Proton and Fluorine-Spin-Lattice Relaxation in Polycrystalline $FeSiF_6 \cdot 6\,H_2O$

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The proton and fluorine nuclear spin-lattice relaxation has been measured in $FeSiF_6 \cdot 6\,H_2O$ in the temperature range $130\ K \leqq T \leqq 420\ K$ with standard pulse methods at 30 MHz. The relaxation times, $T_1(^1H)$ and $T_1(^{19}F)$, decrease with decreasing temperature according to the expression $T_1 = a(I) \exp(-\Delta/T)$ $(I = {}^1H, {}^{19}F)$. They show no significant dependence on the Larmor frequency. Thus, the unpaired Fe^{2+} electrons are mainly responsible for the proton and fluorine spin-lattice relaxation. The relaxation mechanism is described by an Orbach process. The ratio $T_1(^{19}F)/T_1(^1H)$ is relatively constant over the whole temperature range investigated. This is explained by the strong H ... F bonds in $FeSiF_6 \cdot 6\,H_2O$. The sharp increase of $T_1(^1H)$ and $T_1(^{19}F)$ at 224 K is attributed to the phase transition, which probably alters the crystal field at the Fe^{2+} centers.

I. Introduction

Besides several other studies on $FeSiF_6 \cdot 6\,H_2O$, [1] and the literature cited therein, previous spin-lattice relaxation time measurements performed on the proton spin system near He-temperature are also given by Skaeveland et al. [2], and on the fluorine spin system in the temperature range $150\ K \leqq T \leqq 300\ K$ by Birkeland and Svare [3]. However, these authors did not measure both the proton and fluorine spin-lattice relaxation simultaneously. Further, Birkeland and Svare observed the fluorine spin-lattice relaxation times to be virtually independent of temperature which is in contrast to our results. Therefore, in this work* we present our experimental data on proton and fluorine spin-lattice relaxation in the temperature range $130\ K \leqq T \leqq 420\ K$. From these data information on the relaxation mechanism and the involved Fe^{2+} energy levels is expected.

II. Crystal Structure

The crystal structure of $FeSiF_6 \cdot 6\,H_2O$ has been determined by a single crystal neutron diffraction method [5]. The structure is described as a slightly distorted CsCl structure composed of the octahedral complexes $(SiF_6)^{2-}$ and $(Fe \cdot 6\,H_2O)^{2+}$ (Figure 1). The room temperature space group is $R\bar{3}m$ when a static disorder involving a rotation about the threefold axis is postulated for both ionic complexes.

Looking along the threefold axis the crystal is built up by parallel columns of alternating cation and anion complexes. Each octahedron forms three hydrogen bonds to the neighboring octahedra above and below in the same column, whereas only one hydrogen bond exists for each of the six nearest octahedra in the neighboring columns. Further, each hydrogen atom participates in one O—H ... F bond, whereas each fluorine atom is involved in two such bonds (Figure 1). From the room temperature

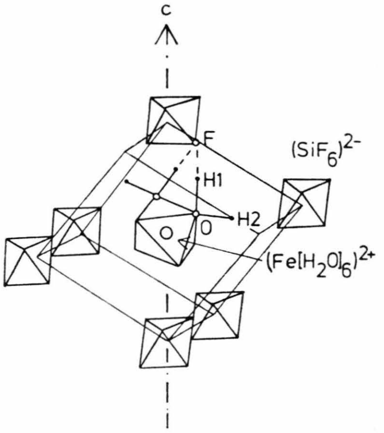

Fig. 1. Section of the $FeSiF_6 \cdot 6\,H_2O$ crystal structure at room temperature (after Hamilton [5]). The $(SiF_6)^{2-}$ octahedra at two corners of the cube are omitted for clarity.

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structure data given by Hamilton [5] the shortest distances between Fe and H, and Fe and F were calculated to be 2.78 Å and 4.08 Å, respectively.

Jehanno and Varret [6] observed a phase transition in $FeSiF_6 \cdot 6\,H_2O$ near 240 K. They described the low temperature form of $FeSiF_6 \cdot 6\,H_2O$ by the monoclinic space group $P_{2_{1/c}}$ which is, however, closely related to the high temperature form with space group $R\bar{3}m$. The main difference between the two crystal structures appears in that the mutual orientation of the anion and cation octahedra is different. In the low temperature form there are two different orientations of the $(SiF_6)^{2-}$ anions, whereas in the high temperature form only one orientation exists [7]. In contrast to that, the interatomic distances seem to be nearly the same in both structures.

III. Experimental Procedure and Results

The sample, $FeSiF_6 \cdot 6\,H_2O$, used in this study was prepared by dissolving metallic iron in H_2SiF_6 with 10% excess. A polycrystalline powder of light-greenish colour was obtained while evaporating the saturated solution at room temperature. The spin-lattice relaxation time measurements were taken at 30 MHz on a Bruker pulse NMR spectrometer. The temperature varied between $130\ \mathrm{K} \leqq T \leqq 420\ \mathrm{K}$ with an accuracy of ± 1 K. The relaxation times, T_1, were determined using standard pulse methods with pulse lengths of 2–4 µsec.

In the investigated temperature range the nuclear magnetization $M(t)$ has approached its equilibrium value, $M(t \to \infty) \equiv M(t=0)$, exponentially with time t, at least in the range $0.1 \leqq M(0) - M(t)/M(0) \leqq 0.95$. Plotting the differences of the nuclear magnetization at time t from its equilibrium value semilogarithmically as a function of t, the relaxation time T_1 was obtained from the slope of that plot. The proton and fluorine spin-lattice relaxation times, $T_1(^1H)$ and $T_1(^{19}F)$, determined in that way are shown in Figure 2. Within a certain limit of error they exhibit the same dependence on temperature and differ only by an approximate factor of 4. This can be clearly seen in the temperature range above the phase transition temperature $T = 224$ K. This temperature was also determined by a differential thermoanalysis and is in good agreement with the value given by Rubins et al. [1]. Below that temperature the difference between

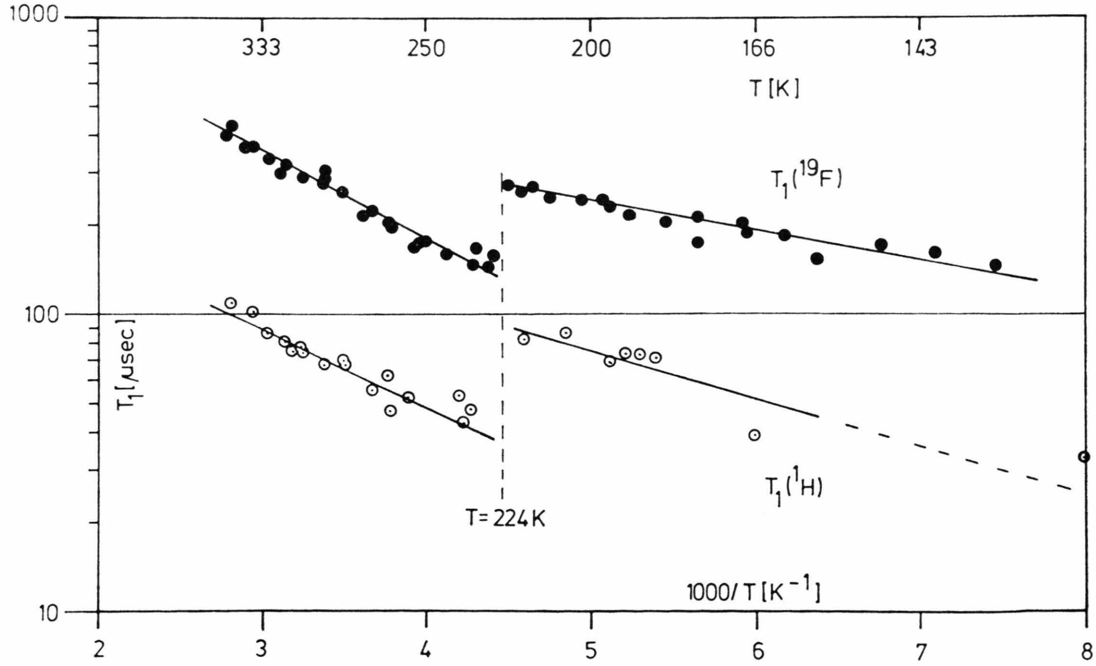

Fig. 2. The spin-lattice relaxation times, $T_1(^1H)$ and $T_1(^{19}F)$, in $FeSiF_6 \cdot 6\,H_2O$ as a function of the reciprocal temperature. The solid lines were calculated using Eqs. (8) and (10) (see text).

Table 1. Frequency dependence of the spin-lattice relaxation times, $T_1(^1H)$ and $T_1(^{19}F)$, at room temperature.

ν/MHz	10	30	45	60
$T_1(^1H)/\mu sec$	77.7	70.8	68.2	66.2
	67.5	64.7	60.5	65.5
	76.8	68.6	65.6	66.9
	77.3		69.9	
MEAN T_1	74.8 ± 3	68.0 ± 2	66.1 ± 2	66.2 $+1$
$T_1(^{19}F)/\mu sec$	382.0	312.6	329.5	297.4
	326.7	332.2	325.0	297.8
	359.5	338.6		300.3
	314.6			
MEAN T_1	345.7 ± 15	327.8 ± 8	327.0 ± 2	298.5 ± 1

$T_1(^1H)$ and $T_1(^{19}F)$ seems to become slightly temperature dependent. However, it should be noted that below 160 K $T_1(^1H)$ is too short to be measured accurately by the applied techniques.

The dependence of the observed spin-lattice relaxation times on the nuclear resonance frequency was studied at room temperature (Table 1). Although the small variation of T_1 with the Larmor frequency is slightly larger for the fluorine than for the proton spin-lattice relaxation we assume that the tumbling of both the octahedral anion and cation complexes does not affect the spin-lattice relaxation. Only at higher temperatures the motion, especially of the $(SiF_6)^{2-}$ anion, may become more effective.

IV. Discussion

As pointed out by Vega and Fiat [8] the nuclear relaxation mechanism in tumbling paramagnetic complexes is a superposition of two random processes. The first is due to the time dependent magnetic field induced by the paramagnetic center [9]. The second arises from the thermal average of the electron spin polarization which can be described in terms of the molecular susceptibility χ (χ-mechanism). The so-called χ-relaxation rate, $1/T_1$, increases quadratically with the external field. This was not observed experimentally. The possibility that the relaxation is caused by thermal motions of one or several of the constituents, $(SiF_6)^{2-}$, H_2O, and/or $(Fe \cdot 6\,H_2O)^{2+}$, or via these motions by the χ-mechanism can, therefore, be eliminated. Thus, the fluctuation with time of the magnetic field induced by the unpaired electron spins is the dominating relaxation process for both the proton and fluorine spin system. The equation describing that relaxation mechanism has the form [9]

$$1/T_1 \approx \frac{\gamma_I^2 g^2 \mu_B^2 S(S+1)}{r^6} \cdot \left(\frac{3\,\tau_c}{1+\omega_I^2 \tau_c^2} + \frac{7\,\tau_c}{1+\omega_S^2 \tau_c^2} \right). \tag{1}$$

γ_I is the gyromagnetic ratio of the nuclear spin system I (^1H or ^{19}F), S is the effective electron spin, and ω_I and ω_S are the nuclear and electron spin resonance frequencies, respectively. μ_B is the Bohr magneton and g the spectroscopic splitting factor. τ_c is given by the temperature dependent electron spin relaxation time T_{1e} [10] and the temperature independent time τ_S for the spin flips between electron neighbors, according to

$$1/T_{1e} + 1/\tau_S = 1/\tau_c\,. \tag{2}$$

As already supposed by Birkeland and Svare [3], and indicated by the temperature dependent spin lattice relaxation times (Fig. 2) T_{1e}^{-1} dominates, yielding $1/T_{1e} \approx 1/\tau_c$. From the data for τ_c estimated by Birkeland and Svare $\omega_I \tau_c \ll 1$ follow which results in

$$1/T_1 = \sum_i \frac{2\,\gamma_I^2 g^2 \mu_B^2 S(S+1)}{15\, r_i^6} \cdot \left(3\,\tau_c + \frac{7\,\tau_c}{1+\omega_S^2 \tau_c^2} \right), \tag{3}$$

for the powder average of the dipolar relaxation rate due to electron spins S at distances r_i from the nuclear spins I. Utton [11] measured the proton spin lattice relaxation rates at 4.2 K, 77 K, and 292 K, and obtained 0.117 $10^3\,sec^{-1}$, 12.9 $10^3\,sec^{-1}$, and 11.1 $10^3\,sec^{-1}$, respectively, for $1/T_1$. This means that the proton spin-lattice relaxation times run through a minimum which may be located below 120 K. Thus, the relaxation times in Fig. 2 belong to the "high temperature" branch where $\omega_S \tau_c \ll 1$. Equation (3) is then reduced to

$$1/T_1 = \sum_i \frac{20}{15} (1/r_i)^6 \gamma_I^2 \mu_B^2 g^2 S(S+1)\, \tau_c \tag{4}$$

which can also be written in the more general form

$$1/T_1(I) = a(I)\, \tau_c\,. \tag{5}$$

I denotes the nuclear spin system under investigation. To obtain a rule for the factor $a(I)$ we require the sum $\sum_i r_i^{-6}$ and the mean square of the magnetic moment including the anisotropy of the g-factor. This effect was considered by Sternlicht [12] who extended (3) accordingly. However, the anisotropy of the susceptibility in $FeSiF_6 \cdot 6\,H_2O$ is negligible in the range $130\ \mathrm{K} \leqq T \leqq 420\ \mathrm{K}$ [13]. Therefore, this effect was not taken into account. The sum $\sum_i r_i^{-6}$ can be calculated by lattice sums.

Taking the value for $g^2 S(S+1)$ given by Birkeland and Svare [3], the proton and fluorine spin-lattice relaxations. Eq. (4), differ only in the gryomagnetic ratios and in the $Fe^{2+} - I$ distances ($I = {}^1H$, ${}^{19}F$). The gyromagnetic ratios, $\gamma({}^1H) = 4.25\ 10^6$ Hz/G and $\gamma({}^{19}F) = 4.002$ Hz/G, are not very different, whereas in the high temperature crystal the Fe^{2+}-H distance of about 2.78 Å is considerably shorter than the Fe^{2+}-F distance of about 4.08 Å. Thus, the main difference between the proton and fluorine relaxation is supposed to be due to the different $Fe^{2+} - I\,(I = {}^1H, {}^{19}F)$ distances and, in a first approximation, the ratio of the proton and fluorine spin-lattice relaxation may be written as

$$T_1({}^{19}F)/T_1({}^1H) \approx \sum_i r_{\text{Fe-H}}^{-6} \Big/ \sum_i r_{\text{Fe-F}}^{-6}\,. \tag{6}$$

Assuming negligible variations of the metal-ligand distances with varying temperature (see section II) this ratio is virtually constant as can be seen in Figure 2.

From the high temperature structure data of the Fe-H and Fe-F distances we estimate the ratio $T_1({}^{19}F)/T_1({}^1H)$ to be between 10 and 12. The corresponding ratio deduced from the spin-lattice relaxation times in the range $420\ \mathrm{K} \geqq T > 224\ \mathrm{K}$ is about 4 (Figure 2). To explain the difference it must be considered that each hydrogen is involved in one, and each fluorine in two, O---H ... F bonds. Thus, the proton and fluorine relaxation rates are constrained by

$$2(1/T_1({}^1H)) = (1/T_1({}^{19}F))\,. \tag{7}$$

Taking this into account, the ratio $T_1({}^{19}F)/T_1({}^1H)$ is between 5 and 6 and agrees within reasonable limits of error with the ratio obtained from the spin-lattice relaxation time measurements. This indicates that the proton and fluorine relaxation in $FeSiF_6 \cdot 6\,H_2O$ depends strongly on the metal-ligand distances and that the relaxation pathway for the fluorine spin system runs through the O---H ... F bonds.

Above 224 K the dependence of the relaxation times on the reverse temperature (Fig. 2) was fitted by

$$T_1({}^1H) = 0.00057 \exp(-640/T) \tag{8.1}$$

for the proton spin-lattice relaxation, and by

$$T_1({}^{19}F) = 0.00304 \exp(-702/T) \tag{8.2}$$

for the fluorine spin-lattice relaxation. The errors of the preexponential and exponential factors are given in Table 2. They are rather large because of the experimental difficulties in measuring short relaxation times with standard pulse methods. However, the ratio of the preexponential factors in (8.1, 2) is nearly 5 in agreement with the above estimation.

Assuming $1/\tau \approx 1/T_{1e}$, substitution of (5) into (8) yields the longitudinal electron spin-lattice relaxation time at the Fe^{2+} center, which can generally be expressed as

$$T_{1e} = a' \exp(\Delta/T)\,. \tag{9}$$

A spin-lattice relaxation of this form is described by the Orbach process [14]. This is a two step process in which transitions between two states, $|a\rangle$ and $|b\rangle$, occur via a third intermediate state $|c\rangle$. Assuming that state $|c\rangle$ has an energy Δ with respect to the initial states, $|a\rangle$ and $|b\rangle$, and the energy splitting δ_{ab} between $|a\rangle$ and $|b\rangle$ is much less than

Table 2. Parameters used to describe the temperature dependence of the proton and fluorine spin-lattice relaxation according to the relation $T_1 = a(I) \exp(-\Delta/T)$.

	${}^1H$ system			${}^{19}F$ system			
	$a({}^1H)$ / sec	Δ / K	Δ / cm^{-1}	$a({}^{19}F)$ / sec	Δ / K	Δ / cm^{-1}	Δ_{av} / cm^{-1}
$T > 224$ K	0.00057 ± 0.00036	610 ± 188	424 ± 130	0.003 ± 0.002	702 ± 213	488 ± 148	460 ± 140
$T < 224$ K	0.00044 ± 0.00011	351 ± 171	244 ± 119	0.00077 ± 0.0004	200 ± 99	139 ± 69	190 ± 100

Δ and kT, the relaxation time is proportional to $\exp(\Delta/T)$.

In (8) the factor $a(I)$ is different for the proton and fluorine spin system, whereas the parameter Δ is determined by the splitting of the Fe^{2+} states under action of the ligand field and spin orbit coupling and, therefore, independent of the spin system under investigation. The best fit Δ values obtained from $T_1(^1H)$ and $T_1(^{19}F)$ measurements in the range $420\ K \geqq T > 224\ K$ are different (Table 2). However, regarding the limits of error we may assume an average Δ value of $460\ cm^{-1}$ above 224 K.

As pointed out by Rubins et al. [1], the splitting pattern in Fig. 3 was constructed from experimental data assuming that the cubic crystal field splitting of ^5D is much greater than that of $^5T_{2g}$, which in turn is much greater than the spin orbit coupling constant. The cubic splitting 10 Dq is given as $10400\ cm^{-1}$ [15]. Under the action of a trigonal crystal field, $^5T_{2g}$ splits into a ^5A and ^5E term, which may be split further by spin orbit coupling. The separation between ^5E and ^5A of $760\ cm^{-1}$ was determined by susceptibility measurements in the range $80\ K \leqq T \leqq 300\ K$ [16], as well as being calculated from Mößbauer data obtained at temperatures ranging from 4 K to 300 K [17] where a spin orbit coupling constant of $100\ cm^{-1}$ and $80\ cm^{-1}$, respectively, was used. From susceptibility [18], electron spin resonance [1], and spin-lattice relaxation time measurements [2] near 4 K the splitting of ^5A was determined to be about 10 and $40\ cm^{-1}$. Thus, based on the splitting pattern in Fig. 3 and on the average Δ value of $460\ cm^{-1}$, one of the ^5E sublevels may be involved as the intermediate state $|c\rangle$ in the relaxation process above 224 K.

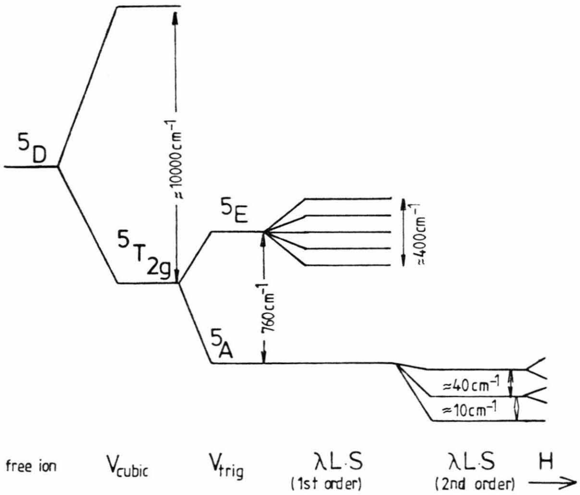

Fig. 3. Splitting pattern of the ^5D term under action of the crystal field and spin orbit coupling (after Rubins [1]). The approximate splittings of the states, ^5D, $^5T_{2g}$, ^5E, and ^5A, are given.

Below 224 K the proton and fluorine spin-lattice relaxation were fitted by

$$T_1(^1H) = 0.00044 \exp(-350/T) \qquad (10.1)$$

and

$$T_1(^{19}F) = 0.00077 \exp(-200/T), \qquad (10.2)$$

respectively. The errors of the factors are given in Table 2. The ratio, $T_1(^{19}F)/T_1(^1H)$, taken from the experimental data (Fig. 2) is nearly 4 in the range $224\ K > T > 180\ K$. This agrees with the experimental ratio for $T > 224\ K$ and indicates only a small variation of the interatomic distances with varying temperature and crystal structure as was pointed out in Section II. However, it should be noted that the ratio $T_1(^{19}F)/T_1(^1H) \approx 4$, is not confirmed by the ratio of the fitted preexponential factors in (10).

Further, below 224 K the difference in Δ deduced from the $T_1(^1H)$ and $T_1(^{19}F)$ data is larger than that above 224 K (Table 2). As already mentioned this is due to experimental difficulties while measuring relaxation times in the range of microseconds using the applied techniques. However, below 224 K an average Δ value of $190\ cm^{-1}$ is reasonable. Taking into account the change in the mutual orientation of the anion and cation complexes, at phase transition a different splitting of the Fe^{2+} terms under action of the crystal field and spin orbit coupling and, thus, a change of Δ can be expected. At 224 K Δ decreases when lowering the temperature. This may be accompanied by a decrease of the transition probabilities between the states $|a\rangle$ and $|b\rangle$ via state $|c\rangle$, which in turn then increases the relaxation times as observed experimentally. However, the exact splitting pattern and hence the identification of the energy levels involved in the relaxation process below 224 K have yet to be established.

In summary, the relaxation times, $T_1(^1H)$ and $T_1(^{19}F)$, in $FeSiF_6\ 6H_2O$ depend on the distance between the paramagnetic Fe^{2+} centers and the protons and fluorine atoms, respectively. The relaxation pathway for the fluorine spin system runs through the O---H ... F bonds in accordance with the strong hydrogen fluorine bond in this compound. Motional contributions of one of the constituents, H_2O, $(Fe \cdot 6\,H_2O)^{2+}$, $(SiF_6)^{2-}$, to the spin-lattice relaxation could not be observed in the temperature range $130\text{ K} \leqq T \leqq 420\text{ K}$. The relaxation mechanism was interpreted to be an Orbach process. The decrease of the energy level splitting Δ at phase transition very likely arises from a change in the crystal field at the Fe^{2+} centers, which, however, should be confirmed by corresponding experiments.

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