. The inversion recovery method was used for the measurements of T_1.

Results and Discussion

^2H NMR Spectra

Figure 1 shows ^2H NMR spectra of each phase. The spectrum at 255 K showed the typical shape of a large

0932-0784 / 98 / 0600-0453 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

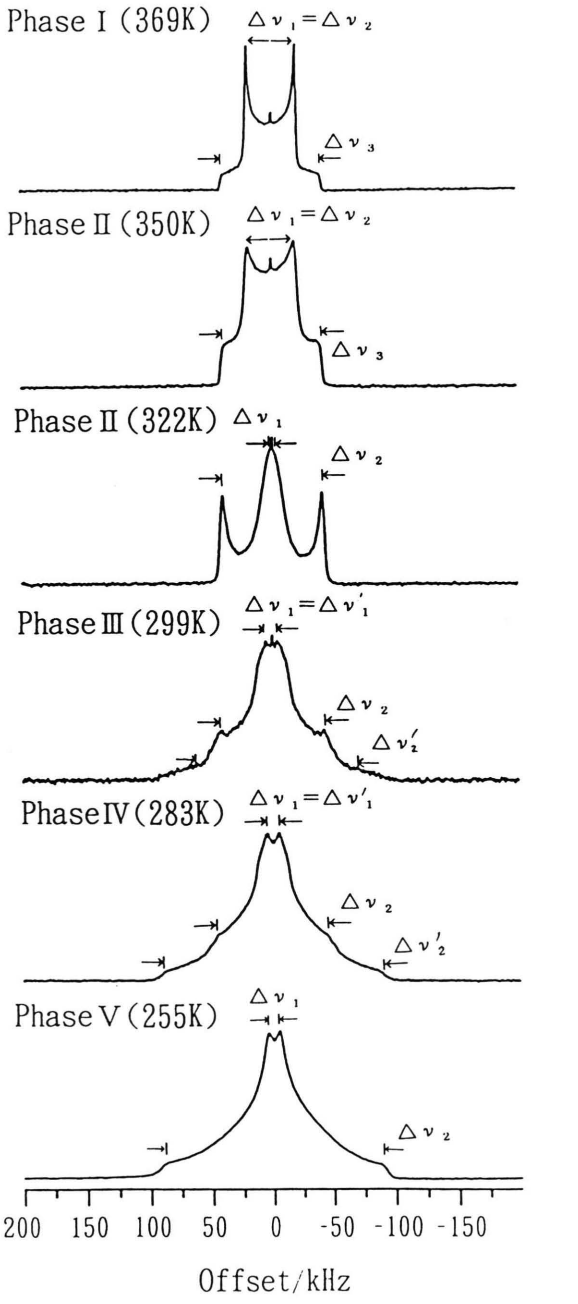

Fig. 1. ^{2}H NMR spectra in each phase of $[Mg(H_2O)_6][SiF_6]$.

η value due to the rapid 180° flip of H_2O molecules. The temperature change of the spectral lineshape can be caused by the reorientation of $[Mg(H_2O)_6]^{2+}$. Figure 2 shows the temperature dependences of the averaged e^2Qq/h and η, which were estimated from the spectral width shown in Fig. 1 by the equations [11]

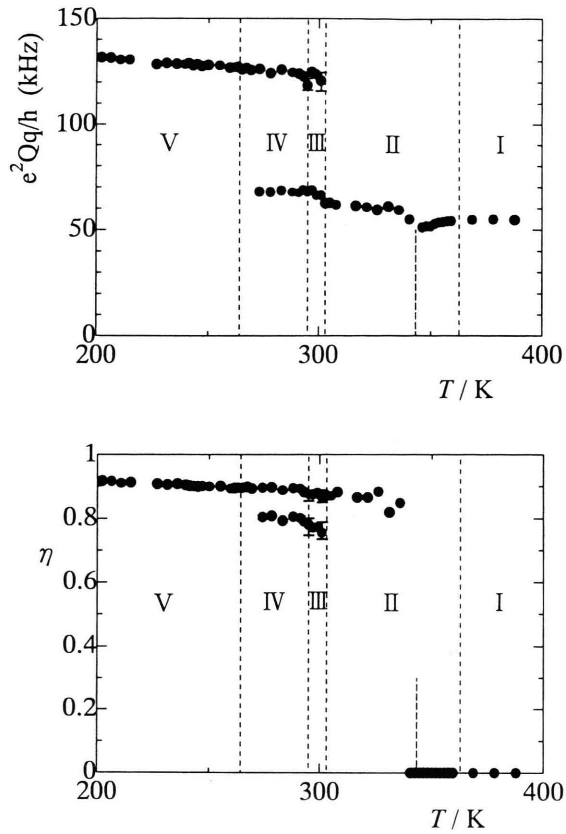

Fig. 2. Temperature dependence of the motional averaged quadrupole coupling constant e^2Qq/h and the asymmetry parameter η in $[Mg(D_2O)_6][SiF_6]$.

$$\Delta\nu_1 = \frac{3e^2Qq}{4h}(1-\eta), \quad (1)$$

$$\Delta\nu_2 = \frac{3e^2Qq}{4h}(1+\eta), \quad (2)$$

$$\Delta\nu_3 = \frac{3e^2Qq}{2h}. \quad (3)$$

e^2Qq/h and η changed continuously at the I - II and the III - IV transitions and discontinuously at other transitions. The continuity of e^2Qq/h and η at the I - II phase transition is consistent with the fact that the normal-incommensurate transition is of second order. For the III - IV transition, a large change in the structure between phase III and IV has not also been observed by ESR [2]. Additional discontinuities of e^2Qq/h and η were observed at 343 K. A drastic change of ESR spectra has been reported at the same temperature [2 - 4] and the existence of a phase transition is predicted. For the reorientation of $[Mg(H_2O)_6]^{2+}$ can be considered to occur most frequently around the C_3 axis, since the spectra at high temperature showed an axially symmetric lineshape and only one component of e^2Qq/h and η [11]. A simulation of ^{2}H NMR spectra in phase II was performed, using the three-site jump model around the C_3 axis of $[Mg(H_2O)_6]^{2+}$ with the averaged e^2Qq/h and η values due to the fast 180° flip of H_2O. $e^2Qq/h = 127$ kHz and $\eta = 0.9$ were obtained from the spectrum at 255 K. The principal axes system of the EFG tensor (3,2,1), averaged for the fast 180° flip of H_2O, was assigned as follows: The 1 axis is perpendicular to the water molecular plane, the 2 axis stays in the water plane and the 3 axis is parallel to the bisector of HOH. For the static quadrupole principal axes (x, y, z) it was assumed that the z axis is parallel to O-H bond and the y axis perpendicular to the water molecular plane. The site frequency ω_i is written by the second-order Wigner rotation matrix $D^{(2)*}_{nm}(\Omega)$ [12] as

$$\omega_i = \sqrt{\frac{3}{2}} \sum_{n,m=-2}^{2} D^{(2)*}_{0n}(\psi,\theta,\phi) D^{(2)*}_{nm}(\alpha,\beta,\gamma) T^{(2)}_{m\mathrm{Q}}, \tag{4}$$

$$T^{(2)}_{0\mathrm{Q}} = \sqrt{\frac{3}{8}}\, e^2Qq/\hbar, \quad T^{(2)}_{\pm 2\mathrm{Q}} = (\eta/2) e^2Qq/\hbar, \tag{5}$$

where (α, β, γ) and (ψ, θ, ϕ) are the Euler angles for the transformation from the molecular axes to the principal axes system of the quadrupolar tensor and from the laboratory axes to the molecular axes, respectively. $\beta = 78.9°$, and $\gamma = 46.6°$ were estimated from the result of the neutron diffraction analysis [8]. The frequencies of the three sites were specified by $\alpha = 0°$, 120°, and 240°. The quadrupole echo signal $G(t, \theta, \phi)$ is written as [13]

$$G(t,\theta,\phi) = \boldsymbol{P} \cdot \exp[\hat{\boldsymbol{A}} t] \exp(\hat{\boldsymbol{A}} \tau) \exp(\hat{\boldsymbol{A}}^* \tau) \cdot \boldsymbol{1}, \tag{6}$$

$$\hat{\boldsymbol{A}} = \begin{pmatrix} i\omega_1 - 2k & k & k \\ k & i\omega_2 - 2k & k \\ k & k & i\omega_3 - 2k \end{pmatrix}, \tag{7}$$

$$\boldsymbol{P} = (P_1, P_2, P_3), \quad \boldsymbol{1} = (1,1,1). \tag{8}$$

Here, $\boldsymbol{P}$ is a vector of site populations, and we assumed $P_1 = P_2 = P_3 = 1/3$. The signal of a powder sample, $G(t)$ was given by averaging over (θ,ϕ) and the spectra were obtained by Fourier transform of $G(t)$. Figure 3 shows the temperature dependence of the observed and simulated spectra of ^{2}H NMR. The good agreement between the observed and calculated spectra shows that the applied model is appropriate. The temperature dependence of the jumping rate k for the reorientation of $[Mg(H_2O)_6]^{2+}$ is shown in Figure 4. Assuming an Arrhenius relation, k is given

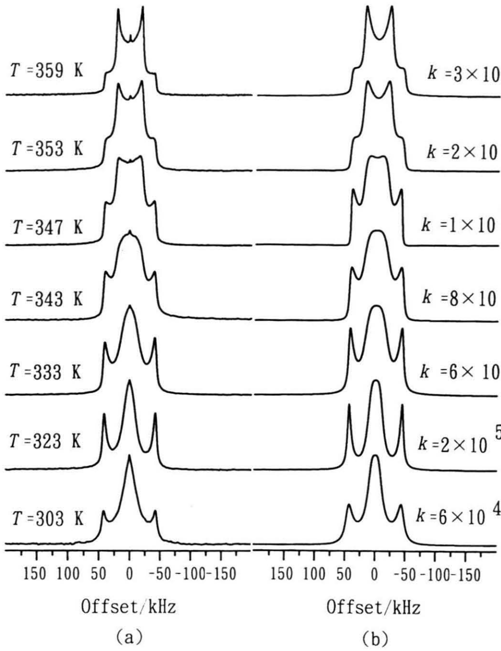

Fig. 3. Temperature dependence of ^{2}H NMR spectra in Phase II of $[Mg(D_2O)_6][SiF_6]$. (a) and (b) show the observed and simulated spectra, respectively.

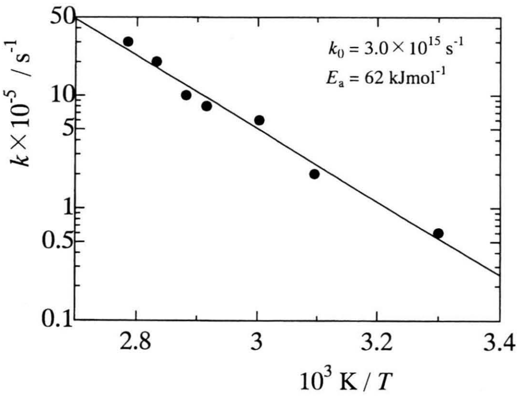

Fig. 4. Temperature dependence of the jumping rate (k) for the reorientation of $[Mg(H_2O)_6]^{2+}$ in phase II.

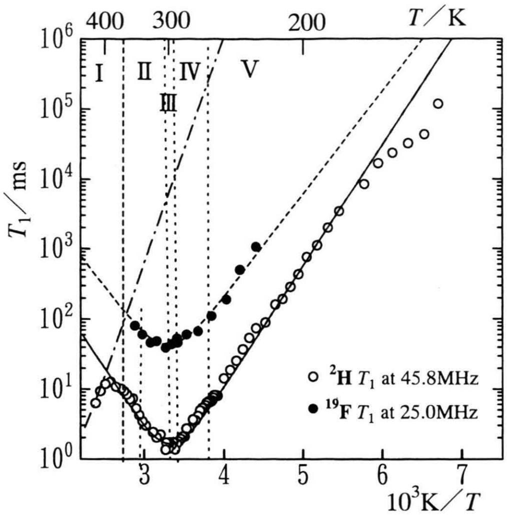

Fig. 5. Temperature dependence of the ^{2}H and ^{19}F NMR T_1 in $[Mg(D_2O)_6][SiF_6]$. The solid and broken lines show the theoretical curves.

by

$$k = k_0 \exp(-E_a/RT), \tag{9}$$

where, k_0 and E_a are the jumping rate at infinite temperature and the activation energy for the reorientation around the C_3 axis of the $[Mg(H_2O)_6]^{2+}$ ions. By fitting (9) to the temperature dependence of k, $k_0 = 3.0\times10^{15}$ s^{-1} and $E_a = 62$ kJmol^{-1} were obtained.

^{2}H, ^{19}F T_1 in $[Mg(D_2O)_6][SiF_6]$

Figure 5 shows the temperature dependences of ^{2}H and ^{19}F T_1 in $[Mg(D_2O)_6][SiF_6]$ (denoted as T_{1D} and T_{1F}). Both T_{1D} and T_{1F} showed a minimum at ca. 306 K, and T_{1D} decreased rapidly with increasing temperature above ca. 390 K. A drastic change of T_1 for both nuclei was not observed at the phase transition temperatures. T_{1F} can be considered to be determined dominantly by the fluctuation of the ^{19}F-^{19}F dipolar interactions caused by the reorientation of $[SiF_6]^{2-}$. In this case, T_{1F} is written as [14]

$$T_{1F}^{-1} = \frac{2}{3}\gamma_F^2 \Delta M_2 \left\{ \frac{\tau_F}{1+\omega_F^2\tau_F^2} + \frac{4\tau_F}{1+4\omega_F^2\tau_F^2} \right\}, \tag{10}$$

where ω_F and γ_F are the angular NMR frequency and the gyromagnetic ratio of ^{19}F. ΔM_2 is the amount of second moment reduction, and τ_F is the correlation time of the reorientation of $[SiF_6]^{2-}$, expressed as

$$\tau_F = \tau_{0F} \exp(E_{aF}/RT). \tag{11}$$

The least-squares fitting was performed with (10), (11) and $\tau_{0F} = 6.0\times10^{-14}$ s and $E_{aF} = 28$ kJmol^{-1} were obtained. T_{1D} can be considered to be dominated by the fluctuation of the EFG due to the reorientation of $[Mg(H_2O)_6]^{2+}$ and the 180° flip of H_2O above and below ca. 390 K. When the relaxation of the ^{2}H nuclear spin is caused by the 180° flip of H_2O, T_{1D} is given by using the static quadrupole interaction parameters e^2Qq_{stat}/h and η_{stat} in the absence of averaging by the 180° flip of H_2O. Assuming $\eta_{stat} = 0$, T_{1D} can be written as [15]

$$T_{1D}^{-1} = C_Q \left\{ \frac{\tau_D}{1+\omega_D^2\tau_D^2} + \frac{4\tau_D}{1+4\omega_D^2\tau_D^2} \right\}, \tag{12}$$

$$C_Q = \frac{1}{10}\left(\frac{3e^2Qq_{stat}}{4\hbar}\right)^2 (\sin 2\beta')^2, \tag{13}$$

where ω_D is the angular NMR frequency of ^{2}H. β' is the angle between the O-H bond and the flipping axis. The correlation time τ_D is written as

$$\tau_D = \tau_{0D} \exp(E_{aD}/RT). \tag{14}$$

Below 360 K, a least-squares fitting was performed using (12) - (14) with C_Q, τ_{0D} and E_{aD} as parameters. τ_{0D} and E_{aD} were obtained as 4.0×10^{-15} s and 33 kJmol^{-1}, respectively. The e^2Qq_{stat}/h value was estimated to be 240 kHz from the obtained C_Q value, using $\beta' = 53.9°$ given by the neutron diffraction analysis [8]. The principal values of the EFG tensor ($eq_{33}, eq_{22}, eq_{11}$), averaged for the 180° flip of H_2O, are written by using eq_{stat} and η_{stat} [11] as

$$eq_{11} = -\frac{1}{2} eq_{stat}(1+\eta_{stat}), \tag{15}$$

$$eq_{22} = \frac{1}{4} eq_{stat}[(1-3\cos 2\beta') + \eta_{stat}(1+\cos 2\beta')], \tag{16}$$

$$eq_{33} = \frac{1}{4} eq_{stat}[(1+3\cos 2\beta') + \eta_{stat}(1-\cos 2\beta')]. \tag{17}$$

In the case of $\beta' = 53.9°$, $|eq_{11}| > |eq_{22}| > |eq_{33}|$ holds. From the spectrum at 255 K, using (15) - (17), e^2Qq_{stat}/h and η_{stat} were estimated as 248 kHz and 0.05, respectively. The result that the e^2Qq_{stat}/h and

Table 1. Activation energies E_a and correlation times τ_0 at the limit of infinite temperature for each motion in $[Mg(D_2O)_6][SiF_6]$.

Motional mode	E_a/kJmol^{-1}	τ_0/s	Method
reorientation of $[SiF_6]^{2-}$	28	6.0×10^{-14}	$^{19}F\ T_1$
180° flip of H_2O	33	4.0×10^{-15}	$^{2}H\ T_1$
reorientation of $[Mg(H_2O)_6]^{2+}(C_3)$	62 (phase II)	1.1×10^{-16}	^{2}H spectra
reorientation of $[Mg(H_2O)_6]^{2+}$	62 (phase I)	—	$^{2}H\ T_1$

η_{stat} values obtained from T_1 measurements agree with those obtained from the spectrum is considered to indicate that T_{1D} is determined by the fluctuation of the EFG due to the 180°flip of H_2O in this temperature range. Above 390 K, an activation energy E_a for the reorientation of $[Mg(H_2O)_6]^{2+}$ was obtained as 62 kJmol^{-1} from the slope of the logT_{1D} vs. $1/T$ plot. The τ_0 and E_a values for the 180° flip of H_2O and the reorientations of $[SiF_6]^{2-}$ and $[Mg(H_2O)_6]^{2+}$ obtained from T_1 and the spectra are listed in Table 1. Here, τ_0 for the reorientations of $[Mg(H_2O)_6]^{2+}$ in phase II was obtained by converting k_0 to τ_0 with the relation $\tau = (3k)^{-1}$. A large change of E_a for the reorientation of $[Mg(H_2O)_6]^{2+}$ between phase I and II was not observed. The correlation time for the reorientation of $[Mg(H_2O)_6]^{2+}$ changes from the order of 10^{-5} s to 10^{-7} s in phase II. On the contrary, those for the 180° flip of H_2O and the reorientation of $[SiF_6]^{2-}$ become the order 10^{-8} s in phase V. Therefore, the reorientation of $[Mg(H_2O)_6]^{2+}$ about the C_3 axis can be considered to play an important role in the successive phase transitions.

^1H,^{19}F T_1 in $[Mg(H_2O)_6][SiF_6]$

The magnetization recoveries of both ^1H and ^{19}F showed a non-exponential time dependence due to the cross relaxation between ^1H and ^{19}F [16]. In phase V, those of both nuclei could be separated into two components, and T_1 of each component could be estimated. In the other phases, however, T_1 was determined from the initial portion of the magnetization recoveries, which showed an exponential time dependence, since the separation of the two components was difficult. Figure 6 shows the temperature dependences of ^1H and ^{19}F T_1. At low temperatures, T_1 may be determined by the reorientation of $[SiF_6]^{2-}$ [10]. Above ca. 340 K, ^1H T_1 decreased rapidly. In this temperature range, the relaxation of ^1H is probably dominated by the reorientation of $[Mg(H_2O)_6]^{2+}$. The observed relaxation rate T_1^{-1} can be explained by the eigen values (R_1, R_2) of the relaxation matrix [17]

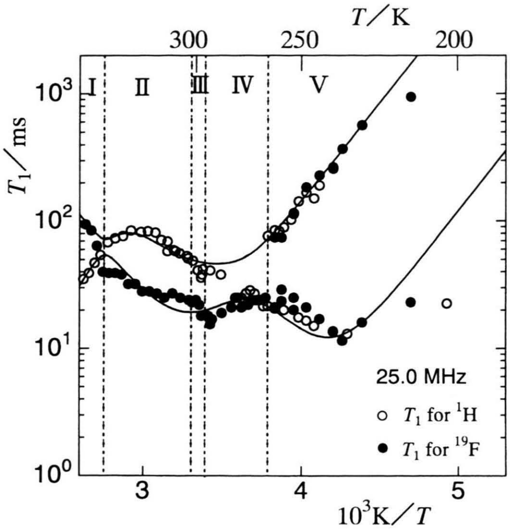

Fig. 6. Temperature dependence of the ^1H and ^{19}F NMR T_1 in $[Mg(H_2O)_6][SiF_6]$. The solid lines show the theoretical curves.

$$\boldsymbol{R} = \begin{pmatrix} R_H & R_{HF} \\ R_{FH} & R_F \end{pmatrix}, \tag{18}$$

where

$$R_H = C_{HH}\gamma_H^2 g(\omega_H, \tau_H) + C_{HF}\gamma_H^2 g_H(\omega_{HF}, \tau_H) + C'_{HF}\gamma_H^2 g_H(\omega_{HF}, \tau_F), \tag{19}$$

$$R_F = C_{FF}\gamma_F^2 g(\omega_F, \tau_F) + C'_{FH}\gamma_F^2 g_F(\omega_{HF}, \tau_F) + C_{FH}\gamma_F^2 g_F(\omega_{HF}, \tau_H), \tag{20}$$

$$R_{HF} = C'_{FH}\gamma_F^2 g(\omega_{HF}, \tau_F) + C_{FH}\gamma_F^2 g(\omega_{HF}, \tau_H), \tag{21}$$

$$R_{FH} = C_{HF}\gamma_H^2 g(\omega_{HF}, \tau_H) + C'_{HF}\gamma_H^2 g(\omega_{HF}, \tau_F), \tag{22}$$

$$g(\omega_i, \tau_j) = \frac{\tau_j}{1+\omega_i^2\tau_j^2} + \frac{4\tau_j}{1+4\omega_i^2\tau_j^2}, \tag{23}$$

$$g(\omega_{HF}, \tau_j) = \frac{-\tau_j}{1+(\omega_H-\omega_F)^2\tau_j^2} + \frac{6\tau_j}{1+(\omega_H+\omega_F)^2\tau_j^2}, \tag{24}$$

$$g_i(\omega_{HF}, \tau_j) = \frac{\tau_j}{1+(\omega_H-\omega_F)^2\tau_j^2} + \frac{3\tau_j}{1+\omega_i^2\tau_j^2} + \frac{6\tau_j}{1+(\omega_H+\omega_F)^2\tau_j^2}. \tag{25}$$

Table 2. Activation energies E_a, correlation times τ_0 at the limit of infinite temperature, and motional constant C for the reorientation of $[Mg(H_2O)_6]^{2+}$ and $[SiF_6]^{2-}$ in $[Mg(H_2O)_6][SiF_6]$

Motional mode	E_a/kJmol^{-1}	τ_0/s	C/G^2
reorientation of $[SiF_6]^{2-}$	30	3.0×10^{-14}	$C_{FF} = 6.0$ $C'_{FH} = 1.0$ $C'_{HF} = 1.2$
reorientation of $[Mg(H_2O)_6]^{2+}$	50	6.0×10^{-15}	$C_{HH} = 19$ $C_{FH} = 0$ $C_{HF} = 0$

γ_H and γ_F are the gyromagnetic ratios of ^{1}H and ^{19}F, respectively and C_{ij}, C'_{ij} $(i, j$ = H, F) are the parameters related to the second moments. τ_j (j = H, F) represents the correlation times of the reorientation of $[Mg(H_2O)_6]^{2+}$ and $[SiF_6]^{2-}$. τ_j for each motion may be discribed by

$$\tau_j = \tau_{0j}\exp(E_{aj}/RT). \quad (26)$$

The fitting calculations of R_1^{-1} and R_2^{-1} to the observed ^{1}H and ^{19}F T_1 were performed by using (18)-(26) with C_{ij}, C'_{ij} $(i, j$ = H, F), τ_{0j}, and E_{aj} (j=H,F) as parameters. The determined parameters are given in Table 2. Here, τ_{0H} was estimated by using $C_{HH} = 19\,G^2$, which was obtained from the experimental result of the second moment reduction ΔM_2 [9], using the relation $C = (2/3)\Delta M_2$. The activation energy for the reorientation of $[SiF_6]^{2-}$ in $[Mg(H_2O)_6][SiF_6]$ was similar to that of $[Mg(D_2O)_6][SiF_6]$. For the reorientation of $[Mg(H_2O)_6]^{2+}$, however, the activation energy for the protonated compound was smaller than that of the deuterated compound. The difference of mass between H and D can be considered to contribute largely in the change of the activation energy for the reorientation of $[Mg(H_2O)_6]^{2+}$.

[1] A. Kassiba, R. Hrabanski, D. Bonhomme, and A. Hader, J. Phys. Condens. Matter **7**, 3339 (1995).
[2] M. Suhara, T. Bandoh, T. Kitai, T. Kobayashi, and H. Katsuda, Phase Transitions **37**, 111 (1992).
[3] A. M. Ziatdinov, V. G. Kuryavyi, and R. L. Davidovich, Sov. Phys. Solid State **27**, 1288 (1985).
[4] A. M. Ziatdinov, V. G. Kuryavyi, and R. L. Davidovich, Sov. Phys. Solid State **30**, 1833 (1988).
[5] S. Syoyama and K. Osaki, Acta Cryst. **B28**, 2626 (1972).
[6] G. Jehanno and F. Varret, Acta. Cryst. **A31**, 857 (1975).
[7] G. Chevrier and G. Jehanno, Acta. Cryst. **A35**, 912 (1979).
[8] G. Chevrier, J. Sol. St. Chem. **99**, 276 (1992).
[9] J. M. Dereppe, P. W. Lobo, and M. V. Meerssche, J. Chim. Phys. **61**, 1076 (1964).
[10] D. B. Utton and T. Tsang, J. Chem. Phys. **56**, 116 (1972).
[11] R. G. Barnes, Advances in Nuclear Quadrupole Resonance, Vol. 1, ed. by J. A. S. Smith, Heyden, London 1974, p. 335.
[12] M. E. Rose, Elementary Theory of Angular Momentum, Wiley, New York 1957.
[13] M. S. Greenfield, A. D. Ronemus, R. L. Vold, R. R. Vold, P. D. Ellis, and T. E. Raidy, J. Magn. Reson. **72**, 89 (1987).
[14] N. Bloembergen, E. M. Purcell, and R. Pound, Phys. Rev. **73**, 679 (1948).
[15] D. A. Torchia and A. Szabo, J. Magn. Reson. **49**, 107 (1982).
[16] A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press, London 1961.
[17] S. Albert and H. S. Gutowsky, J. Chem. Phys. **59**, 3585 (1973).