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Neutron scattering study of the reorientational motions for NH_3 groups in $(\text{NH}_3(\text{CH}_2)_3\text{NH}_3)\text{MnCl}_4$

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Résumé. — Des expériences de diffusion incohérente quasi-élastique des neutrons ont été réalisées à partir de cristaux orientés et d'échantillons polycristallins des composés $(\text{NH}_3(\text{CH}_2)_3\text{NH}_3)\text{MnCl}_4$ et $(\text{NH}_3(\text{CD}_2)_3\text{NH}_3)\text{MnCl}_4$ sur le domaine de température 4-300 K. Des spectromètres à rétro-diffusion et à temps de vol ont été utilisés; les spectres ont été enregistrés à l'aide de différentes résolutions (entre 1 et 170 μeV) et sur un large domaine de transfert de moment (entre 0,17 et 2,57 $\text{\AA}^{-1}$).

On conclut que les groupes NH_3 effectuent des mouvements de réorientation en dessous de 300 K. Les spectres expérimentaux ont été reproduits, de manière satisfaisante, par un modèle de sauts de $2\pi/3$ des groupes NH_3 , avec un temps de corrélation de 10^{-11} s à 300 K et une énergie d'activation d'environ 27 kJ/mole.

Enfin, une comparaison de ces résultats avec ceux de la littérature, provenant essentiellement d'études antérieures par RMN et Raman, est présentée.

Abstract. — Incoherent quasi-elastic neutron scattering experiments have been performed on oriented crystals and on polycrystalline samples of $(\text{NH}_3(\text{CH}_2)_3\text{NH}_3)\text{MnCl}_4$ and $(\text{NH}_3(\text{CD}_2)_3\text{NH}_3)\text{MnCl}_4$ compounds in the 4-300 K temperature range. Backscattering and time of flight spectrometers were used; spectra were obtained using different resolutions (1-170 μeV) and a large range of momentum transfers (0.17-2.57 $\text{\AA}^{-1}$).

It is concluded that NH_3 groups reorientate below 300 K; the experimental spectra have been satisfactorily fitted with a model of $2\pi/3$ jumps of the NH_3 groups, associated with a correlation time of 1×10^{-11} s at 300 K and an activation energy roughly equal to 27 kJ/mol.

Finally a comparison with literature data, mainly from NMR and Raman results, is presented.

1. Introduction.

The propylene diammonium metal tetrachloride layer compounds having formula $(\text{NH}_3(\text{CH}_2)_n\text{NH}_3)\text{MCl}_4$ with $n = 2, 3, 4, 5$ and $M = \text{Cu, Mn, Fe, Cd, ...}$ belong to the perovskite structural family. Their magnetic properties [1, 2] and their structural phase transitions have been extensively studied [2, 6]. These compounds crystallize in a two dimensional structure consisting of nearly isolated layers of corner-sharing MCl_6 octahedra parallel to the (a, c) planes. The interlayer bonding in the b -direction is only achieved by the alkylene-diammonium cations through NH...Cl hy-

drogen bonds. For the 1-3 propylenediammonium manganese tetrachloride compound (Fig. 1), noted hereafter as PDA MnCl_4 , the sequence of phase transitions presented in table I results from calorimetric [3] and Raman experiments [7]. The structures of the corresponding phases have been investigated by different authors :

(i) Willet and Riedel [2], from a neutron diffraction study, have shown that the room temperature phase III is disordered. Also, from broad line proton NMR measurements, they conclude that this disorder is of a dynamical nature, the PDA ions undergoing rotational motions around their long b -axes.

Table I. — Phase sequence and structural data on PDA MnCl_4 .

Phase I		Phase II		Phase III		Phase IV	
$T/\text{K} \leftarrow$		$336 \leftarrow$	$306 \leftarrow$	$110 (^{\circ}) \leftarrow$			
Imma ^(b)		Fmmn ^(b)		Imma ^(a)			
$Z = 2$		$Z = 2$		$Z = 2$			
				Pnma ^(b)	Ordered ^(c)		
				$Z = 4$			
				Disordered ^(c)			

Z gives the primitive unit cell multiplicity,

^(a) from ref. [2],

^(b) from ref. [5],

^(c) from ref. [7].

Fig. 1. — Simplified picture of the structure of $(\text{NH}_3(\text{CH}_2)_3\text{NH}_3)\text{MnCl}_4$ showing two layers of MnCl_6 octahedra and only the skeleton of one propylene diammonium cation (hydrogen atoms are omitted).

(ii) Sourisseau and Lucazeau [6, 7], from an infrared and Raman study, have shown that the fully ordered phase is obtained below 100 K and that at about 110 K a phase transition must occur; this low temperature ordered phase was identified as phase IV. From a systematic study of the temperature dependence of Raman frequencies and half-widths, it was concluded that the dynamical disorder is associated with NH_3 groups below 300 K. Assuming that the broadening of Raman bands is entirely due to NH_3 jumps, an activation energy of 4.2 kJ/mol was derived and found similar to the six fold potential barrier ($V_6 \approx 5.02$ kJ/mol) associated with the NH_3 torsional movements. However no arguments were given to rule out the possibility of a three fold barrier $V_3 \approx 20.08$ kJ/mol [7]. Above 110 K, it is believed that NH_3 movements are coupled with reorientations of PDA ions and that this could explain the observation

Fig. 2. — Comparison of the theoretical (full-lines) and experimental ($\square$ points) EISF for different reorientational movements of the NH_3 mobile protons in powdered samples. a) on a circle of radius 0.942 Å for $2\pi/3$ jumps, b) on a circle of radius 0.942 Å for $2\pi/6$ jumps.

of a unique N-H stretching frequency. There will be in a first approximation an equiprobability of the possible positions of PDA ions. Above 336 K (phase I), from the point of view of their long axis rotational degree of freedom, PDA and NH_3 groups are in a quasi liquid state.

(iii) Kind, Plesko and Roos [5] have concluded from NQR and NMR experiments that in phase III the chains are almost ordered and are in one out of the four potential wells of the cavity. These four orientations exist within an unit cell and are related by symmetry operations of the Pnma group. A dynamical disorder of the chains between two orientations was only observed above 306 K. Moreover these authors do not observe at low temperature any anomaly in their ^{35}Cl NQR frequencies and conclude that there is no phase transition at 110 K as proposed in reference 7.

We have thus undertaken incoherent quasi-elastic neutron scattering (IQENS) experiments in order to get a better insight into the dynamical disorder, in particular to evaluate to what extent the PDA ions are involved. Our preliminary neutron scattering results on PDA MnCl_4 (using ^{12}H and $^6\text{D}^6\text{H}$ derivatives) have already been reported [8, 9].

2. Experimental conditions.

Polycrystalline samples of $(\text{NH}_3(\text{CH}_2)_3\text{NH}_3)\text{MnCl}_4$ [2] and $(\text{NH}_3(\text{CD}_2)_3\text{NH}_3)\text{MnCl}_4$ [10] compounds were freshly prepared and controlled by infrared spectroscopy before and after IQENS experiments in order to check that neither hydration nor H/D exchange had taken place. Powder samples were contained in circular thin walled aluminium cans (5 cm in diameter) and their thickness was adjusted to ensure a transmission of about 90 %. Oriented mosaic samples composed of platelet crystals (with the (a, c) basal plane) were also contained in slab shaped aluminium containers and they were oriented either at 135° ($Q_{\parallel}$) or at 45° ($Q_{\perp}$) with respect to the incident beam (Fig. 3). The measured transmissions in these cases were found equal to only 75 %.

Neutron scattering experiments were performed at the Institut Laue-Langevin (ILL, Grenoble, France) with the backscattering (BS) high resolution IN10 instrument and the time of flight (TOF) IN5 and IN6 spectrometers [11]. The experimental conditions are summarized in table II. In the BS instrument seven detectors were set at scattering angles between $2\theta = 9.75^\circ$ and 153° . Ten detector positions ranging

Fig. 3. — Schematic drawing of the orientations of the monocrystalline platelets with respect to the incident neutron beam. *a*) $3\pi/4$ configuration called « Q parallel » to the layer planes ($Q_{\parallel}$), *b*) $\pi/4$ configuration called « Q perpendicular » to the layer planes ($Q_{\perp}$), Δ_1 and Δ_2 are the axes of rotation for the NH_3 groups with respect to the base planes.

from $2\theta = 23.5^\circ$ to 129° were used in the IN5 TOF spectrometer while sixteen and twenty four counters at angles between $2\theta = 12^\circ$ and 114° were utilized in the IN6 TOF spectrometer with incident wavelengths 5.9 Å and 4.1 Å, respectively. Angles that were contaminated by Bragg reflections were eliminated from the data. The spectra were corrected by standard programs for detector efficiency, sample container efficiency, scattering absorption and self-shielding [12, 13]. A BS spectrum of the sample at 4 K was used as a resolution run while all the TOF spectra were normalized to the elastic scattering from vanadium.

3. Theoretical background and EISF curves.

The incoherent scattering law, $S_{\text{inc}}(Q, w)$ for a polycrystalline sample in the quasi-elastic region takes the form

$$S_{\text{inc}}(Q, w) = \exp(-Q^2 \langle u^2 \rangle) \times \{ S_{\text{inc}}^{\text{rot}}(Q, w) + B(Q) \}, \quad (1)$$

where the first term is the Debye-Waller factor in which $\langle u^2 \rangle$ is the mean square hydrogen vibrational amplitude and $B(Q)$ is the inelastic background contribution. The rotational scattering function, $S_{\text{inc}}^{\text{rot}}(Q, w)$ has been calculated for different models of proton reorientations and the problem of random one dimensional rotation in a N -fold cosine potential has been treated by Dianoux and Volino [14, 15]. Here we will however use the simple rotational jump model. In this model of rotational jumps between a finite number N of allowed sites, the scattering law consists of an elastic term and a series of broadened terms. It takes the following form for a powder sample [16].

$$S_{\text{inc}}^{\text{rot}}(Q, w) = A_0(Q) \delta(w) + \frac{1}{\pi} \sum_{i=1}^{N-1} A_i(Q) L(\tau_i^{-1}). \quad (2)$$

where

$$A_i(Q) = \frac{1}{N} \sum_{p=1}^N j_0\left(2Qa \sin \frac{\pi p}{N}\right) \times \cos\left(\frac{2\pi ip}{N}\right), \quad (3)$$

Table II. — *Experimental conditions.*

Compound (geometry)	Instrument	Incident wavelength (Å)	Resolution FWHM (μeV)	Temperature range (K)	Momentum range (Å ⁻¹)
$(\text{NH}_3(\text{CD}_2)_3\text{NH}_3)\text{MnCl}_4$ $(\text{NH}_3(\text{CH}_2)_3\text{NH}_3)\text{MnCl}_4$ Powders	IN10	6.28	1.0	4-280	0.17-1.95
$(\text{NH}_3(\text{CH}_2)_3\text{NH}_3)\text{MnCl}_4$ Platelets (135° and 45°)	IN5	$\left\{ \begin{array}{l} 10.05 \\ 5.14 \end{array} \right.$	$\left\{ \begin{array}{l} 20 \\ 130 \end{array} \right.$	$\left\{ \begin{array}{l} 250-304 \\ 250-304 \end{array} \right.$	$\left\{ \begin{array}{l} 0.25-1.13 \\ 0.49-2.21 \end{array} \right.$
Powders (45°)	IN5	5.14	130	292	0.49-2.21
$(\text{NH}_3(\text{CH}_2)_3\text{NH}_3)\text{MnCl}_4$ Platelets (135° and 45°)	IN6	$\left\{ \begin{array}{l} 5.9 \\ 4.1 \end{array} \right.$	$\left\{ \begin{array}{l} 68 \\ 170 \end{array} \right.$	$\left\{ \begin{array}{l} 299 \\ 299 \end{array} \right.$	$\left\{ \begin{array}{l} 0.24-1.75 \\ 0.32-2.57 \end{array} \right.$

j_0 is the spherical Bessel function of the first kind of order zero $\left(j_0(x) = \frac{\sin x}{x}\right)$ and $L(\tau_i^{-1})$ is a Lorentzian function,

$$L(\tau_i^{-1}) = \frac{\tau_i}{1 + w^2 \tau_i^2}, \quad (4)$$

in which τ_i^{-1} is the HWMH and the characteristic times are given by

$$\tau_i = \frac{\tau_c}{2 \sin^2 \left(\frac{\pi \cdot i}{N} \right)}, \quad (5)$$

where τ_c is the correlation time between two successive jumps of a proton. It is known [14-16] that the first term of broadening in the summation over all the possible jumps gives the largest contribution and thus, the experimental HWHM of the quasi-elastic peaks may be sometimes approximated by $1/\tau_1$. Moreover, in the limiting case $N \rightarrow \infty$, this jump probability can be identified with the rotational diffusion coefficient, D_r . The term $A_0(Q)$ in the above expression 2 represents the elastic incoherent structure factor, EISF; it is the purely elastic fraction of the integrated elastic-plus-quasielastic intensity. The EISF is directly related to the geometry of the molecular motion and is a measure of the time averaged spatial distribution of the protons [17]. EISF values as a function of $\bar{Q}$ ($\text{\AA}^{-1}$) can be compared with the calculated ones for different models. In fact, $2\pi/3$ and $2\pi/6$ are the most probable jump angles for uniaxial rotation of NH_3 groups in PDA MnCl_4 . Thus, figure 2 shows the theoretical EISF curves for a random walk of N-H protons among 3 and 6 equidistant sites on a circle of radius $a = 0.942 \text{ \AA}$ assuming that the CH_2 backbone of the PDA ion is rigidly fixed. Under these conditions, the theoretical expression is

$$\text{EISF} = \rho + (1 - \rho) A_0(Q), \quad (6)$$

where ρ is the ratio of the number of fixed protons to the total number of protons. As the NH_3 groups exhibit a very small radius of gyration we cannot discriminate between both jump models within the Q range used but, from the good agreement with the experimental points, we conclude that only half of the protons ($\rho = 0.5$) in PDA cations are involved in the dynamical process. These protons are surely those of NH_3 groups since a (weak) broadening in the quasi-elastic region has been observed in the high resolution experiments using the deuterated powder sample $(\text{NH}_3(\text{CD}_2)_3\text{NH}_3)\text{MnCl}_4$ (see later).

In the « semicrystalline » case of flat platelets, the amplitude factors $A_i(Q)$ were first derived by Barnes [16]:

$$A_i(Q) = \frac{1}{N} \sum_{p=1}^N J_0 \left(2 Q a \times \sin v \times \sin \frac{\pi p}{N} \right) \times \cos \left(\frac{2 \pi i p}{N} \right) \quad (7)$$

where v is the angle between $\mathbf{Q}$ ($\mathbf{Q} = \mathbf{k} - \mathbf{k}_0$) and the axis of rotation. Therefore, we have oriented the platelets with angles equal to $3\pi/4$ and $\pi/4$ with respect to the incident beam in order to discriminate between Q parallel ($Q_{\parallel}$) and Q perpendicular ($Q_{\perp}$) spectra. However, one must take care in PDA MnCl_4 that the axes of rotation of NH_3 groups are tilted from the base planes with angles roughly equal to 60° for one group and to 120° for the other one [2]. For arbitrary Q corresponding to a detector position at an angle of $2\theta^\circ$ degrees $\left(\bar{Q} = \frac{4\pi \sin \theta}{\lambda_0} \right)$ we thus obtain the following analytical expressions:

$$\begin{aligned} A_0(Q_{\parallel} \text{ for } 2\theta^\circ) &= \\ &= \frac{1}{2} \left\{ \frac{1}{N} \sum_{p=1}^N J_0 \left(2 Q a \sin(\theta^\circ + 15^\circ) \sin \left(\frac{\pi p}{N} \right) \right) + \right. \\ &\quad \left. + \frac{1}{N} \sum_{p=1}^N J_0 \left(2 Q a \sin(\theta^\circ + 75^\circ) \sin \left(\frac{\pi p}{N} \right) \right) \right\}. \quad (8) \end{aligned}$$

$$\begin{aligned} A_0(Q_{\perp} \text{ for } 2\theta^\circ) &= \\ &= \frac{1}{2} \left\{ \frac{1}{N} \sum_{p=1}^N J_0 \left(2 Q a \sin(75^\circ - \theta^\circ) \sin \left(\frac{\pi p}{N} \right) \right) + \right. \\ &\quad \left. + \frac{1}{N} \sum_{p=1}^N J_0 \left(2 Q a \sin(\theta^\circ - 15^\circ) \sin \left(\frac{\pi p}{N} \right) \right) \right\}. \quad (9) \end{aligned}$$

We can check easily that for the particular detector position at $2\theta = 90^\circ$, the angles v between $\mathbf{Q}$ and the axes of NH_3 rotation are equal to 60° and 120° in the former case ($Q_{\parallel}$) while both angles v are equal to 30° in the latter one ($Q_{\perp}$) as is expected from geometrical considerations (Fig. 3). The corresponding theoretical EISF curves obtained via the above relations and the expression (6), with the assumption that ρ is again equal to 0.5, are plotted on figure 4. These curves apply to the $2\pi/3$ jump model but almost identical curves are obtained for the $2\pi/6$ model over the $0-2.5 \text{ \AA}^{-1}$ Q range. Once more we cannot discriminate between both jump models but experimental points

Fig. 4. — Comparison of the theoretical (full-lines) and experimental ($\bigcirc$ points for $\lambda_0 = 5.14 \text{ \AA}$ and $\bigcirc$ points for $\lambda_0 = 4.1 \text{ \AA}$) EISF for $2\pi/3$ jumps of the NH_3 groups and using oriented crystals of PDA MnCl_4 , a) results for the configuration « Q perpendicular » (« $Q_{\perp}$ »), b) results for the configuration « Q parallel » (« $Q_{\parallel}$ »).

either for $Q_{\parallel}$ or for $Q_{\perp}$ compare nicely with the theoretical curves and confirm that at about 300 K the mobile protons of PDA are those of the NH_3 groups.

4. Results and discussion.

4.1 BACK SCATTERING RESULTS. — A very weak broadening in the quasi-elastic region has been detected with the high resolution (1 μeV) IN10 instrument using the partly deuterated (^6H - ^6D) powder sample $(\text{NH}_3(\text{CD}_2)_3\text{NH}_3)\text{MnCl}_4$ at 280 K (Fig. 5). However, the weakness of this effect and the poor statistics prevent any significant analysis in order to determine the dynamical process in which the NH_3 groups are involved. Moreover, the experimental profiles obtained with hydrogenated samples (^1H) differed slightly from those of the resolution. In any case, no tunnelling effect was observed at low temperature indicating that the potential barriers must be relatively high and insofar as these results are significant a correlation time $\tau_c^{(280\text{K})}$ of about 10^{-10} - 10^{-11} s can be suggested. Moreover, we have measured the normalized elastic intensity without Doppler drive for different Q values and over the whole temperature range 4-280 K in order to check whether a diffusional motion is really taking place. In such experiments the incident neutron beam is monochromatic and only the neutrons which do not display energy changes are backscattered. Thus, for nonzero Q values the neutrons scattered with energy changes are not collected by the detectors and do not contribute to the elastic intensity. On figure 6, we have plotted $-\text{Ln}(\text{Int}_{\text{elast}})$ versus Q^2 at different temperatures using the normalizations with the run at 4 K and the monitor counting rates (M_1). In fact, the ratios (D_i/M_1) of the counting rates in the detector D_i and in the monitor 1 (M_1) have been measured in the temperature range 4-250 K and for

Fig. 5. — Comparison of the resolution (dotted line) and of the PDA $\text{MnCl}_4(^6\text{H}^6\text{D})$ spectra taken with a powdered sample at 4 K and 280 K, respectively, on the backscattering IN10 spectrometer ($\lambda_0 = 6.28 \text{ \AA}$) for a scattering angle of 153° ($Q = 1.946 \text{ \AA}^{-1}$). The two peaks have been normalized to the same maximum intensity. The very weak broadening and the poor statistics prevent any quantitative analysis of the inelastic contribution which is expected to spread over a much larger energy range.

each detector the variations of the elastic intensity were estimated with respect to the value of this ratio at 4 K, i.e. $\text{Int}_{\text{elast}} = (D_i/M_1)_T / (D_i/M_1)_{4\text{K}}$. The non-linear temperature dependence observed on these curves for $T \geq 85 \text{ K}$ indicates that the usual Debye-Waller factor is not sufficient to explain the decreases of the elastic intensity. Thus, NH_3 groups undergo a rotational motion leading to what appears as an unusual amplitude factor as soon as the first phase transition at 110 K is approached. Finally, we conclude that the weak broadening in the quasi-elastic region is connected with pure NH_3 motions and that the energy transfer range for this scattering is much larger than 12.5 μeV as soon as the NH_3 groups start to jump. This weak effect is in agreement with the very small radius of gyration ($a < 1.0 \text{ \AA}$) of NH_3 groups.

Fig. 6. — Variations of the elastic intensity versus $Q^2/(\text{\AA}^{-2})$ at different temperatures for a powdered sample of PDA MnCl_4 . In fact, the peak intensities have been normalized to the countings on the monitor 1 and compared with the ratio obtained at 4 K (see text).

4.2 TIME OF FLIGHT RESULTS. — TOF experiments on IN5 and IN6 instruments were carried out using different resolutions (Table II) in order to study the dynamics of NH_3 groups near the room temperature phase III. Most of these experiments were performed on monocrystalline platelets and, as illustrated on figures 7 and 8, quasielastic broadenings are clearly observed essentially for configurations with Q parallel to the base planes. Similarly, some spectra of a powder sample were analysed and quasi-elastic contributions were again detected mainly in the high Q range, 1.7-2.2 $\text{\AA}^{-1}$ (Fig. 9).

The corrected IQENS spectra were fitted with those calculated by folding the scattering law for uniaxial rotational motion of N-H protons with the instrumental resolutions. The parameters used in the fitting procedures are the following ones :

F is a scaling or amplitude factor which normalizes the calculated intensity to the experimental function.

B corresponds to an inelastic background correction of the base line, which may be proportional to Q or Q^2 , and which, eventually, takes into account a non-negligible multiple scattering contribution.

Fig. 7. — Comparison of two sets of quasi-elastic neutron scattering spectra recorded on the time of flight IN5 instrument using different orientations of monocrystalline platelets of PDA MnCl_4 with respect to the incident beam : a) and b) $\lambda_0 = 10.05 \text{ \AA}$ and $Q = 0.88 \text{ \AA}^{-1}$ for perpendicular and parallel orientations, respectively, c) and d) $\lambda_0 = 5.14 \text{ \AA}$ and $Q = 1.73 \text{ \AA}^{-1}$ for perpendicular and parallel orientations, respectively. The dotted lines indicate the quasi-elastic broadening contributions.

Fig. 8. — Quasi-elastic neutron scattering spectra recorded on the time of flight IN6 instrument with a) $\lambda_0 = 5.9 \text{ \AA}$ ($Q = 1.54 \text{ \AA}^{-1}$) and b) $\lambda_0 = 4.1 \text{ \AA}$ ($Q = 2.21 \text{ \AA}^{-1}$) and using oriented crystals of PDA MnCl_4 in the « Q parallel » configuration. In each case the experimental spectrum is compared with the vanadium elastic peak (dotted lines).

Fig. 9. — Corrected quasi-elastic neutron scattering spectra for polycrystalline samples of PDA MnCl_4 at 292 K taken on the IN5 spectrometer with $\lambda_0 = 5.14 \text{ \AA}$ for different Q values (1.73, 2.12 and $2.21 \text{ \AA}^{-1}$, respectively). The dotted lines represent the quasi-elastic contributions.

$\langle u^2 \rangle$ is the mean square vibrational amplitude of the projection of the proton displacements on $\mathbf{Q}$; it appears in the Debye-Waller factor, $\exp(-Q^2 \langle u^2 \rangle)$.

ρ is the ratio of the number of fixed protons to the total number of protons.

D_r is a parameter governing the width of the first Lorentzian of the scattering function and is equal to (τ_1^{-1}) ; thus, τ_c values are derived through the relation (5).

a is the radius of gyration of mobile N-H protons and has been estimated from neutron diffraction results [2]. This parameter was always observed to tend to the expected value, $0.942 \text{ \AA}$.

N is the number of equivalent sites for the protons on the circle of radius a .

v is the angle between $\mathbf{Q}$ and the axes of rotation of NH_3 groups for platelet experiments.

Using equations (2) and (3) one obtains the general expression (10) for the scattering law :

$$S_{\text{inc}}(Q, w) = F \exp(-Q^2 \langle u^2 \rangle) \times \left\{ [\rho + (1 - \rho) A_0(Q)] G(w) + (1 - \rho) \frac{1}{\pi} \times \left[\sum_{i=1}^{N-1} A_i(Q) L(\tau_i^{-1}) \right] \otimes G(w) \right\} + B(Q) \quad (10)$$

where the characteristic times τ_i are defined in equation (5) and $G(w)$ is the elastic resolution function measured for each scattering angle ($\otimes$ represents the convolution product). For IN5 spectra $G(w)$ is replaced in the convolution product by a triangular function having a width equal to the width averaged over all the scattering angles. A further complication comes from the fact that for a TOF instrument, at a given scattering angle, the resolution width varies with the energy transfer, $\hbar w$. This is taken care of in the evaluation of equation (10). The fitting procedure was first performed for each angle, and then a new set of input parameters was introduced in order to fit all the angles at the same time. Finally, the results of the different fits were compared as the incident wavelength was changed.

It is clear that the theoretical models for $2\pi/3$ and $2\pi/6$ jumps have led to the best consistency for all the data. Some fits using the theoretical model of $2\pi/2$ jumps of the alkylene chains were tried without success. In the same way, the ratio ρ was always found to tend towards 0.5. In this respect, the model of reorientations of PDA as a whole (corresponding to the value $\rho = 0.0$), as suggested from broadline NMR results [2], was tried but no convergence was observed. In table III we report the final D_r values (meV) obtained for the best fits at different temperatures, wavelengths and orientations of the platelets. The agreement between these values is satisfactory. For instance, whatever the orientation of the platelets, D_r at 300 K is found equal to 0.092 meV for $\lambda_0 = 5.14 \text{ \AA}$ (IN5) or to 0.091 meV for $\lambda_0 = 5.9 \text{ \AA}$ (IN6). From these values, the corre-

Table III. — Results of the different fits within the $2\pi/3$ jump model of NH_3 groups in PDA MnCl_4 .

Compound	Instrument	Incident λ_0 (Å)	Temperature (K)	D_r (meV) ^(b)	$\tau_1 \times 10^{12}$ (s) ^(a)	$\tau_c \times 10^{12}$ (s) ^(a)
Powder	IN5	5.14	292	0.064	10.29	15.43
Platelets	IN5	5.14	275	0.034	19.36	29.04
($Q_{\parallel}$ and $Q_{\perp}$)	IN5	5.14	301	0.093	7.10	10.67
—	IN5	10.05	304	0.100	6.58	9.87
—	IN6	4.1	299	0.092	7.15	10.73
—	IN6	5.9	299	0.091	7.20	10.80

$$^{(a)} \tau_1 (\text{s}) = \frac{0.658 \times 10^{-12}}{D_r (\text{meV})} \text{ and } \tau_c = \tau_1 \times 2 \sin^2(\pi/3) = \tau_1 \times 1.5.$$

^(b) D_r is the HWHM of the first Lorentzian in the expression of $S_{\text{inc}}^{\text{rot}}(Q, \omega)$. The values reported here are those which give the best fits.

lation times τ_c were derived over the 275-304 K temperature range. The figure 10 shows that their temperature dependence seems to follow an Arrhenius type law, $\tau_c = \tau_{\infty} \exp(E_A/KT)$. The correlation time at 300 K is found equal to 1.0×10^{-11} s while the activation energy deduced from the slope of the Arrhenius plot is equal to 26.6 kJ/mol. In fact, this energy value is a rough estimate since it has only been obtained over a restricted temperature range (Table III).

5. Conclusions.

The consistency between all the above results obtained using several incident wavelengths and different temperature ranges allows us to propose reliable conclusions. We confirm that reorientational movements of only the protons of NH_3 groups are taking place in phases III and IV of PDA MnCl_4 . This result is in agreement with Deuteron-NMR-NQR results [5] but in disagreement with broadband proton NMR conclusions. Also in our previous Raman study [7] some large amplitude librational movements of the alkylene chains coupled with NH_3 torsions had been suggested. We conclude also that the dynamics of NH_3 groups in the room temperature phase III are governed by a correlation time $\tau_c^{300\text{K}} \simeq 1 \times 10^{-11}$ s and by an activation energy of 26.6 kJ/mol. We are not able to discriminate between the $2\pi/3$ and $2\pi/6$ jump models over the Q range investigated but the $2\pi/3$ model is physically the most probable. In this respect the activation energy can be compared with the V_3 potential barrier against the torsion as deduced from the torsional frequency $V_3^0 = 20.08 \text{ kJ} \cdot \text{mol}^{-1}$. Therefore, these IQENS results show that the activation energy derived from the Raman band broadenings [7] is once more [18, 19] underestimated and that the temperature dependence of Raman band widths cannot be satisfactorily interpreted within a simple Arrhenius type law.

Fig. 10. — Arrhenius plot of the correlation times (τ_c) against reciprocal temperatures (in the narrow range 275-304 K). The slope of the straight line gives an estimate of the activation energy for NH_3 rotation.

Finally, it is noteworthy that the dynamics of NH_3 groups in phase IV could be determined using the wide Q range available on the IN13 instrument [11]. We also plan to perform additional experimental work at higher temperature. It would be interesting to check if a dynamical disorder of the chains between two orientations with the same or with different probabilities in time really exists in the crystalline phases I and II of PDA MnCl_4 . Experiments with the deuterated derivative $(\text{ND}_3(\text{CH}_2)_3\text{ND}_3)\text{MnCl}_4$ would be surely conclusive.

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