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REORIENTATIONS IN  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$   
STUDIED BY THE PROTON MAGNETIC  
RESONANCE AND THE QUASIELASTIC  
NEUTRON SCATTERING METHODS

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METHODS

BADANIE RUCHÓW REORIENTACYJNYCH W  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  METODAMI  
MAGNETYCZNEGO REZONANSU PROTONOWEGO I KWAZIELASTYCZNEGO  
ROZPRASZANIA NEUTRONÓW

ИССЛЕДОВАНИЯ РЕОРИЕНТАЦИОННЫХ ДВИЖЕНИИ В  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$   
МЕТОДОМ ЯДЕРНОГО МАГНИТНОГО РЕЗОНАНСА И МЕТОДОМ КВАЗИУПРУГОГО  
РОССЕЯНИЯ НЕЙТРОНОВ

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***Wydanie I***

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1)  $[Mg(H_2O)_6](ClO_4)_2 \cdot 2H_2O$

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Proton magnetic relaxation measurements carried out for  $[Mg(H_2O)_6](ClO_4)_2$  revealed two processes responsible for  $T_1$  vs temperature dependence: One connected with  $H_2O$   $180^\circ$  flips about the symmetry axis and one connected with a tumbling of the complex cation. Quasielastic neutron scattering measurements gave another evidence of  $H_2O$   $180^\circ$  flips. The reorientational correlation times, which in the 273 K - 325 K region are of the order of picoseconds, as derived from NMR coincide perfectly well with those derived from QNS.

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Pomiary magnetycznego rezonansu jądrowego (NMR) dla  $[Mg(H_2O)_6](ClO_4)_2$  wykryły dwa procesy odpowiedzialne za temperaturową zależność czasu  $T_1$ : jeden związany z przeskokami molekuł  $H_2O$  o kąt  $180^\circ$  wokół osi symetrii i jeden związany z ruchem "kociołkującym" całego kationu kompleksowego. Pomiary kwazielastycznego rozpraszania neutronów (QNS) dostarczyły również ewidencji przeskoków molekuł  $H_2O$  o kąt  $180^\circ$ . Czasy korelacji reorientacyjnej, które w zakresie temperatur 273 - 325 K są rzędu pikosekund, uzyskane metodą NMR, wykazują doskonałą zgodność z odpowiednimi czasami uzyskanymi metodą QNS.

Измерения ядерного магнитного резонанса ЯМР для  $[Mg(H_2O)_6](ClO_4)_2$  обнаружили два процесса отвечающие за температурную зависимость времени  $T_1$ : один связанный с перепрыжками молекул  $H_2O$  на  $180^\circ$  вокруг оси симметрии, а один связанный с движением комплексного целого катиона. Измерения квазиупругого рассеяния нейтронов (КРН) дали тоже подтверждение перепрыжков молекул  $H_2O$  на  $180^\circ$ . Времена реориентационной корреляции, которые в пределе температур 273 - 325 К порядка пикосекунд, полученные методом ЯМР показывают отличное согласие с соответствующими временами, полученными методом КРН.

## 1. INTRODUCTION

The divalent metal perchlorate hexahydrates  $[\text{Me}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  with  $\text{Me}^{2+} = \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}$  or  $\text{Ni}^{2+}$  have at room temperature similar pseudohexagonal crystal lattices. A number of phase transitions for this group of salts have been detected by Mössbauer studies [1, 2], magnetic susceptibility [3, 4], specific heat [5-7], crystal field splitting in electron spin resonance [8-11] and Raman scattering [12].

To help in clarifying the structures and the nature of the phase transitions, we have studied the magnesium salt  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  with proton spin-lattice relaxation (NMR) and incoherent quasielastic neutron scattering (QNS). The perchlorates are very hygroscopic and show a great tendency to triple twinning. This makes it difficult to get good and reproducible experimental data, but  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  appears to be one of the more stable salts in the series.

$[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  has the space group  $\text{Pmn}2_1$  ( $\text{C}_{2v}^7$ ) at room temperature [13]. Phase transitions have been detected for this salt at  $T_{01} = 325 \text{ K}$  [7],  $T_{02} = 272 \text{ K}$  [8,7] and at  $T_{03} = 103 \text{ K}$  [1,7,9], but only the room temperature structure is known.

In the 325 K phase transition the  $\text{ClO}_4^-$  anions seem to play a dominating role. The Raman bands contour analysis applied to this salt [12] showed a large  $\text{ClO}_4^-$  reorientational mobility above the phase transition and their abrupt slowing down at the phase transition. The main aim of the present study is to observe motions of and in the complex cation, via the methods sensible selectively to protons, i.e. the NMR and QNS methods.

Two types of motion is likely for the  $\text{Mg}(\text{H}_2\text{O})_6$  complex shown in Fig. 1. One ligand water molecule may flip by  $180^\circ$  around the Mg-O symmetry axis. We expect this motion to be easier and faster than the tumbling motion of the whole complex where the ligand water molecules exchange places. The advantage of the proton relaxation measurements is to differentiate between the two motions. The correlation times can also be de-

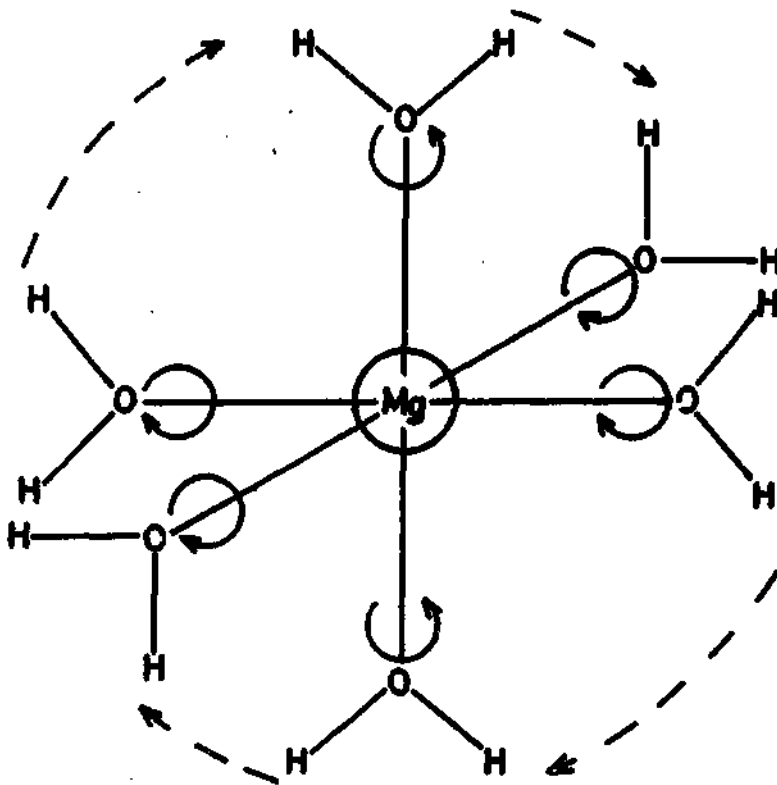


Fig. 1.  $\text{Mg}(\text{H}_2\text{O})_6$  complex with possible modes of motion indicated: 180° flip of each  $\text{H}_2\text{O}$  (solid arrows) and tumbling motion of the whole complex (dashed arrows).

rived and will be shown to be in good agreement with the times derived from quasielastic neutron scattering.

## 2. PROTON RELAXATION MEASUREMENTS

The NMR measurements were carried out in the Physics Department of the University of Trondheim, Norway.

The spin-lattice relaxation rate from the two types of motion for the  $Mg(H_2O)_6$  complex modulating the proton dipolar interaction is

$$\tau_1^{-1} = \sum_{in} C_1(n) \left[ \frac{\tau_1(n)}{1 + \omega_0^2 \tau_1^2(n)} + \frac{4\tau_1(n)}{1 + 4\omega_0^2 \tau_1^2(n)} \right] \quad (1)$$

Here  $\omega_0 = \gamma B_0$  is the measuring frequency, the coefficients  $C_1(n)$  are related to the change in dipolar coupling to the neighbour  $i$  over a cycle of the motion of type  $n$ , and the correlation time is assumed to vary as

$$\tau_1(n) = \tau_{\infty}(n) \exp(E_n/kT) \quad (2)$$

The relaxation rate in the rotating frame is more sensitive to slow motion

$$\tau_{1\rho}^{-1} = \sum_{in} C_1(n) \left[ \frac{5}{2} \frac{\tau_1(n)}{1 + \omega_0^2 \tau_1^2(n)} + \frac{\tau_1(n)}{1 + 4\omega_0^2 \tau_1^2(n)} + \frac{3}{2} \frac{\tau_1(n)}{1 + 4\omega_1^2 \tau_1^2(n)} \right] \quad (3)$$

Here  $\omega_1/\gamma = B_1$  is the effective field in the rotating frame.

For an isolated water molecule where the proton-proton vector  $\vec{r}_0$  is randomly reoriented we have

$$C_0 = (\mu_0/4\pi)^2 (3/10) \gamma^4 \hbar^2 / r_0^2 = 1.0 \times 10^{10} s^{-2} \text{ with } r_0 = 1.6 \text{ \AA}.$$

But only tumbling of the whole complex can give random reorientation and this relaxation efficiency. Water  $180^\circ$  flips alone do not change the dipolar interaction and contribute nothing

to the relaxation rate. For  $180^\circ$  flips only the weaker interaction with next nearest neighbours at  $r_1 \approx 2.8 \text{ \AA}$  gives relaxation with total  $C_1(180^\circ) \approx 10^9 \text{ s}^{-2}$ . Hence from (1) we expect minima in  $T_1$  of order 15 ns from tumbling motion and of order 150 ns from  $180^\circ$  flips. We use this difference to label the observed minimum in  $T_1$ .

The room temperature crystal space group  $Pm\bar{2}_1$  permits piezoelectricity [13, 14] and pulse measurements on a piezoelectric powder may cause "ringing" that obscures the free induction decay signal. The electric field in the coil excites mechanical oscillations in each crystallite, and this couples back to the coil after the pulse. Hence we could not measure the magnetic relaxation times in dry powder of  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  below the phase transition  $T_{01}$  which has hysteresis from about 324 to about 328 K. Above  $T_{01}$  the structure must be non-piezoelectric. Likewise, we did not see piezoelectricity below  $T_{03}$  which showed hysteresis from about 110 to 120 K. But the failure to observe piezoelectric "ringing" should not always be taken as a proof of non-piezoelectricity. For example, the "ringing" could be shorted out by moisture and electrolytic conduction on the surfaces of the hygroscopic crystallites down to about 160 K, and for this it was only necessary to leave the samples in the air for a while. Drying the samples in vacuum would then restore the "ringing" in the  $Pm\bar{2}_1$  phase. Another way of avoiding the piezoelectric "ringing" was to put the sample in a liquid without protons like  $\text{CCl}_4$ , which is a poor solvent for ionic salts. This would mechanically dampen oscillations so that the magnetic signal could be observed.

The  $T_1$  and  $T_{1p}$  of protons in powders of  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  measured with the usual pulse sequences are shown in Fig. 2 and Fig. 3. Around 133 K there is a minimum in  $T_1$  of about 200 ns which must be caused by  $180^\circ$  flips. The solid line here is fitted with (1) and (2) to give  $E_a(180^\circ) = 3.2 \text{ kcal/mol}$  and factor  $\tau_{180}(180^\circ) = 2 \times 10^{-14} \text{ s}$ . The resulting correlation time for  $180^\circ$  flips is also shown in Fig. 2 as function of inverse tem-



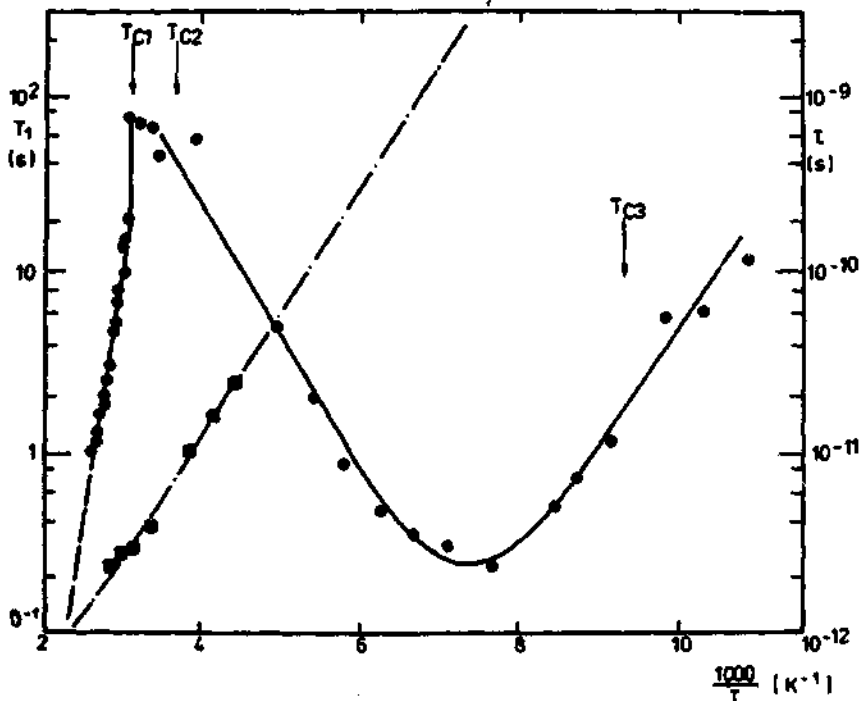


Fig. 2. Measured proton  $T_1$  at 30 MHz fitted with Eqs. (1) and (2) (full line, left hand scale) as function of inverse temperature. Dash-dot line (right hand scale) is derived correlation time  $\tau$  ( $180^\circ$ ). Squares ( $\blacksquare$ ) are correlation times determined by the QNS method.

perature. The effect of the slower tumbling above  $T_{01}$  is seen in  $T_1$  and  $T_{1\rho}$  in Fig. 3. We cannot go to high enough temperature to see the minimum in  $T_1$ , but the extrapolation according to (1), (2) and (3) give  $\tau_{\text{min}} = 35$  ns with  $E_a(\text{tumbl.}) = 12$  kcal/mol and  $\tau_{\infty}(\text{tumbl.}) = 3 \times 10^{-14}$  s. While  $T_{\text{min}}$  is high and  $\tau_{\infty}(\text{tumbl.})$  short compared to expectations, these results are not too unreasonable.

Below the phase transition  $T_c \approx 325$  K  $T_1$  increase by a factor of about four to a value probably determined by impurities. The correlation time of the tumbling motion is therefore increased below  $T_{01}$  by a factor of at least four. Little change in  $T_1$  is seen at the phase transitions  $T_{c2}$  and  $T_{c3}$ .

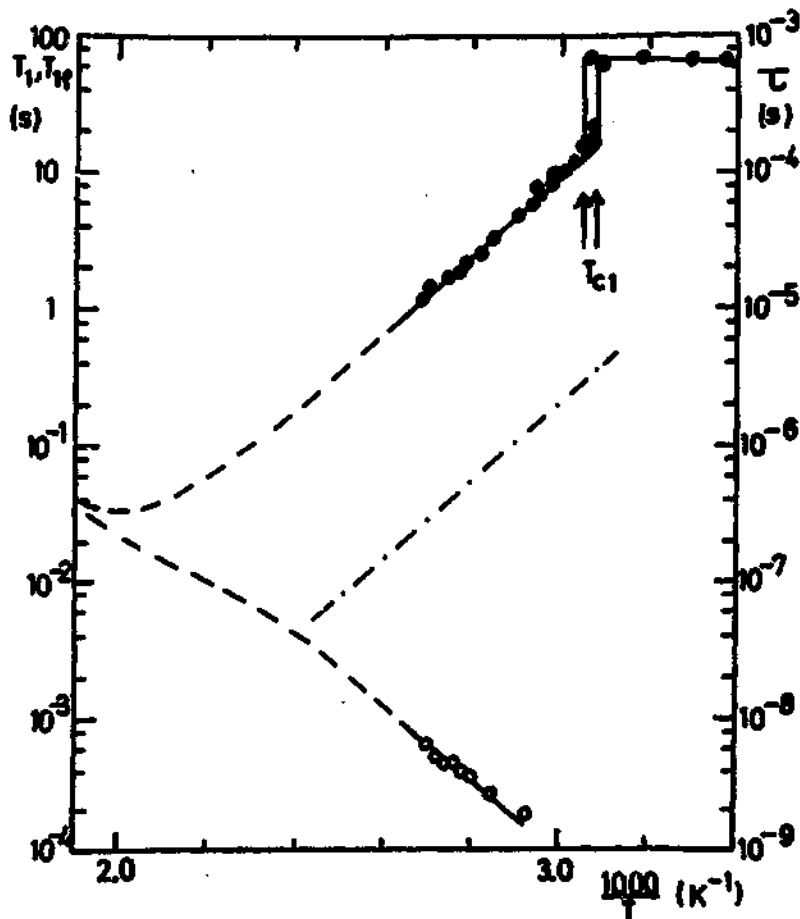


Fig. 3. Proton  $T_1$  (filled points) and  $T_{1\rho}$  (open points) at 30 MHz above room temperature with dashed lines as extrapolation according to Eqs. (1), (2) and (3) (left hand scale). Dash-dot line (right hand scale) is derived correlation times  $\tau$  (tumbl.).

### 3. QUASIELASTIC NEUTRON SCATTERING MEASUREMENTS

The QNS measurements were carried out in the Institutt for Energiteknikk at Kjeller, Norway, by using the time-of-flight spectrometer "TOF" installed at the JEEP II reactor. The spectrometer cooperates with a liquid hydrogen cold source and

with the pyrolytic graphite monochromator. The analysing system is composed of the curved slits chopper and the  $^3\text{He}$  counters. The chopper was situated between the monochromator and the sample. The incident neutron wavelength was  $4.189 \text{ \AA}$  which corresponds to  $4.661 \text{ meV}$ .

The powdered sample was closed in a thin flat aluminium sample-holder mounted inside of either an oven or a cryostat possessing a temperature regulation and control. The temperatures in which the measurements were made were:  $353 \text{ K}$ ,  $333 \text{ K}$ ,  $313 \text{ K}$ ,  $295 \text{ K}$ ,  $261 \text{ K}$ ,  $242 \text{ K}$ ,  $224 \text{ K}$  and  $128 \text{ K}$ . The measurements were carried out at only one scattering angle  $80^\circ$ , which corresponded to the neutron momentum transfer  $1.924 \text{ \AA}^{-1}$ . The instrumental resolution for measurements in the oven was  $0.173 \text{ meV}$  and for measurements in the cryostat  $0.152 \text{ meV}$ .

The scattered neutron spectrum recorded in the time-of-flight scale was transformed into the energy scale. Then the background in form of a straight line passing through points far from the wings of the quasielastic peak was subtracted. To the resulting spectrum a model scattering function convoluted by the instrumental function was fitted. As a model scattering function that corresponding to instantaneous proton jumps connected with  $180^\circ$  reorientations of  $\text{H}_2\text{O}$  groups around their symmetry axes was chosen. The corresponding formula is:

$$\frac{d^2\sigma}{d\Omega d\omega} \sim \frac{1}{2} \left( 1 + \frac{\sin 2\pi d}{2\pi d} \right) \delta(\omega) + \frac{1}{2\pi} \left( 1 - \frac{\sin 2\pi d}{2\pi d} \right) \frac{\Gamma}{\Gamma^2 + (\hbar\omega)^2} \quad (4)$$

where  $d^2\sigma$  is the cross-section corresponding to neutron scattering into the solid angle  $d\Omega$  and with the energy change  $\hbar d\omega$ , the neutron energy and momentum transfers are  $\hbar\omega$  and  $\hbar\vec{k}$  respectively,  $d$  is the radius of the proton trajectory at the  $180^\circ$  reorientational jump and  $\Gamma$  is connected with the average residence time  $\tau$  between the jumps by the formula

$$\tau = \frac{2\hbar}{\Gamma} \quad (5)$$

The quality of fits was controlled by the  $\chi^2$  test. From the fitting procedure the  $\tau$  values, and hence the  $\tau_c$  values, were obtained.

Fig. 4 shows, for all temperatures, the experimental QNS peaks together with the fitted model of  $H_2O$   $180^\circ$ -jumps. The peaks for all temperatures are normalized to equal heights.

The obtained correlation times  $\tau_c$  (residence times between instantaneous  $180^\circ$  jumps) are presented as squares ( $\blacksquare$ ) in Fig. 2. It should be pointed out that these values ( $\blacksquare$ ) are situated close to the dash-dot line representing the correlation times evaluated from the NMR experiment. Thus, a very good agreement between the two methods has been achieved.

#### 4. DISCUSSION AND CONCLUSIONS

1. We have found in  $[Mg(H_2O)_6](ClO_4)_2$  activation energies  $E_a(180^\circ) = 3.2$  kcal/mol and  $E_a(\text{tumbl}) = 12$  kcal/mol for respective  $180^\circ$  flips of  $H_2O$  molecules around their symmetry axes and for tumbling of the whole  $Mg(H_2O)_6$  complex. The ratio  $E_a(\text{tumbl})/E_a(180^\circ) \approx 4$  may crudely represent the ratio of the numbers of hydrogen bond that must be broken in the two types of motion, two for  $180^\circ$  flips and of the order eight for tumbling.

2. The NMR measured correlation time  $\tau_c(180^\circ)$  is in very good agreement with the residence time  $\tau_c$  between  $180^\circ$  angular jumps derived from quasielastic neutron scattering.

3. Dayal et al. [8] found a non-linear variation with temperature of the crystal field parameter  $D$  of  $Mn^{2+}$  in  $[Mg(H_2O)_6](ClO_4)_2$  between 103 and 272 K. This is likely to be related to the excitation of the  $H_2O$  torsional oscillations in this temperature range.

4. There is no direct evidence of any dependence of the  $H_2O$   $180^\circ$  flips on the phase transitions. The results may be interpreted as connected with a gradual slowing down of the flips with lowering temperature. The cation tumbling, on the

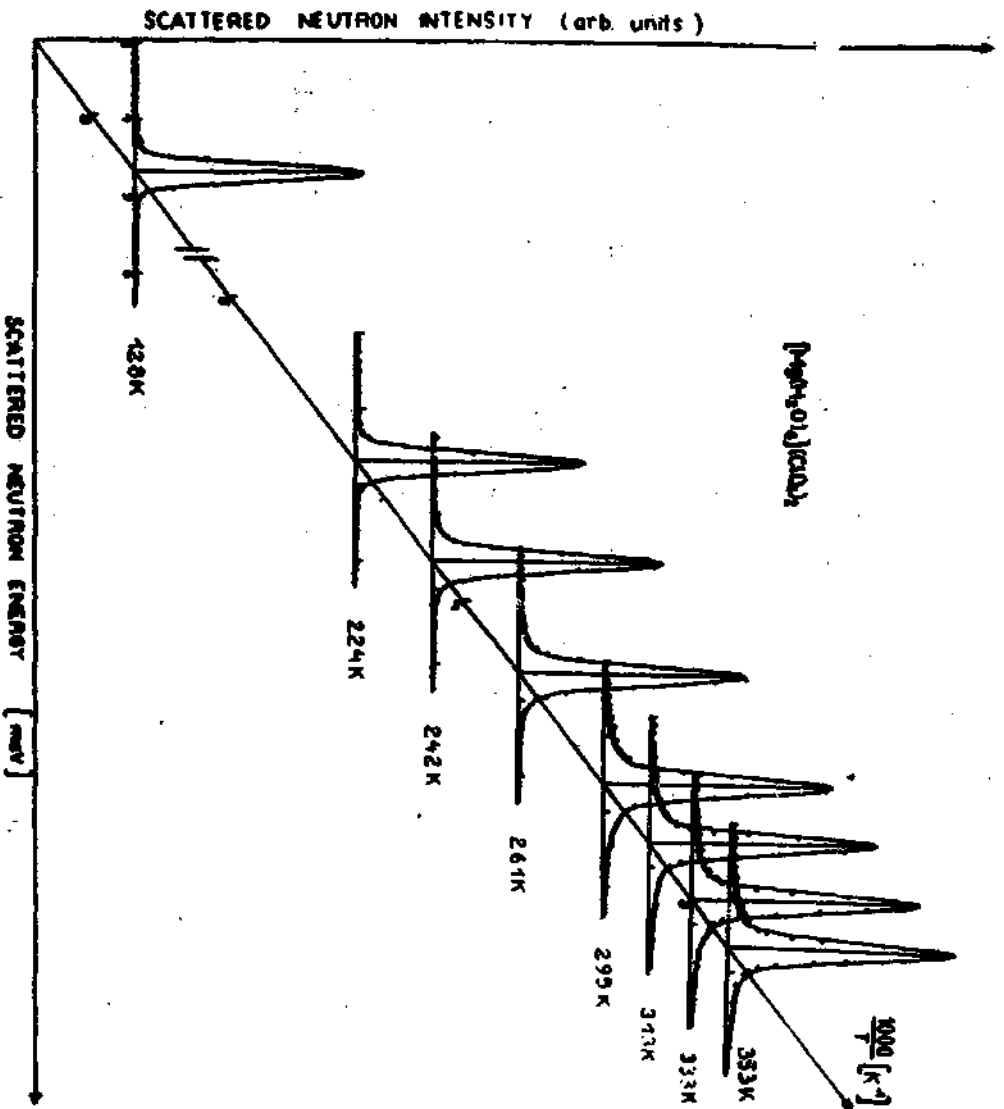


FIG. 4. Experimental QNS peaks together with the model curves (solid lines) obtained by fitting of Eq. (4) to the experimental points. Scattering angle  $90^\circ$ .

other hand, is strongly perturbed by the transition occurring at 325 K.

5. The barrier to  $H_2O$   $180^\circ$  flips in  $[Mg(H_2O)_6](ClO_4)_2$  is significantly higher than the barrier to  $NH_3$   $120^\circ$  jumps in an analogous  $[Mg(NH_3)_6](ClO_4)_2$  compound [15] (3.2 kcal/mole and 0.5 kcal/mole respectively).

6. We found  $[Mg(H_2O)_6](ClO_4)_2$  to be piezoelectric at room temperature, in agreement with the space group  $Pm\bar{3}$ .

7. The NMR relaxation properties as well as the QNS studies of other perchlorates will be published elsewhere.

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