Coupled Proton and Fluorine Nuclear Spin-Lattice Relaxation in Polycrystalline Magnesium and Zinc Fluorosilicate Hexahydrate

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Coupled proton and fluorine nuclear spin-lattice relaxation mechanisms have been studied in polycrystalline MeSiF$_6$·6H$_2$O (Me = Zn, Mg) at 30 MHz over the temperature range 130 K ≤ T ≤ 420 K. The results indicate that below 280 K in the magnesium complex and below 390 K in the zinc complex, respectively, the reorientations of the [SiF$_6$]$^{2-}$ ions are the dominant relaxation mechanism. Reorientations of individual water molecules have not to be taken into account as an effective relaxation mechanism. The phase transition in MgSiF$_6$·6H$_2$O at 298 K is reflected by a change in the spin-lattice relaxation rate ($T_1^{-1}$). In MgSiF$_6$·6H$_2$O the relaxation behavior becomes purely exponential above the phase transition temperature, whereas in ZnSiF$_6$·6H$_2$O there is a non-exponential relaxation behavior over the whole temperature range investigated. The activation energies and frequency factors obtained from ($T_1^{-1}$) measurements are consistent with the data obtained by use of the Waugh-Fedin relation.

1. Introduction

As part of an extended program to study nuclear spin relaxation mechanisms we investigated the coupled $^1$H,$^{19}$F spin-lattice relaxation in polycrystalline MgSiF$_6$·6H$_2$O and ZnSiF$_6$·6H$_2$O. The results are presented in this paper.

In MgSiF$_6$·6H$_2$O a phase transition occurs near 298 K. The low and high temperature forms of the crystal lattices are closely related, and the space groups are $P2_1/ c$ and $R\overline{3}m$. A recent X-ray investigation of ZnSiF$_6$·6H$_2$O gave the space group as $R\overline{3}m$.

Both crystals consist of nearly octahedral $[\text{Me}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{SiF}_6]^{2-}$ ions arranged in a slightly distorted CsCl-structure. The densest packing is in columns where cations and anions alternate along the threefold axis in ZnSiF$_6$·6H$_2$O and along the pseudo-trigonal axis in MgSiF$_6$·6H$_2$O, respectively. Three hydrogen bonds connect each pair of adjacent octahedra in a column while one hydrogen bond connects one octahedron to each of its six neighboring octahedra in other columns, i.e. each hydrogen atom participates in one OH···F bond, whereas each fluorine atom is involved in two such bonds. In ZnSiF$_6$·6H$_2$O there is a disorder of fluorine octahedra between two positions unrelated by any symmetry element and with unequal occupancy. In the low temperature crystal structure of MgSiF$_6$·6H$_2$O the cations are surrounded by six anions with two different orientations. In the high temperature form MgSiF$_6$·6H$_2$O exhibits also a disorder.

The spin-lattice relaxation rate measurements were undertaken to study motional relaxation processes with respect to the hydrogen bonds. Another purpose of this investigation was to see whether the reported phase transition in MgSiF$_6$·6H$_2$O is reflected by a change in the spin-lattice relaxation rate ($T_1^{-1}$).

Previous NMR studies on powdered MgSiF$_6$·6H$_2$O were made by Utton and Tsang who, however, did not consider the phase transition at 298 K in the interpretation of their results. Thompson and Nolle examined proton and fluorine spin-lattice relaxation times in single-crystal ZnSiF$_6$·6H$_2$O containing iron and manganese impurities at different concentrations. They attributed the motional relaxation to tumbling of the complexes in an interval extending about 100 K below room temperature with an activation energy of 6 kcal/mole for the $^{19}$F complex and 4.8 kcal/mole for the $^1$H complex. The later value seems to be extremely low.

2. Experimental Procedure and Results

Commercially obtained samples of both hexahydrates were purified by recrystallization from aqueous solution and dried with CaCl$_2$. A Bruker BKR 320 s pulse spectrometer was used to obtain proton and fluorine spin-lattice relaxation rates ($T_1^{-1}$) at 30 MHz. For all measurements, a $90^\circ$-t-$90^\circ$ pulse sequence was employed. The temperature was varied between 130 K and 420 K by means of a simple gas-flow cryostat and we estimate temper...
temperature measurements to be accurate to ±1 K. Because of possible sample dehydration, measurements at higher temperatures were not made. Relaxation rates as a function of temperature, estimated to be accurate to ±5%, are shown in Figs. 1 and 2.

![Fig. 1. Relaxation rates \((T_1^I)^{-1}\) and \((T_1''^I)^{-1}\) as a function of reciprocal temperature for polycrystalline MgSiF₆·6H₂O. The phase transition at 298 K is denoted by \(T_{\text{II}}\). Curve A is related to the proton spin-lattice relaxation rate \([T_1^1(\text{H})]^{-1}\) above phase transition. Relaxation rates obtained from measurements of the proton and fluorine spin system are denoted by triangles (▲) and circles (○), respectively.](image1)

Additionally, we measured the half width of the free induction decay (FID) as a function of temperature in analogy to the NMR line width measurements. So, we were able to determine the temperature \(T_c\) at half narrowing of the FID. Applying the Waugh-Fedin relation

\[
\frac{V_{a\text{cal/mole}}}{\text{cal/mole}} = 37 \frac{T_c}{\text{K}}
\]

the activation energies \(V_{a}\) of the cation and anion reorientation were obtained. The results are given in Table 2.

![Fig. 2. Relaxation rates \((T_1')^{-1}\) and \((T_1'')^{-1}\) as a function of reciprocal temperature for polycrystalline ZnSiF₆·6H₂O. Relaxation rates obtained from measurements of the proton and fluorine spin system are denoted by triangles (▲) and circles (○), respectively.](image2)


d\langle I_z \rangle \over dt = -(T_1^{II})^{-1} \langle I_z - I_0 \rangle - (T_1^{IS})^{-1} \langle S_z - S_0 \rangle ,
\]

\[
d\langle S_z \rangle \over dt = -(T_1^{SI})^{-1} \langle I_z - I_0 \rangle - (T_1^{SS})^{-1} \langle S_z - S_0 \rangle .
\]

Here, \(I\) and \(S\) refer to the proton and fluorine spins, respectively. The observed relaxation rates \((T_1')^{-1}\) and \((T_1'')^{-1}\) are eigenvalues of the relaxation matrix \(R\):

\[
R = \begin{pmatrix}
(T_1^{II})^{-1} & (T_1^{IS})^{-1} \\
(T_1^{SI})^{-1} & (T_1^{SS})^{-1}
\end{pmatrix}.
\]

To determine the matrix elements, they must be related to fluctuations of the local dipolar fields, i.e., to molecular motions which dominate the spin-lattice relaxation. In the compounds investigated, there are three types of molecular motions which may effect spin-lattice relaxation:

i) reorientation of water molecules,
ii) reorientation of the \([\text{SiF}_6]^2^-\) octahedra,
iii) reorientation of the \([\text{Me}(\text{H}_2\text{O})_6]^2+\) octahedra.

In the case of MgSiF₆·6H₂O, Dereppe, Lobo, and van Meersche calculated the contributions of these three types of motions to the proton second moment. The part which is due to the rotation of water mole-
cules about the \( C_2 \) axis was calculated to 6.44 G. \(^2\)
This value could not be realized in the course of the experimental second moment. Hence, these authors considered the motion of water molecules at low temperatures to be improbable and they suggest, that the water molecules and the water octahedra start to reorient at the same temperature of about 285 K.

In the case of \( \text{ZnSiF}_6 \cdot 6 \text{H}_2\text{O} \), Thompson and Nolle\(^4\) pointed out that their results could be better explained by taking into account a rapid reorientation of each water molecule about its symmetry axis. Muthukrishnan and Ramakrishna\(^8\) also assumed a motion of water molecules in \( \text{ZnSiF}_6 \cdot 6 \text{H}_2\text{O} \) which starts as the temperature is raised above 100 K. However, based on the temperature dependence of the proton and fluorine NMR second moments in \( \text{ZnSiF}_6 \cdot 6 \text{H}_2\text{O} \) which is very similar to the NMR second moments in \( \text{MgSiF}_6 \cdot 6 \text{H}_2\text{O} \), we assume that below 350 K in \( \text{ZnSiF}_6 \cdot 6 \text{H}_2\text{O} \) and below 285 K in \( \text{MgSiF}_6 \cdot 6 \text{H}_2\text{O} \), the local dipolar fields are modulated primarily by motions of the \([\text{SiF}_6]^{2-}\) octahedra.

In terms of this relaxation model, the expression for \( (T_1^{\text{SS}})^{-1} \) is comprised by two terms, one based on the fluorine-fluorine interaction and one on the proton-fluorine interaction. Both, \( (T_1^{\text{IS}})^{-1} \) and \( (T_1^{\text{SI}})^{-1} \) are cross-relaxation terms which are constrained as follows:

\[
(T_1^{\text{IS}})^{-1} = \frac{1}{2} (T_1^{\text{SI}})^{-1}. \tag{5}
\]

The factor 1/2 in Eq. (5) arises from the ratio of the number of the hydrogen bonds in which the protons and the fluorine atoms are involved. Lastly, \( (T_1^{\text{II}})^{-1} \) contains terms arising only from proton-fluorine interactions.

To evaluate the various expressions for \( (T_1)^{-1} \) in Eq. (4), spectral density functions are required, and these were obtained in the usual way\(^3,6,9\). Writing our results in terms of the second moments \( M_2^{\text{inter}} \) and \( M_2^{\text{intra}} \), due to intermolecular and intramolecular interactions, respectively, we obtained the following expressions for the matrix elements:

\[
(T_1^{\text{SS}})^{-1} = \frac{3}{4} M_2^{\text{intra}} \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega^2 \tau_c^2} \right] + \frac{\tau_c}{2} \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{3 \tau_c}{1 + 4 \omega^2 \tau_c^2} \right],
\]

\[
(T_1^{\text{II}})^{-1} = \frac{3}{4} M_2^{\text{inter}} \left[ \frac{\tau_c}{2} \left[ \frac{3 \tau_c}{1 + 4 \omega^2 \tau_c^2} \right] + \frac{\tau_c}{1 + \omega^2 \tau_c^2} \right]
\]

\[
(T_1^{\text{IS}})^{-1} = \frac{1}{2} (T_1^{\text{SI}})^{-1} = \frac{3}{4} M_2^{\text{inter}} \left[ -\frac{3 \tau_c}{1 + 4 \omega^2 \tau_c^2} + \frac{\tau_c}{2} \right].
\]

where

\[
\omega_1 \approx \omega_2 \approx \omega, \quad \omega_1 + \omega_2 \approx 2 \omega, \quad \omega_1 - \omega_2 = \omega', \tag{9}
\]

and

\[
2 M_2^{\text{inter}} = M_2^{\text{S inter}}.
\]

At low temperatures (e.g., below 200 °C), the conditions

\[
\omega \tau_c \gg 1 \quad \text{and} \quad \omega' \tau_c \gg 1
\]

are assumed to be fulfilled, and the \( \omega' \) terms in Eqs. (6), (7), and (8) will be dominant. Using a perturbation expansion for the recovery of the magnetization, we obtained the following expressions:

\[
\frac{\langle I_0 - I_z \rangle}{\langle I_0 \rangle} = \frac{3}{2} \exp(-t/T_1') + \frac{3}{2} \exp(-t/T_1''), \tag{10}
\]

\[
\frac{\langle S_0 - S_z \rangle}{\langle S_0 \rangle} = \frac{3}{2} \exp(-t/T_1') + \frac{3}{2} \exp(-t/T_1''). \tag{11}
\]

The above equations show that proton and fluorine relaxation rates are characterized by the same pair of time constants. As an example of this, recovery functions of the magnetization in \( \text{MgSiF}_6 \cdot 6 \text{H}_2\text{O} \) and \( \text{ZnSiF}_6 \cdot 6 \text{H}_2\text{O} \) are shown in Fig. 3, and compared with calculated curves obtained using the more general equations:

\[
\left( \frac{M_0 - M_x}{M_0} \right)_I = A_I \exp(-t/T_1') + B_I \exp(-t/T_1''), \tag{10,1}
\]

\[
\left( \frac{M_0 - M_x}{M_0} \right)_S = A_S \exp(-t/T_1') + B_S \exp(-t/T_1''). \tag{11,1}
\]

Equation (10,1) and Eq. (11,1) were fitted to the experimental data by the method of least-squares. The computed values for the parameters \( A_I, B_I, A_S, \) and \( B_S \) are in fair agreement with the theoretical ones.

Using the perturbation expansion and the low temperature conditions as mentioned above the eigenvalues \( (T_1')^{-1} \) and \( (T_1'')^{-1} \) of the matrix R.
can be approximated by

\[ (T_1')^{-1} = C_1 \left( \frac{\tau_c}{1 + \omega^2 \tau_c^2} \right) \] and

\[ (T_1'')^{-1} = C_2 \left( \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega^2 \tau_c^2} \right), \]  

where

\[ C_1 = \frac{7}{6} M_2^{18 \text{ inter}} \]  

and

\[ C_2 = \frac{5}{6} M_2^{18 \text{ inter}} + \frac{1}{6} M_2^{8 \text{ intra}}. \]

To calculate the constants \( C_1 \) and \( C_2 \) we used the wellknown expressions for the second moments of unlike spins

\[ M_2^{18 \text{ inter}} = \frac{7}{6} \gamma_1^2 \gamma_2^2 \hbar^2 \sum_{i} r_{ik}^{-6} \]  

and of like spins

\[ M_2^{8 \text{ intra}} = \frac{9}{30} \gamma_1^4 \gamma_2^2 \hbar^2 \sum_{ij} r_{ij}^{-6}, \]

respectively.

The intermolecular H-F distances \( r_{ik} \) and the intramolecular F-F distances \( r_{ij} \) were obtained from the crystal structure data for MgSiF\(_6\)-6H\(_2\)O\(^2\) and for ZnSiF\(_6\)-6H\(_2\)O\(^2\). The calculated and experimental values of \( C_1 \) and \( C_2 \) are compared in Table 1.

Table 1. Experimental and calculated values of the parameters \( C_1 \) and \( C_2 \).

<table>
<thead>
<tr>
<th></th>
<th>MgSiF(_6)-6H(_2)O</th>
<th>ZnSiF(_6)-6H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^6 C_1 ) ( \text{exp.} / \text{sec}^{-2} )</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>( 10^6 C_1 ) ( \text{cal.} / \text{sec}^{-2} )</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>( 10^6 C_2 ) ( \text{exp.} / \text{sec}^{-2} )</td>
<td>4.1</td>
<td>3.9</td>
</tr>
<tr>
<td>( 10^6 C_2 ) ( \text{cal.} / \text{sec}^{-2} )</td>
<td>8.3</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Calculated relaxation rates \( (T_1')^{-1} \) and \( (T_1'')^{-1} \), obtained by inserting the experimental parameters \( C_1 \) and \( C_2 \) into Eqs. (12) and (13) are shown as solid lines in Figs. 1 and 2.

Using Eqs. (12) and (13), correlation times \( \tau_c \) were evaluated as a function of temperature with the
The behavior at higher temperatures is more complicated. In MgSiF$_6$·6H$_2$O, a phase transition occurs at about 298 K and the recovery function of the magnetization becomes purely exponential, whereas in ZnSiF$_6$·6H$_2$O, the spin-lattice relaxation is non-exponential in the whole temperature range investigated. For this reason, the discussion below is restricted to ZnSiF$_6$·6H$_2$O.

In the temperature range 290 K ≤ T ≤ 390 K where the conditions $\omega' \tau_c < 1$ and $\omega \tau_c < 1$ are assumed to be fulfilled a weak non-exponential relaxation behavior was observed. Then, the diagonal elements of $R$ in Eq. (4) may be used to approximate the eigenvalues. Relaxation rates and correlation times calculated using Eqs. (6) and (7), and the above approximation, are drawn as dashed lines in Figs. 2 and 4.

To check the coupled relaxation mechanism over the entire temperature range investigated, $(T_1')^{-1}$ and $(T_1'')^{-1}$ were calculated using the general solution of Eq. (4):

$$
\lambda_{1,2} = M \left( T_1^{(I)} \right)^{-1} + \left( T_1^{(S)} \right)^{-1}
$$

$$
\pm \left( \left[ \left( T_1^{(I)} \right)^{-1} + \left( T_1^{(S)} \right)^{-1} \right]^2 - 4 \left( T_1^{(I)} \right)^{-1} \left( T_1^{(S)} \right)^{-1} \right)^{1/2}
$$

with

$$(T_1')^{-1} = \lambda_1, \quad (T_1'')^{-1} = \lambda_2.$$  

Computed relaxation rates, obtained from Eq. (19) with the matrix elements in Eqs. (6) – (8) are shown as solid lines in Figure 5. Agreement with the experimental values of $(T_1')^{-1}$ and $(T_1'')^{-1}$ is satisfactory, except in the temperature ranges above 390 K and below 160 K, respectively. Above 390 K, the reorientation of $[\text{Zn} (\text{H}_2\text{O})_6]^{2+}$ ions becomes efficient at producing relaxation and the non-exponentiality of the relaxation behavior increases again. Below 160 K, the observed relaxation rates are dominated by contributions from paramagnetic impurities and become nearly temperature independent and purely exponential.

Evaluation of the $(T_1^{(\text{H})})^{-1}$ data for MgSiF$_6$·6H$_2$O in the temperature range above 298 K was based on the fact that the magnetization recovered exponentially and on the assumption that reorientation of $[\text{Mg} (\text{H}_2\text{O})_6]^{2+}$ ions was the dominant relaxation mechanism. A. maximum for the proton relaxation rate (Fig. 1) was obtained without noticeable sample dehydration as determined by repeated room temperature measurements of $(T_1^{(\text{H})})^{-1}$.

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**Table 2. Activation energies and preexponential factors for cation and anion reorientation as derived from spin-lattice relaxation and $T_c$ measurements.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method Reorienting Ion</th>
<th>$V_a$ kcal/mole</th>
<th>$\tau_e^0$ sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSiF$_6$·6H$_2$O</td>
<td>$(T_1')^{-1}$ [SiF$_6^{2-}$]</td>
<td>6.7</td>
<td>6·10$^{-14}$</td>
</tr>
<tr>
<td></td>
<td>$(T_1')^{-1}$ [Mg(H$_2$O)$_6$]$^{2+}$</td>
<td>6.1</td>
<td>.</td>
</tr>
<tr>
<td>ZnSiF$_6$·6H$_2$O</td>
<td>$(T_1')^{-1}$ [SiF$_6^{2-}$]</td>
<td>5.1</td>
<td>1.2·10$^{-13}$</td>
</tr>
<tr>
<td></td>
<td>$(T_1')^{-1}$ [Zn(H$_2$O)$_6$]$^{2+}$</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td></td>
<td>$(T_1')^{-1}$ [Zn(H$_2$O)$_6$]$^{2+}$</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td></td>
<td>$T_c$ [Zn(H$_2$O)$_6$]$^{2+}$</td>
<td>12.2</td>
<td>.</td>
</tr>
</tbody>
</table>

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**Fig. 4.** Correlation times for internal cation and anion reorientation in the compounds MeSiF$_6$·6H$_2$O (Me = Zn, Mg). Curve a is related to the correlation times of the $[\text{Mg} (\text{H}_2\text{O})_6]^{2+}$ reorientation above phase transition temperature. Curves b and c are related to the correlation times of the $[\text{SiF}_6^{2-}]$ reorientation in MgSiF$_6$·6H$_2$O and in ZnSiF$_6$·6H$_2$O, respectively. The correlation times obtained from $(T_1')^{-1}$ and $(T_1'')^{-1}$ data in ZnSiF$_6$·6H$_2$O using Eqs. (6) and (7) are denoted by curve d. Circles (•) and triangles (△) are from $(T_1'')^{-1}$ and $(T_1')^{-1}$ data, respectively.
The phase transition temperature was not possible. This suggests the existence of an additional pathway for fluorine relaxation such as spin-rotation or chemical shift anisotropy.

The dipolar model discussed above explains satisfactory the coupled H-F relaxation behavior in MgSiF$_6$·6H$_2$O and ZnSiF$_6$·6H$_2$O in the respective temperature ranges 170 K – 300 K and 170 K – 390 K. In contrast to the model developed by Thompson and Nolle the motions of water molecules were not taken into account as an effective relaxation mechanism. However, in order to decide whether a 180° flipping motion of individual water molecules takes place or not additional experiments are necessary.

The activation energies obtained from $^1$H and $^{19}$F spin-lattice relaxation rate measurements agree with those calculated by Equation (1). Unfortunately, the activation energy for [Zn(H$_2$O)$_6$]$^{2+}$ reorientation could not be obtained from relaxation rate measurements because of the sample dehydration and decomposition at high temperatures. But, the value of 12.2 kcal/mole calculated from Eq. (1) is supposed to be correct.

From the comparison of the activation energy values for the complexes in MgSiF$_6$·6H$_2$O and in ZnSiF$_6$·6H$_2$O follows qualitatively that a higher barrier against water octahedra reorientation is connected with a lower barrier hindering [SiF$_6$]$^{2-}$-reorientation and vice versa. This may be due to a different strong binding of the water ligands to the central atoms in the two cations. A stronger binding of the water ligands corresponds to weaker H-F bonds and therefore to a higher barrier against water octahedra reorientation and to a lower barrier against [SiF$_6$]$^{2-}$-octahedra reorientation.

However, a more detailed discussion has to take into account the crystal disorder in ZnSiF$_6$·6H$_2$O and in MgSiF$_6$·6H$_2$O above phase transition temperature as well as the exact sizes and moments of inertia of the complex ions.

Acknowledgement

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11 S. Folek and K. Kowol, J. Thermal Analysis 7, 199 [1975].