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Deuteron Magnetic Resonance of $NiSiF_6 \cdot 6D_2O$ and $NiSnCl_6 \cdot 6D_2O$

Takehiko CHIBA[*1] and Gen SODA[*2]

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo

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Deuteron magnetic resonance study was made on single crystals of $NiSiF_6 \cdot 6D_2O$ and $NiSnCl_6 \cdot 6D_2O$. Deuteron quadrupole coupling tensors were determined at various temperatures. In $NiSiF_6 \cdot 6D_2O$, the quadrupole coupling at −116°C is that of stationary D_2O, at 23°C and at 70°C that of D_2O under rapid 180°-flip motion and at 150°C that of rapid $Ni(D_2O)_6{}^{2+}$ reorientation. The eqQ/h values at −116°C, 238.3±1.3 kc and 235.7±1.9 kc do not appear to show marked effect of strong coordination. In $NiSnCl_6 \cdot 6D_2O$, the quadrupole coupling corresponding to D_2O under 180°-flip motion is observed at −53°C, at 25°C, and at 55°C. Spectra corresponding to a stationary D_2O are not observed even at 77°K. From the orientation of quadrupole tensors probable crystal structures of these compounds are proposed. Line width transitions were observed from which the reorientation rate was derived. The estimated activation energies of the 180°-flip motion of D_2O are 7.6 and 4.3 kcal/mol in the fluosilicate and chlorostannate, respectively, and that of $Ni(D_2O)_6{}^{2+}$ reorientation in the fluosilicate is 19 kcal/mol. Additional measurements of ^{19}F and ^1H resonances indicate the setting in of the $SiF_6{}^{2-}$ reorientation at −110°—−120°C in $NiSiF_6 \cdot 6H_2O$, and that of the $Ni(H_2O)_6{}^{2+}$ reorientation in the chlorostannate at approximately the same temperature as the fluosilicate.

It has been shown in recent studies that the deuteron magnetic resonance (DMR) can provide useful informations about the structure and the motion of hydration water in crystals.[1,2] DMR of some O–D···O systems revealed strong dependence

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[*1] Present address: Department of Chemistry, Nihon University, Sakurajosui, Setagaya-ku, Tokyo.

[*2] Present address: Department of Physical Chemistry, Faculty of Science, Osaka University, Toyonaka.

1) T. Chiba, *J. Chem. Phys.*, **39**, 947 (1963).

2) T. Tsang and D. E. O'Reilly, *ibid.*, **43**, 4234 (1965).

of the deuteron quadrupole coupling on the hydrogen bond strength.3) Temperature dependence of the line-width was used to determine the barrier to the motion of water molecule in crystals.1-3)

When the position of a water molecule is fixed by hydrogen bondings of X···H–O–H···Y, the activation energy to reorientation may be considered to be the work required to break these hydrogen bondings. Then the activation energy would be a good measure of the strength of the hydrogen bond.

The purpose of the present study is (1) to see the effect of strong coordination of a water molecule to a metal ion on the deuteron quadrupole coupling, and (2) to study the motion of a water molecule where hydrogen bond is to atoms other than oxygen, for instance, to chlorine where hydrogen bond is supposed to be weak, and also to study other possible motions such as an over-all rotation of a cluster ion.

It may be noted that frequently used technique for the study of motions in crystals is the measurement of temperature dependence of the spin-lattice relaxation time T_1, which in the present case is inapplicable, because of the strong relaxation due to the presence of paramagnetic ions.

The compounds studied here are $NiSiF_6 \cdot 6D_2O$ and $NiSnCl_6 \cdot 6D_2O$. The crystal structures of these compounds are isomorphous, consisting of $Ni(H_2O)_6{}^{2+}$ and $(SiF_6)^{2-}$ or $(SnCl_6)^{2-}$ group ions. According to Pauling's early X-ray analysis,4) the crystal is trigonal of space group $R\bar{3}$, assuming distorted CsCl-like structure. One formula unit is contained in a unit cell. All the water molecules are in equivalent positions.

Experimental

Preparation of the Crystals. A single crystal of $NiSiF_6 \cdot 6D_2O$ (which had been grown from a solution of this compound synthesized from $BaSiF_6$ and $NiSO_4$ in heavy water) was kindly supplied by K. Kume. The crystal exhibits {110} and {1$\bar{1}$0} faces.

$NiSnCl_6 \cdot 6D_2O$. A solution of this compound was prepared by adding an equivalent amount of $NiCl_2$ into heavy water solution of $SnCl_4$. A single crystal was grown by slowly lowering the temperature of the saturated solution. The crystal exhibits dominant {100} faces.

Measurement of DMR. The apparatus and the method of the measurement of DMR have been described elsewhere.5) Spectra of quadrupole-split lines are measured at various angles of rotation of the probe perpendicular to the static magnetic field H_0(rotation pattern). Orientation of the crystal on the mounting head of the probe is determined using a reflection goniometer. Measurement of the DMR was made at H_0 of 16600 G.

Results

Deuteron Quadrupole Coupling Tensor. $NiSiF_6 \cdot 6D_2O$. The appearance of the spectral lines is fairly broad throughout the temperature range studied indicating the rapid relaxation due to the presence of paramagnetic ions. Spectra with fairly good signal-to-noise ratio were obtained, however, since high rf level operation was possible.

The crystal structure is such that quadrupole coupling tensors can be transformed to one another by three-fold rotations about the [111] direction; therefore, it is sufficient for the determination of quadrupole coupling tensors to measure the rotation pattern for only one crystal setting provided that the axis of rotation does not coincide with the [111] direction.

A crystal-fixed coordinate (X_C, Y_C, Z_C) is defined here as,

X_C parallel to $[1\bar{1}0]$,
Y_C parallel to $[11\bar{2}]$,
Z_C parallel to $[111]$.

The laboratory-fixed coordinate (X_L, Y_L, Z_L) is such that H_0 is in the plane of X_LY_L, and θ, the angle of rotation of H_0 is measured from X_L. For the crystal setting in this experiment the transformation matrix $\boldsymbol{U}$ from the crystal-fixed system to the laboratory-fixed system was determined optically as:

	X_C	Y_C	Z_C
X_L	0.4759	−0.8644	0.1624
Y_L	0.7805	0.3300	−0.5309
Z_L	0.4054	0.3794	0.8317

Figure 1(a) shows the rotation pattern of the spectra at −116°C. The paramagnetism of the crystal produces a small shift of central frequency, thus distorting the symmetry of the rotation pattern of high and low frequency satellites as seen in the figure. The effect of paramagnetic ions on the measurement of the quadrupole splitting will now be considered.

The bulk susceptibility of a nonspherical sample can produce a local field component perpendicular to the external field at the nucleus. If this field is large, correct angular dependence of quadrupole splitting may not be obtained. From a crude estimation, however, the shape effect in the present experiment is found to be negligible.

The internal field due to contact and dipolar interactions can give rise to a paramagnetic shift. This shift is small, however, as seen in the figure in the present study, less than 20 kc/sec. Therefore, the nucleus-electron spin interaction can be treated as a first-order perturbation, just like the quadrupole interaction. The effect is only to shift the Larmor frequency, and the correct rotation pattern of

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3) T. Chiba, *ibid.*, **41**, 1352 (1964).
4) L. Pauling, *Z. Kristallogr.*, **72**, 482 (1930).
5) T. Chiba, *J. Chem. Phys.*, **36**, 1122 (1962).

quadrupole splitting can be obtained from the frequency difference between the upper and lower satellites just as in the absence of paramagnetic ions. The situation is analysed in more rigorous manner in the forthcoming paper on $CuSO_4 \cdot 5D_2O$.⁶⁾ Paramagnetic shifts in ^1H and ^{19}F resonances of $NiSiF_6 \cdot 6H_2O$ have been studied in detail at the liquid helium temperature by Kume and Sugawara.⁷⁾ In this study the paramagnetic shift is not analysed.

The rotation pattern of quadrupole splitting is obtained at −116°C, 23°C, 70°C, and at 150°C. At −116°C, six pairs of lines are obtained corresponding to two nonequivalent deuterons (D_1 and D_2) of D_2O. At room temperature and at 70°C, only three pairs are observed which means that the field gradient tensors (q-tensors) of D_1 and D_2 are averaged to give a single q-tensor by a rapid 180°-flip of D_2O (Fig. 1(b)). At 150°C only one pair is observed (Fig. 1(c)). This shows an additional averaging of q-tensors, corresponding to a setting in of rapid motion which interchanges D_2O at different sites. These motions will be discussed in a later section.

The determination of quadrupole coupling tensors is made as follows. First, the spectra at room temperature and at 70°C will be analysed. The curves A, B and C of rotation pattern of quadrupole splitting are formed as differences between A_+ and A_-, B_+ and B_- and C_+ and C_- of Fig. 1(b). Assume that curve A corresponds to a particular one of the three equivalent q-tensors, $q^{(1)}$, then curve B corresponds to a rotation pattern of $q^{(1)}$ in a crystal setting defined by the transformation matrix UC_3 or UC_3^{-1}, where

$$C_3 = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Similarly, curve C corresponds to a crystal setting of UC_3^{-1} or UC_3. Relative sign of the curves A, B and C can be readily found from the fact that the sum of A, B and C should give a rotation pattern of a quadrupole coupling tensor which is axially symmetric about Z_C axis. For the two alternative cases,

$$\left.\begin{array}{l} \text{Curve A} \cdots U \\ \text{Curve B} \cdots UC_3 \\ \text{Curve C} \cdots UC_3^{-1} \end{array}\right\} \text{ and } \left.\begin{array}{c} U \\ UC_3^{-1} \\ UC_3 \end{array}\right\},$$

$q^{(1)}$ can be determined in the crystal-fixed coordinate system by the procedure described elsewhere.⁶⁾ The wrong set gives unrealistic result with large standard deviations and can easily be eliminated.

The low temperature pattern is analysed as follows. Here the assignment of the lines is made by comparison with the estimated rotation pattern from the room temperature data. Since the obtained room temperature quadrupole tensor is a typical of D_2O under rapid 180° flip motion approximate orientation of water molecule can be estimated and the predicted rotation pattern can be drawn by assuming 1) q_{zz} of D_1 and D_2 making an angle of 110° to each other, 2) $\eta=0.1$, and 3) q_{yy} perpendicular to the molecular plane.¹˒³⁾ Here q_{zz} *etc.* are the principal components of q-tensor defined such that $|q_{xx}| \leq |q_{yy}| \leq |q_{zz}$. The agreement of estimated pattern with the experimental one at −116°C is sufficient for the assignment of each curve of rotation pattern to be readily made. The low temperature rotation pattern is then analyzed in the same way as before and the quadrupole coupling tensors for the D_1 and D_2 are determined.

At 150°C the rotation pattern corresponds to the average of the room temperature pattern and is axially symmetric about Z_C axis. eqQ, η and the principal axis directions are given in Table 1.

$NiSnCl_6 \cdot 6D_2O$. General appearance of the spectra is similar to that of the fluosilicate. In this case three pairs of lines were observed at room temperature as in the fluosilicate indicating the averaging of field gradient tensors by a 180°-flip motion of water molecules. It is found that the line broadening due to this motion takes place at considerably lower temperatures than in the fluosilicate. The rotation pattern of the quadrupole splitting for the flipping water molecule is measured at −53°C, 23°C and at 55°C, and the quadrupole coupling tensor is determined in the same way as in the fluosilicate as shown in Table 1. Line broadening is observed in the temperature range of −85—−125°C but spectra corresponding to the stationary deuterons are not observed even at the temperature of liquid nitrogen. Therefore, we were unable to determine quadrupole coupling for each deuteron.

Temperature Dependence of the Linewidth—Motional Effect. $NiSiF_6 \cdot 6D_2O$. As mentioned above, two different motions are observed by DMR, one is a 180°-flip motion of water molecules and the other is a motion which interchanges water molecules at different sites. Fortunately, broadening of spectral lines by these two motions occur in stepwise at different temperature ranges so that separate analysis of the motions can be made.

Temperature dependence of the linewidth at the fast and slow exchange limits of these two motions is observed at various temperatures and at various values of frequency splitting. To reduce the complexity of motional broadening due to dipolar structure the measurements are made at directions where original linewidth is small. These

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6) G. Soda and T. Chiba, *J. Chem. Phys.*, to be published.

7) K. Kume and T. Sugawara, *J. Phys. Soc. Japan*, **19**, 688 (1964).

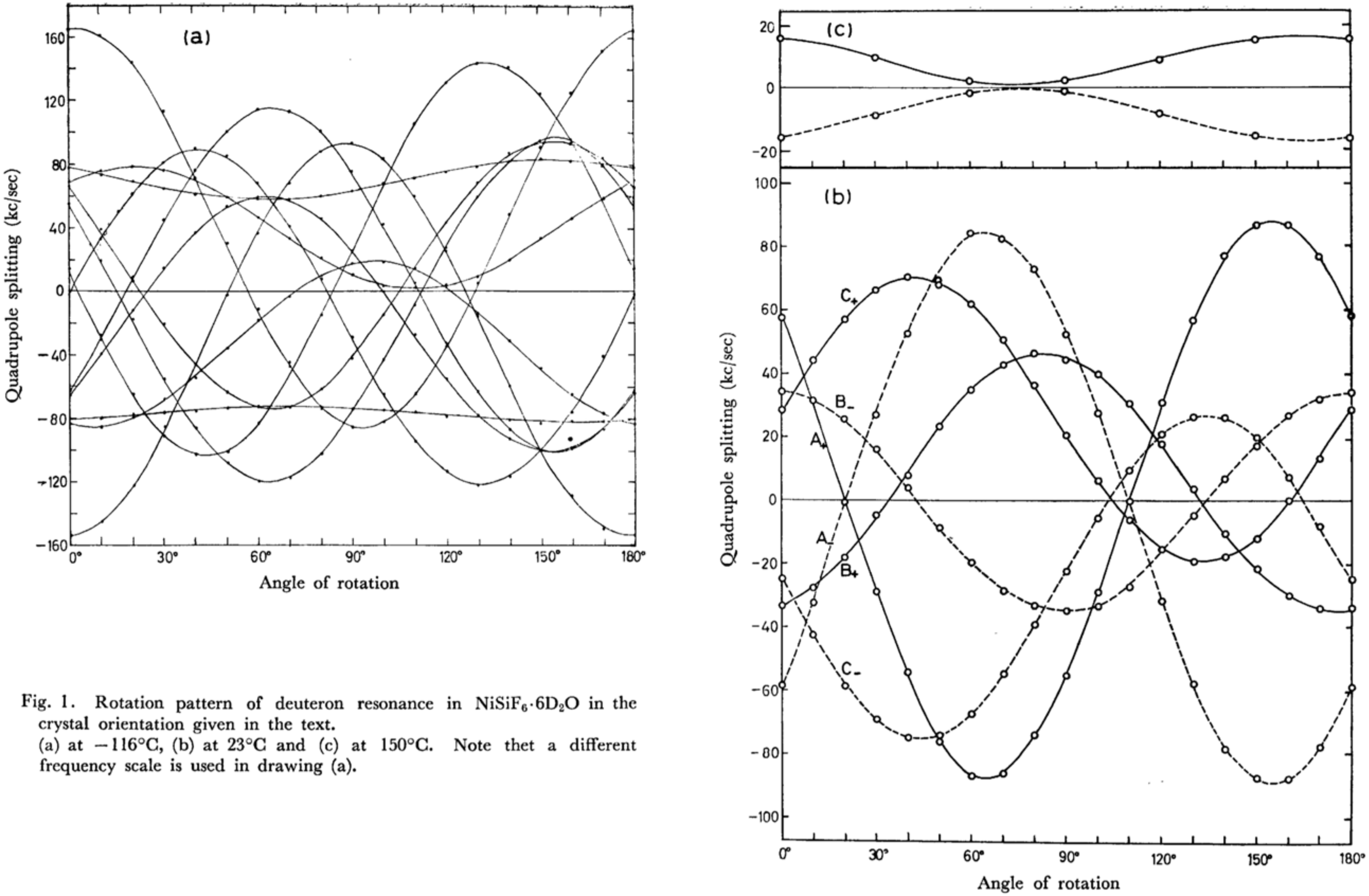

Fig. 1. Rotation pattern of deuteron resonance in $NiSiF_6 \cdot 6D_2O$ in the crystal orientation given in the text.
(a) at −116°C, (b) at 23°C and (c) at 150°C. Note thet a different frequency scale is used in drawing (a).

TABLE 1. DEUTERON QUADRUPOLE COUPLING eqQ/h, ASYMMETRY PARAMETER η AND THE PRINCIPAL AXIS DIRECTIONS* OF FIELD GRADIENT TENSOR IN $NiSiF_6\cdot 6D_2O$ AND IN $NiSnCl_6\cdot 6D_2O$ CRYSTALS

$NiSiF_6\cdot D_2O$					
−116°C			X_C	Y_C	Z_C
D_1 eqQ/h	238.3±1.3 kc	q_{xx}	0.690	0.679	0.250
η	0.100±0.005	q_{yy}	0.721	−0.676	−0.154
		q_{zz}	−0.064	−0.287	0.956
D_2 eqQ/h	235.7±1.9 kc	q_{xx}	0.196	−0.055	0.979
η	0.110±0.005	q_{yy}	0.777	−0.600	−0.189
		q_{zz}	0.598	0.798	−0.075
23°C					
eqQ/h	120.7±0.6 kc	q_{xx}	0.509	0.421	0.751
η	0.950±0.007	q_{yy}	0.443	0.620	−0.648
		q_{zz}	0.738	−0.662	−0.129
70°C					
eqQ/h	115.1±0.5 kc	Same as above within experimental errors.			
η	0.963±0.006				
150°C					
eqQ/h	44.5±0.7 kc	q_{zz} parallel to Z_C.			
η	0				

$NiSnCl_6\cdot 6DO$					
−53°C			X_C	Y_C	Z_C
eqQ/h	129.5±1.2 kc	Same as below within experimental errors.			
η	0.880±0.024				
25°C					
eqQ/h	121.1±0.8 kc	q_{xx}	0.498	0.431	0.752
η	0.906±0.012	q_{yy}	0.390	0.664	−0.638
		q_{zz}	0.775	−0.611	−0.162
55°C					
eqQ/h	118.4±1.1 kc	Same as above within experimental errors.			
η	0.906±0.025				

* The other two sets of principal axis directions which can be obtained from the one listed here by three-fold rotations about Z_C are omitted.

are used to determine the reorientation rate at various temperatures by the procedure used previously.[1,8] For the 180°-flip motion of water molecules the reorientation rate is determined as shown in Fig. 2. Assuming Arrhenius equation for this motion an activation energy of 7.6 kcal/mol with a pre-exponential factor of about 10^{14} sec^{-1} is obtained.

Three quadrupole coupling tensors of room temperature are averaged by a motion at high temperatures. We assume that this motion is a random reorientation of hydrated Ni ion among three equivalent sites in the equilibrium configuration. If the rate of jump from a site to another is denoted by Ω, we get from a theory,[9] for the slow exchange limit,

$$\Omega = \pi \Delta\nu_M, \tag{1}$$

and for the fast exchange limit,

$$\Omega = \frac{2\pi}{9}\,\frac{(\nu_1{}^2+\nu_2{}^2+\nu_3{}^2)}{\Delta\nu_M}, \tag{2}$$

where $\Delta\nu_M$ is the width due to the motion, ν_1 is the frequency difference at site 1, *etc.*, from the center of gravity of the spectra (*i. e.*, $\nu_1+\nu_2+\nu_3=0$). $\Delta\nu_M$ is determined from the line width change as before and the reorientation rates from the above equations are shown in Fig. 2.*3 An activation energy of 19 kcal/mol is obtained.

$NiSnCl_6\cdot 6D_2O$. The line broadening at the fast exchange limit was observed as in the case of the fluosilicate. To estimate the activation energy of reorientation it is necessary to know the frequency difference between the two deuterons of a water molecule at the orientation of the crystal where

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[8] T. Chiba and Y. Kakiuchi, This Bulletin, **41**, 828 (1968).

[9] P. W. Anderson, *J. Phys. Soc. Japan*, **9**, 316 (1954).

*3 For the fast exchange limit $\Delta\nu_M$ is derived from the width between maximum slopes ($\Delta\nu_{msl}$) as $\Delta\nu_M = \frac{\sqrt{3}}{2}\Delta\nu_{msl}$, neglecting dipolar width.

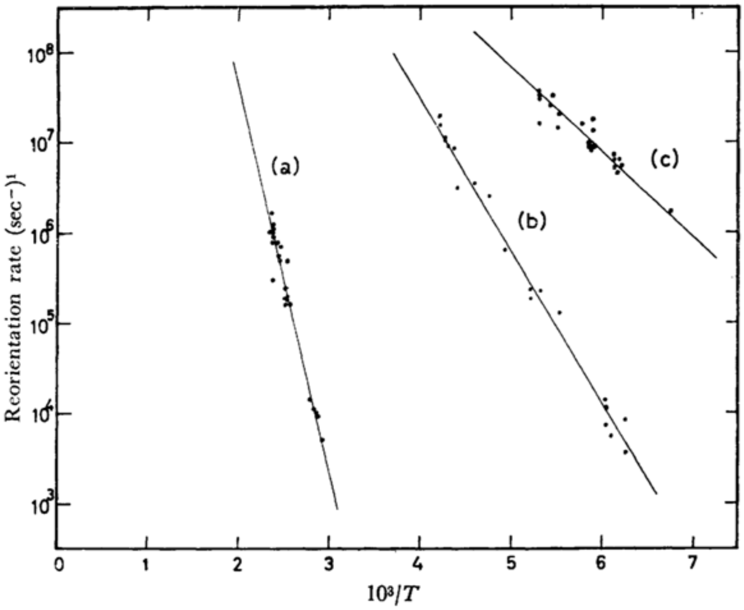

Fig. 2. Temperature dependence of reorientation rates determined from the line width change of DMR.

(a) $Ni(D_2O)_6^{2+}$ reorientation in $NiSiF_6\cdot6D_2O$.
(b) 180° flip motion of D_2O in $NiSiF_6\cdot6D_2O$.
(c) 180° flip motion of D_2O in $NiSnCl_6\cdot6D_2O$.

linewidth is measured. Since the spectra of stationary state were not measured this is estimated from the high temperature quadrupole coupling tensor. It is assumed that the two deuterons of a water molecule have the same quadrupole coupling tensor nearly axially symmetric about each OD bond making an angle of 110° with each other. With this assumption using the quadrupole coupling data at room temperature it is possible to estimate frequency difference between the lines of two deuterons at a given orientation of the crystal. The result is shown in Fig. 2. The activation energy for reorientation is then estimated to be 4.3 kcal/mol.

Discussion

Quadrupole Coupling Tensor. The value of *eqQ* and η are nearly the same as those observed in other water of crystallization. There appears to be no marked effect of coordination on *eqQ* of deuteron.

Crystal structure has not been known for $NiSiF_6\cdot6H_2O$ except the lattice constant and space group ($a=6.255$ Å, $\alpha=96°6'$, space group $R3$).⁴⁾ A neutron diffraction study has recently been done on $FeSiF_6\cdot6H_2O$¹⁰⁾ which was believed to be isomorphous with $NiSiF_6\cdot6H_2O$. It was concluded that ferrous fluosilicate has space group $R\bar{3}m$ instead of $R\bar{3}$, presumably due to statistical distribution of two slightly differently oriented structures. If it were also the case in the nickel salts, it could be easily detected as doubling of the number of satellite pairs*4 and/or from the symmetry of observed field gradient tensor. Since no such effects are indicated in nickel fluosilicate and chlorostannate, the crystal symmetry is not $R\bar{3}m$.

It has been known that to a good approximation the q_{zz} direction is in the bond direction and q_{yy} direction perpendicular to D_1OD_2 plane.³⁾ In the case of $NiSiF_6\cdot6D_2O$ the angle between the direction of q_{zz} of D_1 and that of D_2 is 109.8°, and the deviations of the q_{yy} directions of D_1 and D_2 from the normal to the plane defined by the q_{zz} directions of D_1 and D_2 are 5.9° and 3.8° respectively.

The approximate orientation of water molecule can be determined from the present result. If the dispositions of ions in nickel fluosilicate are assumed to be the same as one of the two mirror image structures of the ferrous salt it is found that the q_{zz} directions do not agree with the OH bond directions (deviation being 13° and 26°). Now, the crystal structure of this salt will be considered under the following assumptions.

1) D-O directions are in the q_{zz} directions.

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10) W. C. Hamilton, *Acta Cryst.*, **15**, 353 (1962).

*4 If a sufficient rapid exchange motion between the mirror image structures is present the number of satellite pairs will not be doubled, however, in that case one of the principal axes of the *q*-tensor should be perpendicular to [11$\bar{1}$], which is readily detectable.

2) Dimension of SiF_6^{2-} ion is the same as that in $FeSiF_6 \cdot 6H_2O$, a regular octahedron with an Si–F distance of 1.71 Å.[10,11]

3) NiO_6 octahedron is regular with an Ni–O distance of 2.07 Å.[11]

4) Ni-O direction must not deviate greatly from the bisector of D_2O*5.

Rotation angles of both positive and negative group ions about the [111] axis are adjusted so as to give reasonable hydrogen-bond distances and angles.

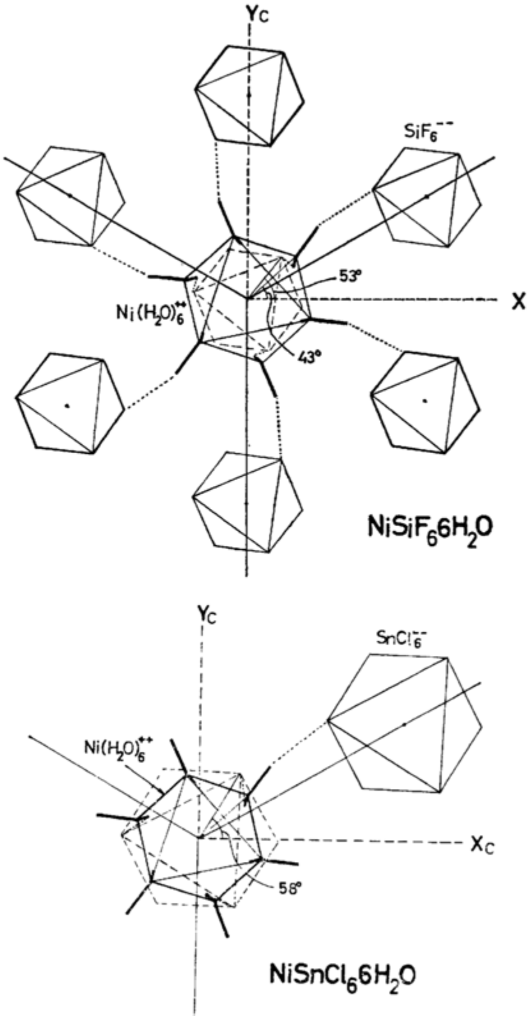

Fig. 3. Proposed crystal structures of $NiSiF_6 \cdot 6H_2O$ and $NiSnCl_6 \cdot 6H_2O$. [111] projection. Hydrogen bonds are indicated by dotted lines. Only one of the six $SnCl_6^{2-}$ ions surrounding $Ni(H_2O)_6^{2+}$ is shown for brevity.

The proposed structure is shown in Fig. 3. The D···F distances are 1.72 Å ($D_1 \cdots F$) and 1.77 Å ($D_2 \cdots F$) with corresponding O–D···F angles of 154° and 156°, respectively. Further improvement of the D···F distances and O–D···F angles may be possible but is hardly meaningful in the present approximations. The hydrogen-bond network in the suggested structure is essentially the same as that of ferrous silicate, one hydrogen-bond being approximately parallel to $[\bar{1}11]$ and the other approximately perpendicular to it.

For $NiSnCl_6 \cdot 6D_2O$, though we were not able to determine *eqQ* for each deuteron of a water molecule, quadrupole coupling tensors and their orientations of D_1 and D_2 are probably nearly the same as those in the fluosilicate as seen from the close agreement of the room temperature values in Table 1.*6 Pauling gives atomic coordinates for the heavy atoms. However, difficulty is encountered when we try to fit our data of directions of quadrupole coupling tensor to his structure.*7 Trial structure as shown in Fig. 3 is proposed assuming $SnCl_6^{2-}$ as regular octahedron with Sn-Cl=2.45 Å[11] and treated in the same way as above. D···Cl distances are 2.02 Å with O–D···Cl angles of 158° and 139°.

It is hoped that more refined structure analysis of these compounds will be made. We were unable to detect NQR spectra of ^{35}Cl in this compound and the attempt to determine Cl–Sn direction by the Zeeman effect of NQR was unsuccessful.

Reorientational Motions. The barrier to reorientation of water molecules is considerably smaller in the chlorostannate than in the fluosilicate, which is well understood from the difference in hydrogen-bond strength in the two crystals.

A reorientational motion of $M(H_2O)_6^{2+}$ group ions similar to the one observed in $NiSiF_6 \cdot 6D_2O$ at high temperature has been detected by the line-shape transition of the proton resonance in the isomorphous zinc and magnesium fluosilicates by Dereppe *et al.*[12] They conclude that motion is excited in both $SiFe_6^{2-}$ and $M(H_2O)_6^{2+}$ groups in these crystals, the activation energies being 6.6 and 11.6 kcal/mol, respectively, for the magnesium salt.

In nickel fluosilicate the barrier to the $M(H_2O)_6^{2+}$ motion is considerably higher. Since the Z_C component of field gradient is preserved it can be concluded that the motion is not a free rotational one, but is a reorientation among equilibrium sites and even the rotational motion of water molecules is not a free motion. A reorientation about any axis which interchanges adjacent three

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11) R. W. G. Wyckoff, "Crystal Structure" (2nd Ed.), Vol. 3, Chapter X, Interscience Publishers, New York (1965).

*5 In $FeSiF_6 \cdot 6H_2O$, Fe–O and the bisector of H_2O are linear within 8.1° (Ref. 10).

*6 At room temperature, q_{xx}, q_{yy} and q_{zz} directions of $NiSiF_6 \cdot 6D_2O$ are in agreement with the corresponding ones of $NiSnCl_6 \cdot 6D_2O$ within 1°, 4°, and 4°, respectively.

*7 An Ni–O distance of 2.40 Å in Pauling's structure is too large compared to the average Ni–O distance of 2.07±0.04 Å of various nickel salts (Ref. 11).

12) J. M. Dereppe, P. W. Lobo and M. V. Meersche, *J. Chim. Phys.*, **61**, 1076 (1964).

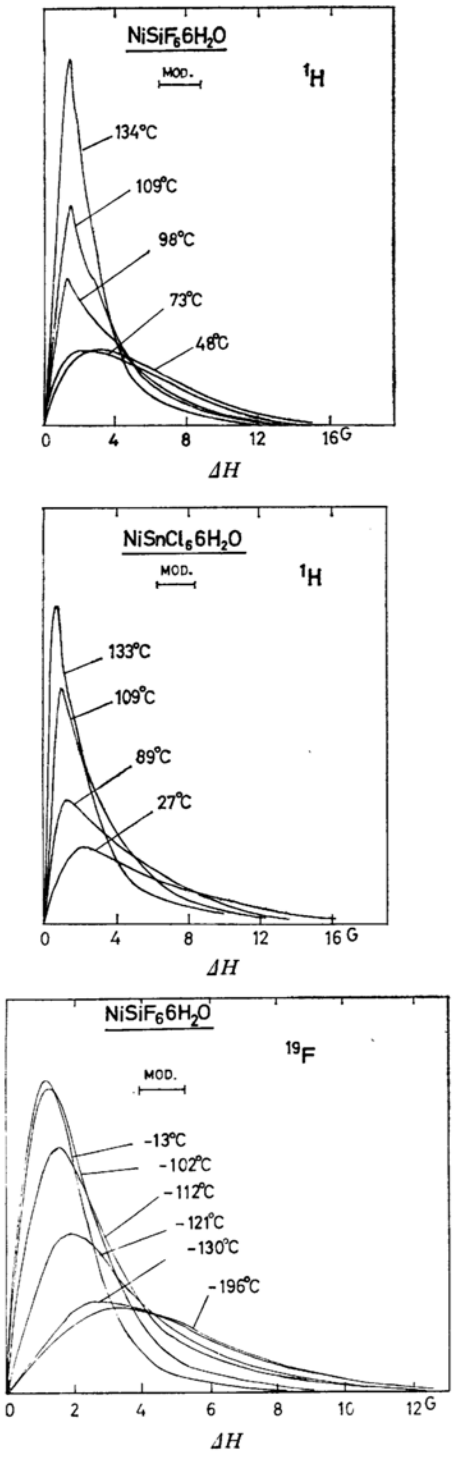

Fig. 4. ^1H and ^{19}F resonance line shapes (a half of the derivative curve) at various temperatures.

water molecules can produce the observed effect. There are four three-fold reorientational modes,[*8] one of which is about the [111] axis, and other three four-fold reorientational modes about the O–Ni–O axes. (All these modes except the one about [111] are not pure rotational modes in a rigorous sense because the $Ni(H_2O)_6{}^{2+}$ ion is not a regular octahedron.) It is not possible to determine which of the two types of motions is operative in the observed averaging process. However, if one considers the number of hydrogen bonds to be broken in the course of reorientation the four-fold motion seems more probable.

For $NiSnCl_6\cdot6D_2O$ no measurement of $Ni(D_2O)_6{}^{2+}$ cluster motion was made on a single crystal. Attempt to observe powder pattern of reorienting $Ni(D_2O)_6{}^{2+}$ was made on chlorostannate up to 140°C but was unsuccessful (the crystal decomposes at the higher temperatures).

The line shape transition of ^1H resonance on $NiSnCl_6\cdot6H_2O$ powder was compared with that of $NiSiF_6\cdot6H_2O$ as shown in Fig. 4. Both has similar temperature dependence. The activation energy of $Ni(D_2O)_6{}^{2+}$ motion in chlorostannate is, therefore, probably nearly the same as that in the fluosilicate.

The line shape transition of ^{19}F resonance of nickel fluosilicate was also measured as shown in Fig. 4. Line width transition centered at -110—-120°C is observed. The temperature of transition is considerably lower than that of magnesium fluosilicate, and the activation energy of $SiF_6{}^{2-}$ reorientation in the nickel salt is likely to be less than 6.6 kcal/mol. As Dereppe *et al.*[12] point out, the activation energies of reorientation of $M(H_2O)_6{}^{2+}$ and $SiF_6{}^{2-}$ should be nearly the same if only the interactions between ions of opposite sign are considered. Their explanation of large difference in activation energies between $Mg(H_2O)_6{}^{2+}$ and $SiF_6{}^{2-}$ reorientations is based on the assumption of the same crystal structure for this salt as the ferrous salt. It is clear that such an explanation is not applicable to the nickel salt where no mirror symmetry is observed. Yet the difference in the activation energy of cation and anion reorientation is much larger in the latter case than in the former. There is also another question. For the 180°-flip of a water molecule the observed activation energy is generally reasonable value considered as the energy required to break two hydrogen bonds of the water molecule. Now, if one simply takes hydrogen-bonding energy alone, both the reorientations of $Ni(H_2O)_6{}^{2+}$ and $SiF_6{}^{2-}$ should require at least four times the activation energy of 180°-flip of D_2O or 30 kcal/mol, because hydrogen-bonds of four water molecules are broken in the course of the four-fold reorientation. Same order of the observed activation energy for the $Ni(H_2O)_6{}^{2+}$ reorientation in the chlorostannate as in the fluosilicate is also difficult to understand.

[*8] In the three-fold reorientation the motion should be that all the six water molecules move together and not that three move independent of three others, since the latter means the breakage of coordination bonds.

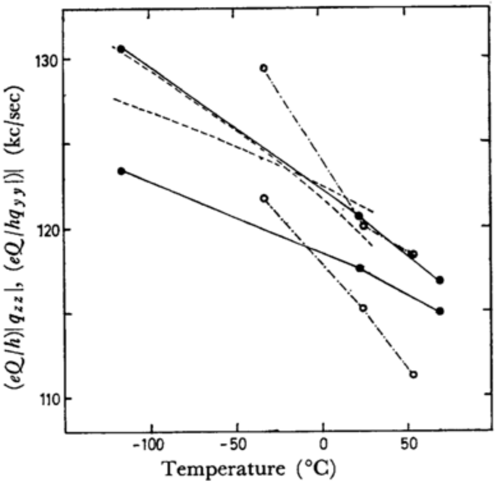

Fig. 5. Temperature dependence of z and y components of averaged quadrupole coupling tensor in D_2O.
—— $NiSiF_6 \cdot 6D_2O$, -·-· $NiSnCl_6 \cdot 6D_2O$,
--- $Ba(ClO_3)_2 \cdot D_2O$ (Ref. 1).

The experimental results in disagreement with the expectation from such a simple picture indicate that various factors, such as electrostatic energy other than hydrogen-bonding energy, steric effect and nonrigidity of the structure, of cluster ions, are the important factors determining the activation energy of reorientation of a large group of atoms. Although no satisfactory explanation of molecular motions in crystals are available at present, nickel fluosilicate presents as interesting example that three types of reorientational motion, that is, the motion of D_2O, $Ni(D_2O)_6{}^{2+}$ and $SiF_6{}^{2-}$ are observed in a single compound.

Torsional Oscillations. $(eQ/h)|q_{zz}|$ and $(eQ/h)|q_{yy}|$ of the quadrupole coupling of D_1OD_2 under 180° flip motion, that is, the quadrupole coupling tensor averaged for D_1 and D_2, are plotted in Fig. 5. (The z direction is perpendicular to the plane of water molecule and the y direction parallel to the direction of D_1–D_2). As discussed in Ref. 1 the temperature dependence of these values can be explained from Bayer's theory[13] in terms of torsional motions of a water molecule. For nickel fluosilicate the temperature dependence of q_{zz} and q_{yy} resembles that of $Ba(ClO_3)_2 \cdot D_2O$ previously obtained.[1] Trend of smaller temperature dependence of q_{yy} compared to q_{zz} is also seen in the present case. This is due to the effect of torsional motion about the D–D axis which only decreases the q_{yy} component. The torsional motions in both cases are probably similar since the activation energy for the two cases is nearly the same (7 kcal/mol for $Ba(ClO_3)_2 \cdot D_2O$).[1,8] Therefore, approximately the same torsional frequencies as obtained in $Ba(ClO_3)_2 \cdot D_2O$ are expected. However, since the oscillation may be more complex and coupling among the modes may be stronger in the present case, no detailed analysis of the torsional frequencies are made. The effect of the torsional motion of $Ni(D_2O)_6{}^{2+}$ cluster on the temperature dependence of quadrupole coupling is estimated assuming a three-fold cosine type potential of barrier height 19 kcal/mol about the [111] direction. It is found that the change in quadrupole coupling is less than one percent over the temperature range of observation and may be negligible.*[9]

In the chlorostannate the observed large temperature dependence can be readily expected from the small hindering potential to 180°-flip motion of water molecules. An approximate calculation assuming a cosine-type potential of 4.3 kcal/mol shows for the temperature range of observations (−53°C to 55°C), about 5% of the observed 9% decrease can be explained by the torsional motion about the bisector of D_2O.

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13) H. Bayer, *Z. Physik*, **130**, 227 (1951).

*[9] The effect is even less when the four-fold reorientation is assumed.