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Motion in Fluosilicates Studied with Nuclear Magnetic Resonance

Svein M. Skjæveland[1] and Ivar Svare

Physics Department, Norwegian Institute of Technology, Trondheim, Norway

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Abstract

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Motional narrowing of H^1 and F^{19} NMR lines in the fluosilicates of Mn, Fe, Co, Ni, Cu and Zn has been studied. Narrowing due to SiF_6^{2-} complex reorientation occurs at about 225 K, 180 K, 200 K, 150 K, 120 K and 150 K, respectively, and rapid $Me(H_2O)_6^{2+}$ reorientation occurs at 225 K, 220 K, 340 K, 375 K, 350 K and 340 K respectively. This variation is correlated with the variation in density of these nearly isomorphic crystals. At nitrogen temperatures the lattices are static and no effect of any Jahn-Teller motion in $CuSiF_6 \cdot 6H_2O$ could be seen.

1. Introduction

We have studied the motional narrowing of the H^1 and F^{19} NMR lines in single crystals and powders of Mn, Fe, Co, Ni, Cu and Zn fluosilicates of general formula $MeSiF_6 \cdot 6H_2O$, and also in the corresponding Ti and Sn salts of Ni. This gives information about the barriers against reorientation of the SiF_6^{2-} and $Me(H_2O)_6^{2+}$ complexes, and the purpose of the investigation was to see if there were any great differences between these salts that could be related to the dynamic Jahn-Teller motion probably present in $CuSiF_6 \cdot 6H_2O$ [1], or to the structural disorder found in $FeSiF_6 \cdot 6H_2O$ [2]. After this work was essentially finished, structure data showing disorder also in the other salts were published [3, 4].

2. Theory

Pauling [5] assumed the fluosilicates to be isomorphous with $NiSnCl_6 \cdot 6H_2O$ which has one molecule in the trigonal unit cell. The trigonal angle is close to 96°. However, a neutron diffraction study of $FeSiF_6 \cdot 6H_2O$ shows a twofold disorder in the orientation of the SiF_6^{2-} and the $Fe(H_2O)_6^{2+}$ complexes [2], and X-ray structure determination of the Co, Ni and Zn fluosilicates shows unusual disorder in SiF_6^{2-} orientations also in these salts [3]. From the ESR-demonstration of dynamic Jahn-Teller effect in Zn-diluted $CuSiF_6 \cdot 6H_2O$ [1] a more complicated structure was expected for the copper salt, and Ray et al. [4] recently gave a hexagonal structure for $CuSiF_6 \cdot 6H_2O$ where three of four $Cu(H_2O)_6^{2+}$ octahedrons are tetragonally distorted.

Some of the fluosilicates show structural transitions at low temperature, e.g. $CoSiF_6 \cdot 6H_2O$ at about 246 K [6]. A NMR-study of $FeSiF_6 \cdot 6H_2O$ in liquid helium indicates considerable changes in proton positions relative to room temperature coordinates [7] even without a sharp transition.

The second moments of the NMR lines for fluosilicate powder samples have been calculated by Dereppe et al. [8] using the coordinates of $FeSiF_6 \cdot 6H_2O$. The nuclear interaction alone should give 31.06 gauss² for H^1 resonance in a rigid lattice, most of which, 25.77 gauss², comes from interaction with the other proton in the same water molecule 1.55 Å away. Rapidly rotating SiF_6^{2-} complexes reduce the rigid $Me(H_2O)_6^{2+}$ proton second moment to 27.28 gauss². The F^{19} second moment should be 13.59 gauss² in a rigid lattice. The dipolar broadening effect of the paramagnetic ions must be added to these moments, and their contribution in powders is approximately [8]

$$\langle \Delta H^2 \rangle_{IS} = (4/5)\mu^4 H_0^2/9k^2T^2r^6 \tag{1}$$

Here $\mu = g\beta[S(S+1)]^{\frac{1}{2}}$ is the magnetic moment of the ions and r is the distance from a nucleus to the nearest ion. For the protons with $r \approx 2.7$ Å in $H_0 = 3\,500$ gauss at 77 K Eq. (1) gives $\langle \Delta H^2 \rangle_{IS} \approx 2.3$ gauss² for the Cu salt, 18 gauss² for Ni-, 95 gauss² for Co-, 150 gauss² for Fe-, and 220 gauss² for $MnSiF_6 \cdot 6H_2O$.

More information can in principle be obtained from second moments of single crystals, but for paramagnetic single crystals it is best to study the line shape. At low temperature the magnetic moments on the ions split the proton line into several components which give information on the proton positions in the static lattice [7].

Complex reorientations or jumps between disorder positions with frequency faster than $(\gamma/2\pi)\Delta H \approx 10^4$–$10^5$ Hz will reduce the dipolar line broadening because the interaction is averaged. In particular, the reduction factor for the intrawater proton second moment in powders is [9]

$$\begin{aligned} F = (2n)^{-2} \{ & [\sum_n (3\cos^2\theta_n - 1)]^2 + 3[\sum_n \sin 2\theta_n \cos\phi_n]^2 \\ & + 3[\sum_n \sin 2\theta_n \sin\phi]^2 + 3[\sum_n \sin^2\theta_n \cos 2\phi]^2 \\ & + [\sum_n \sin^2\theta \sin 2\phi]^2 \} \end{aligned} \tag{2}$$

Here θ and ϕ are the polar angles of the n possible directions of the proton–proton vector relative to any convenient axis system. Eq. (2) will be applied to the suggested deformations of the $Cu(H_2O)_6^{2+}$ complexes [4] to decide whether the distortions are dynamic or not.

The reorientation frequencies can be found from the qualitative line narrowing formula by Gutowsky and Pake [10]

$$\begin{aligned} f_c &= f_0 \exp(-V/RT) \\ &\approx \frac{\gamma \Delta H}{2\pi} \operatorname{cotg} \frac{\pi}{2} \left[\frac{\Delta H^2 - W^2}{U^2 - W^2} \right] \end{aligned} \tag{3}$$

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[1] Present address: Texas A & M University, College Station, Texas 77840, USA.

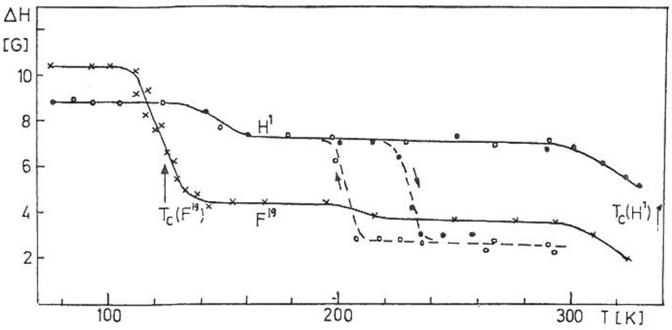

Fig. 1. Line width between maximum slopes of H^1 and F^{19} lines in single crystal of $CuSiF_6 \cdot 6H_2O$ mounted with crystal axis perpendicular to $\boldsymbol{H}_0$. Open circles going down in temperature, filled circles going up.

Here U is the line width below the transition, W is the line width above the transition, ΔH is the line width that varies with temperature, and γ is the gyromagnetic ratio. V is the barrier against reorientation, which for these octahedral complexes is likely to be different for reorientations around 3-fold and 4-fold axes. If different reorientations give about the same narrowing temperature, Eq. (3) is likely to give misleading results and unreasonable vibration frequencies f_0 if the processes cannot be treated separately. Then it is easier and safer to use the approximate formula by Waugh and Fedin [11]

$$V(\text{cal/mole}) \approx 37\ T_c \tag{4}$$

where T_c is the temperature at half narrowing of the proton line width. We use the same relation for the fluorines as well.

The paramagnetic ions may also broaden the NMR lines by causing short nuclear spin relaxation. This contribution is [12]

$$(\Delta H)_{\text{Relax}} = 1/\gamma T_1 = 3\mu^2\gamma\tau \sin^2\theta \cos^2\theta / r^6 \tag{5}$$

Here θ is the angle between $\boldsymbol{H}_0$ and $\boldsymbol{r}$. τ is the correlation time of a paramagnetic ion and it is equal to the shortest of either the electron spin lattice relaxation time T_{1e} or the time between spin flips due to dipolar and exchange interactions between neighbouring ions. We have used $\omega_I\tau \ll 1$. The relaxation broadening will vary with θ in a rigid lattice, and rapid motion will not reduce $(\Delta H)_{\text{Relax}}$ except for some averaging of $\sin^2\theta\cos^2\theta$. We expect $(\Delta H)_{\text{Relax}}$ to be most important in the manganese salt since Mn^{2+} has the largest moment μ and relatively long T_{1e}.

3. Results

Fluosilicate powders and single crystals of hexagonal shapes were slowly grown from solutions in thermostat controlled baths. The resonance measurements were done at about 15 MHz with a Robinson type marginal oscillator and Fieldial controlled Varian magnet. The sample temperature was measured with a Comark thermocouple meter.

$CuSiF_6 \cdot 6H_2O$

These crystals were grown below room temperature to make sure that only the hexahydrate was formed. Typical line widths as function of temperature are shown in Fig. 1. The main narrowing of F^{19} occurs at about 125 K, and Eqs. (3) and (4) give $V = 4.5$ kcal/mole and $f_0 = 4.5 \times 10^{12}\ s^{-1}$. Deuterated salts give the same V and f_0 for F^{19}. The rapid reorientation of SiF_6^{2-} also narrows the H^1 resonance a little at about the same temperature. No thermal hysteresis was seen in the narrowing of the F^{19} line.

A narrow proton line appears around 240 K when the sample is warmed and it disappears at about 220 K when cooled. However, a broad line with unchanged width is still visible up to above room temperature, and most of the intensity is contained in the broad line. We interprete the narrow line as due to inclusions of liquid that freeze well below 273 K because of the salt content and the high pressure in the limited volumes. Different methods of crystal growing and degassing in vacuum could not eliminate the narrow component of the proton line. Heating of $CuSiF_6 \times 6H_2O$ above room temperature caused rapid loss of crystal water and partial transition towards $CuSiF_6 \cdot 4H_2O$, and such samples showed a narrow proton line down to about 260 K.

The broad proton line narrows due to $Cu(H_2O)_6^{2+}$ reorientation at about 350 K corresponding to $V = 13$ kcal/mole, and this motion also reduces the remaining width of the fluorine line.

Attempts to deduce axes of rotation for the $Cu(H_2O)_6^{2+}$ and SiF_6^{2-} complexes from second moments of single crystals were unsuccessful. The experimental powder second moments at 77 K are (36 ± 2) gauss^2 for H^1 and (17 ± 2) gauss^2 for F^{19}. This is slightly more than the rigid lattice theoretical values of Dereppe et al. [8], and we conclude that there can be no reorientation of the complexes and the amplitude of any dynamic Jahn-Teller distortion of $Cu(H_2O)_6^{2+}$ has to be small. In particular, rapid jumps of a complex between the four water orientations given by Ray et al. [4] would reduce the intrawater proton second moment from 25.77 gauss^2 to about 14 gauss^2, and the total calculated second moment to at most 21 gauss^2. Such a reduction is not observed. We conclude that any Jahn-Teller motion in pure $CuSiF_6 \cdot 6H_2O$ is either slower than 10^4 Hz at 77 K, although it is faster than 10^9 Hz in the Zn-diluted salt, or that the amplitude of distortion is considerably less than the difference between the sets of proton coordinates given by Ray et al.

In $CuSiF_6 \cdot 4H_2O$ grown above room temperature we find F^{19} narrowing at about 240 K as reported previously by Rangarajan and Ramakrishna [13].

$FeSiF_6 \cdot 6H_2O$

Powders of iron fluosilicate have been studied with NMR by Dereppe et al. [8], but the field from the Fe^{2+} ion broadens the lines according to Eq. (1) and little information can be obtained. With single crystals we see narrowing of the F^{19} resonance at about 180 K and of H^1 at about 220 K corresponding to barriers of 6.7 and 8.1 kcal/mole respectively from Eq. (4), but the transition regions are broad and give somewhat smaller barriers using Eq. (3). Below 160 K the proton resonance shows structure expanding as $1/T$ which is characteristic of a static paramagnetic complex.

Rangarajan and Ramakrishna [13] found narrowing of both H^1 and F^{19} at about 190 K, but strangely they did not see the broadening effect of Fe^{2+}. Vaughan et al. [14] found that a pressure of 50 kbar would stop the SiF_6^{2-} reorientation at room temperature.

$MnSiF_6 \cdot 6H_2O$

Here the powder resonance of both protons and fluorines narrows at about 225 K corresponding to $V = 8.3$ kcal/mole. Optical measurements show a structural transition with about 10 K hysteresis just at this temperature [15]. However, the NMR narrowing is gradual and shows no hysteresis and we do not think that it is connected with the structural transition.

The proton line in this salt has long wings that cause it to appear less intense than the fluorine line. This is probably an effect of the relaxation broadening Eq. (5). The antiferromagnetic ordering temperature 0.17 K [16] corresponds to an approximate time between exchange spin flips of $\tau \approx 2 \cdot 10^{-10}$ s, and depending upon θ this value of τ gives $(\Delta H)_{\text{Relax}}$ from 0 to 30 gauss. The resonance in crystallites with the largest $(\Delta H)_{\text{Relax}}$ would be difficult to see with our apparatus.

$ZnSiF_6 \cdot 6H_2O$

Muthukrishnan and Ramakrishna [17] report the narrowing temperatures $T_c(H^1) = 350$ K and $T_c(F^{19}) = 140$ K, and we fid similar values $T_c(H^1) = 340$ K and $T_c F^{19}) = 150$ K corresponding to barriers of 12.5 and 5.5 kcal/mole respectively. Motion in this salt has also been studied by Thompson and Nolle [18] with pulse measurements of T_1. They found the F^{19} barrier to be $V(F^{19}) = 0.26$ eV $= 6.0$ kcal/mole and $V(H^1) = 0.21$ eV $= 4.8$ kcal/mole. This value for $V(H^1)$ cannot be the barrier for reorientation of the water octahedron, the observed H^1 relaxation rate must be caused by dipolar interactions with the moving F^{19} nuclei. Hence both 0.21 eV and 0.26 eV are determinations of the SiF_6^{2-} barrier in zink fluosilicate, and their average gives just our result.

$NiSiF_6 \cdot 6H_2O$

We find $T_c(F^{19}) = 150$ K corresponding to $V(F^{19}) = 5.5$ kcal/mole. Chiba and Soda [19] give the same value and $T_c(H^1) = 375$ K which is too high for us to measure.

$CoSiF_6 \cdot 6H_2O$

This crystal has a structural phase transition and cracks at 246 K[6], but this does not effect the NMR line widths appreciably. We find the line narrowing temperatures $T_c(H^1) = 340$ K and $T_c(F^{19}) = 200$ K corresponding to 12.5 kcal/mole and 7.4 kcal/mole respectively. Rangarajan and Ramakrishna [13] strangely did not see any line narrowing up to room temperature in this salt.

$NiTiF_6 \cdot 6H_2O$ and $NiSnF_6 \cdot 6H_2O$

These salts have $T_c(F^{19})$ of 145 K and 190 K respectively. The line narrowing in $NiTiF_6 \cdot 6H_2O$ occurs gradually and does not seem to be connected with the structural phase transition at 120–140 K [20].

4. Discussion

Our data show that in all of these fluosilicates the lattice is essentially static at liquid nitrogen temperature. The SiF_6^{2-} complexes reorients faster than 10^5 Hz when the temperature is raised above 130–230 K, but the water complexes go much slower. The characteristic temperatures T_c are plotted in Fig. 2 together with the barriers from Eq. (4). We note the contrasting behaviour of $T_c(H^1)$ and $T_c(F^{19})$ as the metal ions is changed from Mn^{2+} to Zn^{2+}. All the fluosilicates have essentially the same structure, but their densities differ considerably [2–4.21] and in the same pattern as $T_c(H^1)$ as shown in Fig. 2. We interprete a high density as a result of a strong binding of the water ligands to the metal ion and which also causes a high barrier against reorientation of the water octahedron. But this weakens the H–F bonds and allows easy reorientation of the SiF_6^{2-} complexes. Most of the difference in water bond strength between the transition metal ions is caused by the crystal field splitting of the $3d$ electron states which stabilizes the complexes [22].

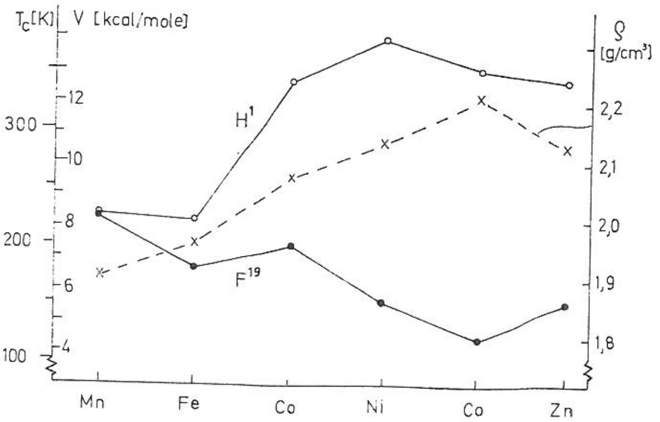

Fig. 2. Line narrowing temperatures T_c and corresponding barriers V in $MeSiF_6 \cdot 6H_2O$ compared with the densities of the crystals.

Each complex is bound into the crystal with 12 hydrogen bonds. But it is not necessary to break all bonds completely for reorientation, evidently the bonds can stretch and partly jump over to new neighbours, and the total barrier to SiF_6^{2-} reorientation in these salts corresponds to only about one hydrogen bond completely broken. Surprisingly, the SiF_6^{2-} barriers are much less than in $(NH_4)_2SiF_6$ even if the NH_4^+ groups there are in rapid motion below 77 K [23]. However, the SiF_6^{2-} reorientation in the metal fluosilicates is probably helped by the disorder that has been shown to be present in most of them at room temperature [2–4], and vice versa the disorder may be a result of rapid reorientation.

The ionic radii are such that Sn^{4+} fits very poorly into an octahedral arrangement of 6 F^-. Hence SnF_6^{2-} is expected to be less spherical than TiF_6^{2-} and SiF_6^{2-} and thus has a higher $T_c(F^{19})$, as observed.

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Note added in proof:

A recent article by K. Muthukrishnan and J. Ramakrishna (J. Chem. Phys. **59**, 5571 (1973)) give approximately the same NMR line narrowing temperatures for some of these fluosilicates as we have found. They derive barriers with Eq. (3) while we use Eq. (4), and therefore their V values differ somewhat from our results.

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Physics Department
N. T. H.
N-7034 Trondheim, Norway