N.M.R. STUDY OF INTERNAL MOTIONS IN ZINC FLUOROSILICATE HEXAHYDRATE

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Nuclear magnetic resonance line splittings, line widths and observed second moments are profoundly influenced by the presence of motion of spins in the crystal lattice. If the correlation frequency is large compared with the rigid lattice linewidth (expressed in frequency units), the motion will result in an averaging of the local fields and hence a narrowing of the resonance line. A study of the temperature dependence of the NMR line-width and observed second moments can therefore, give information about the correlation frequency and the potential barrier hindering the motion.

Dereppe et al. reported to have studied the proton and fluorine resonances as a function of temperature in the hexahydrated fluorosilicates of magnesium, zinc and iron and also in sodium fluorosilicate. They gave the details only in the case of magnesium fluorosilicate hexahydrate. But they mentioned that transitions in the zinc salts took place in the same manner as in the magnesium and iron salts but at a few degrees lower. We find that while the magnesium salt gave results similar to those obtained by Dereppe et al., the zinc salt gave completely different results. In this short note, we therefore, briefly report our results in the zinc salt.

Dilute hydrofluorosilicic acid was prepared by allowing 40% hydrofluoric acid to stand on quartz pieces for several days. The acid was filtered and added to a paste of zinc oxide. When the reaction was over, the resulting solution was filtered by suction and allowed to evaporate. Crystals obtained were purified by recrystallisation. The substance was finely powdered and enclosed in a glass capsule for use in the experiments.

The NMR spectra were recorded using a modified PKW type spectrometer working at 13.5 MHz. The modulation frequency was 330 Hz and the sweep rate was 0.08 gauss/sec. Some of the calculations were performed using the IBM 360/44 computer.
The spectra were recorded in the temperature range 90°K to 420°K. The temperature variation of the observed second moment of the proton resonance is shown in Fig. 1, while that of the fluorine resonance is shown in Fig. 2.

For a simple model\textsuperscript{4-8} it can be shown that

\[
\ln \nu_c = \ln \left( \frac{\gamma_a \Delta H}{2 \pi} \right) - \ln \tan \nu \pi/2 \left( \frac{\Delta \frac{H^2}{U_B} - V_B^2}{U_B^2 - V_B^2} \right)
\]
where $\nu_c$ is the correlation frequency, $\gamma_H$ is the magnetogyric ratio of the resonant nuclei, $\Delta H$, $U_H$ and $V_H$ are the line widths (or second moments) at temperatures within the transition region, below and above the transition respectively. The correlation frequency is, in general, temperature dependent and for a classical description of the motion, it is assumed to have the form

$$\nu_c = \nu_0 \exp(-V/RT)$$

where $V$ is the height of the potential barrier hindering the motion.

The temperature dependence of the correlation frequency for the proton resonance is shown in Fig. 3 while the corresponding plot for the fluorine resonance is shown in Fig. 4. From the plots the height of the potential barrier hindering the proton motion is found to be 15.1 K Cal/mole while that hindering the fluorine motion is 2.533 K Cal/mole. The values of the constant $\nu_0$ for the two cases are $2.018 \times 10^{14}$ cps and $9.977 \times 10^8$ cps respectively.
FIG. 3

Plot of $ln v \times (1000/T^0K)$ for proton motion in zinc fluorosilicate hexahydrate

In can be seen that our results disagree with the statement of Dereppe et al. in that the fluorine transition takes place at a much lower temperature and the proton transition takes place at a much higher temperature when compared with the magnesium salt. Thus, there is considerable difference in the activation energy of reorientation in the two salts and this can be seen by comparing the value of 6.6 K Cal/mole for fluorine and 11.6 K Cal/mole for proton in the magnesium salt with our 2.533 K Cal/mole and 15.1 K Cal/mole respectively in the zinc salt. This confirms the view of Chiba et al. that apart from the interaction of ion clusters of opposite sign, other interactions play a prominent role in these crystals. A detailed investigation of line width and second moment transition in other fluorosilicates is being carried out and the results will be reported shortly.
From figs. 1 and 2 it may be seen that the second moment transition of fluorine (centred around $135^\circ$K) resonance results in a small decrease in the second moment of the proton resonance. Similarly the second moment transition of the proton resonance, (centred at $355^\circ$K) results in a lowering of the local field seen by the reorienting fluorine nuclei.

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