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Recently Mössbauer resonance experiments of Dézsi et.al. [1] and Nozik et. al. [2] showed that on warming up quenched dilute aqueous solutions to about $-80^{o}C$ an irreversible change of the arrangement of ice molecules around the cations takes place. These authors suggested that ice, containing a small amount of impurity, on quenching from liquid state to $-196^{o}C$ has a cubic structure which on warming up transforms at about $-80^{o}C$ to normal hexagonal ice.

While the Mössbauer resonance gives information on the cation sites, the present proton magnetic resonance /PMR/ experiments were performed in order to study the processes as observed in the ice matrix.

The measurements were made on solutions of 0,47 M ferrous chloride in distilled water. In the few ml samples thermal equilibrium was reached in about a minute after quenching.

A wide line NMR spectrometer was used at a frequency of 26 MHz, the modulation amplitude was 0,5 Gauss, the amplitude of the radiofrequency field was chosen so low that signal distortion caused by relaxation effects appeared only at temperatures lower than $-120^{o}C$.

Figure 1. shows two charecteristic PMR spectra.

a./ At $-196^{o}C$ the spectrum did not differ from that of quenched distilled water. The measured second moment of the PMR line, in agreement with [3] on pure ice, was 30 ± 2 Gauss^2, the peak to peak line width $14 \pm 0,5$ Gauss.

b./ On warming up from $-196^{o}C$ the spectrum decomposes to two lines. At about $-100^{o}C$ a strongly asymmetric line with a width of $3 \pm 0,5$ Gauss appears at the center of the spectrum. The broader component of the spectrum remains up to -60°C unchanged, at higher temperatures it shows a motional narrowing [4]. The intensity of the narrow line increases up to -70°C and although the reproducibility was not very good it never exceeded 10 % of that of the whole spectrum.

Keeping the temperature at -70°C the narrow line vanishes within a half to a few hours and does not reappear again. The change is irreversible, on recooling to lower temperatures the spectrum remains unchanged, the narrow line is missing.

c./ On continuing the heating from -70°C after the disappearance of the narrow line, a new narrower symmetric line with a width of about 1.5 Gauss appears at -50°C, with an intensity rapidly increasing with temperature. By recooling from -30°C the intensity of this narrow line decreases slowly and is still well observable at -90°C.

The above described temperature dependence of the PMR spectrum can be well correlated to the previous observations, where a transition temperature lower than -70°C, but with usually a slower transition rate was reported.

One of the most important feature of the results is that the PMR spectra of samples with given temperature histories exhibit two lines indicating the presence of ice molecules in two different states of motion. The asymmetry of the norrow line appearing at temperatures from -100 to -70°C can be attributed to moving ice molecules surrounding the paramagnetic ferrous ions [5]. It follows from the intensity measurements, assuming the system to be homogeneous, that even at maximum intensity of the narrow line only part of the system undergoes a change, namely the ice molecules which are in the first or second coordination shell of iron atoms. The peak to peak linewidth of 3 Gauss precludes the possibility of diffusion at temperatures lower than -70°C [6], the motion is believed to be of a hindered rotational or oscillational type.

The independence of the shape of the broad line from temperature supports but does not prove unambiguously the absence of phase transformation in the bulk of ice. It is probably impossible to distinguish cubic and hexagonal ice [7] by PMR second moment measurements, because of their structural similarity. In spite of this fact the asymmetry and small intensity of the narrow line in the critical temperature region makes highly unlikely a cubic-hexagonal transition in the bulk of ice. Aqueous ferrous chloride solutions have for 30 w % concentration an eutectic point at -36°C [8]. The narrow line characteristic of rapid motion observed at -50°C supports the assumed separation [2] of an eutectic phase at this temperature.

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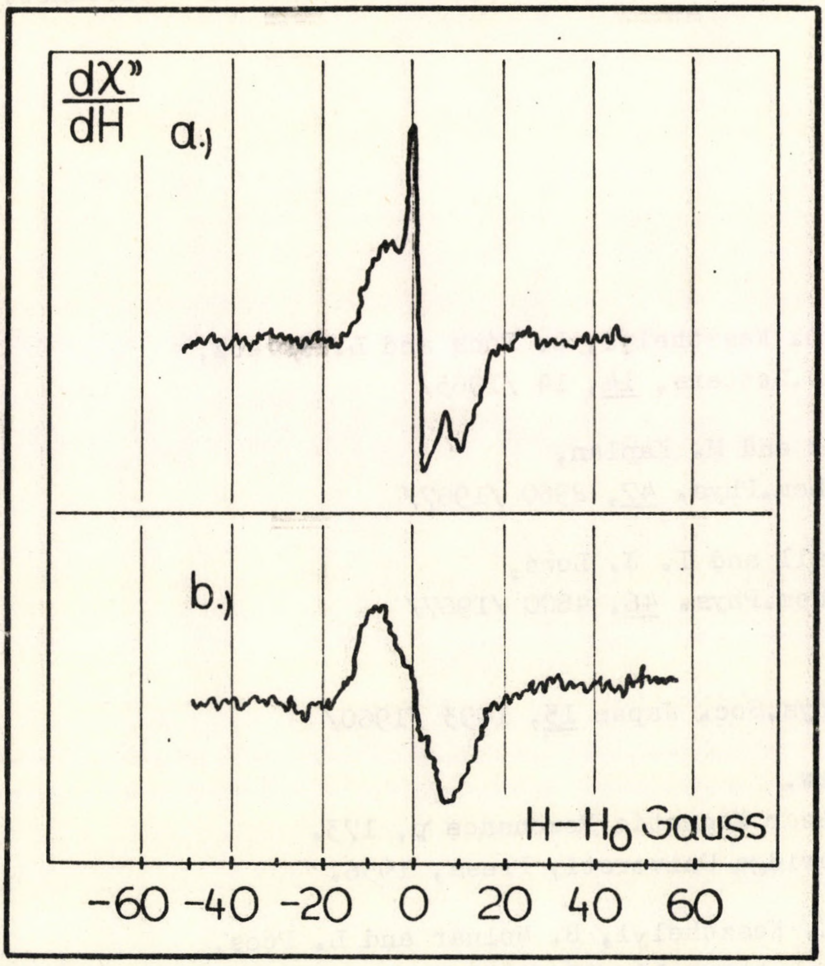

Fig. 1

Spectra of quenched aqueous $FeCl_2$ solution heated to $-71^{o}C$
a./ 10 minutes, b/ 2 hours after thermal equilibrium was reached. /Ho=6100 Gauss/