N.M.R. proton lineshape in (TMTSF)$_2$X : incommensurability of nesting vector and order parameter

J.M. Delrieu, M. Roger, Z. Toffano, A. Moradpour, K. Bechgaard

To cite this version:


HAL Id: jpa-00210268
https://hal.archives-ouvertes.fr/jpa-00210268
Submitted on 1 Jan 1986

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Résumé. — Pour la première fois, dans l'état onde de densité de spin (ODS) des conducteurs organiques (TMTSF)$_2$ClO$_4$ et (TMTSF)$_2$PF$_6$, le vecteur de nesting $Q$ est déterminé à partir d'une analyse détaillée de la forme de raie N.M.R. des protons des groupes méthyles, pour diverses orientations du champ. L'amplitude $\delta$ du paramètre d'ordre est déterminée avec une précision supérieure à celle des travaux précédents qui n'obtenaient aucune information sur le vecteur de nesting et négligeaient le couplage hyperfin. Dans l'état métallique (paramagnétique) la rotation rapide par effet tunnel de deux groupes méthyles inéquivalents donne une raie centrale et deux paires de satellites avec des déplacements variables suivant l'orientation du champ magnétique, en bon accord avec la théorie. Dans l'état onde de densité de spin, les champs locaux dus à la structure magnétique ordonnée entraînent un élargissement important de la raie. Par une étude approfondie de la forme de raie et de son évolution en fonction de l'orientation du champ, nous prouvons que pour ces deux composés, l'ODS est incommensurable; nous déterminons les champs locaux correspondant à chaque groupe méthyle et séparons la contribution dipolaire du terme de contact hyperfin; nous déduisons l'amplitude $\delta$ et le vecteur de onde $Q$ de l'ODS. L'amplitude $\delta = 8.5 \% \pm 2 \%$ (en unité $\mu_B$ par molécule) pour PF$_6$ est très supérieure à certaines estimations ancières. La composante du vecteur de nesting suivant le vecteur de base $b^*$ du réseau réciproque $Q_b = (0.20 \pm 0.05) b^*$ pour PF$_6$ est en contradiction avec les modèles théoriques simples conduisant à $Q_b = 0$ ou $Q_b = 0.5 b^*$, mais correspond aux meilleures conditions de nesting dans le cadre d'un calcul de bande réaliste, dans l'approximation des liaisons fortes. Le vecteur $Q$ est différent dans (TMTSF)$_2$ClO$_4$, en accord avec les prédictions théoriques suivant lesquelles $Q$ dépend de la nature de l'anion et des conditions expérimentales (pression).

Abstract. — For the first time, in the SDW state of the organic conductors (TMTSF)$_2$PF$_6$ and (TMTSF)$_2$ClO$_4$, the nesting vector $Q$ is determined from a detailed analysis of the methyl proton N.M.R. lineshape for various magnetic field orientations. The amplitude $\delta$ of the order parameter is determined with a precision superior to that of previous works which had obtained no information on the nesting vector and neglected the hyperfine coupling. In the paramagnetic metallic state, the fast rotational tunnelling of the two unequivalent methyl groups splits the line into one central line and two pairs of satellites with shifts depending on field orientation, in good agreement with theory. In the SDW state, the local fields due to the ordered magnetic structure lead to an important broadening of the line. By a careful analysis of the lineshape and its evolution in terms of field orientation, we prove, for both compounds, that the SDW is incommensurate; we are able to determine the local fields at each methyl site and separate the dipolar contribution from the hyperfine contact term; we deduce both the amplitude $\delta$ and wave vector $Q$ of the SDW. The amplitude $\delta = 8.5 \% \pm 2 \%$ (in unit $\mu_B$ per molecule) for PF$_6$ is much larger than previous estimates from N.M.R. broadening. The $b^*$ component of the nesting vector $Q_b = (0.20 \pm 0.05) b^*$ is in contradiction with simple theories leading to $Q_b = 0$ or $Q_b = 0.5 b^*$ but agrees with the best nesting conditions obtained with realistic tight binding band calculations. The $Q$ vector is different in (TMTSF)$_2$ClO$_4$, in agreement with the theoretical prediction that $Q$ depends on the nature of anion and experimental conditions such as pressure.

1. Introduction.

The organic conductors (or Bechgaard salts) (TMTSF)$_2$X, where X is a monovalent anion, exhibit very interesting properties and have lead to an explosive growth of research: they show a variety of phase transitions at low temperatures [1-2]: metal to antiferromagnetic Spin Density Wave (SDW) which is suppressed under pressure and replaced by the superconductive state discovered by Jérôme et al. [1-3].
complete understanding of this interplay of SDW and superconductivity is far from being elucidated although more information than in conventional metals can be experimentally obtained, as for example the unique possibility to observe the electronic resonance in the superconducting state [4]. Up to this article very little detailed information had been obtained on the structure of the SDW, like the amplitude $\delta$ of order parameter and the wave vector $Q$. The small size of the samples associated with the small amplitude of the order parameter ($\delta = 8.5\%$ in unit $\mu_B$ per molecule) has suppressed the possibility of neutron diffraction up to this date. In order to compensate the lack of neutron experiments, we reveal in this paper that nuclear magnetic resonance, directly probing the local field created by the SDW, is a very sensitive and powerful method of investigation, in particular when the SDW amplitude is small. Preliminary results have been published in reference [5]. In the future we plan to apply this method at high magnetic field to investigate the structure of the semi-metallic magnetic SDW state. This state appears for pressures where the superconductivity is observed at low fields, it is characterized by plateaus in the Hall resistance at high field, which are reminiscent of the quantum Hall effect [6, 1, 2].

In this paper the methyl proton line-shape is carefully analysed as a function of field orientation, in both the metallic state and in the SDW states. In the metallic state, we observe one central line and two pairs of satellites coming from two inequivalent pairs of methyl groups undergoing fast tunnelling rotation. Our detailed study of linewidth and satellite displacements in terms of magnetic field orientation is compared with theoretical predictions [7, 8] in section 3.

In the SDW state, the line-shapes are very different: additional satellites appear superposed on a strong general broadening: each methyl site sees a different local field created by the SDW ordering of electronic spins. The best theoretical fit of the observed N.M.R. lines, is obtained with an incommensurate SDW. From the evolution of lineshape as the field is rotated, we deduce the experimental local fields seen by the four methyls of the molecule (Sect. 4). The comparison of these fields with theoretical calculations (Sect. 5) allows us to separate the dipolar contribution to the local field from the hyperfine contact term. Up to now, all papers on the N.M.R. in the SDW state of the Bechgaard salts had overlooked the contribution of the hyperfine contact term to the local field [9-11]. As can be expected from crude estimates, we prove that in (TMTSF)$_2$PF$_6$ this term is of the same order as the dipolar field (20 G). This corresponds to a Knight shift of the order 5 to 10 ppm for the methyl proton, in agreement with that (around 10 to 20 ppm) observed on the carbons of methyl group in (TMTSF)$_2$ClO$_4$ [12]. Knowing the dipolar term, theoretical calculations give precise information on the SDW vector $Q$ and amplitude $\delta$. In the SDW state, the magnetization $S_j$ of one molecule centred at site $R_j$ is described by:

$$S_j = \xi \cdot \delta \cdot \mu_B \cos(Q \cdot R_j + \varphi)$$

where $\mu_B$ represents the Bohr magneton, $\xi$ the direction of the magnetization and $0 \leq \delta \leq 1$ the order parameter. The best fit of the observed fields proves for (TMTSF)$_2$PF$_6$ that the order parameter is $\delta = 8.5\% \pm 2\%$ ($\delta$ is 1 for the maximum value of one Bohr magneton per molecule). This value agrees with the order of magnitude deduced from antiferromagnetic resonance [13] and N.M.R. in powder [11] but definitely rules out early estimates of by less than 1%, from N.M.R. experiments on powder [9] (the large anisotropy of the line broadening is much more difficult to see in powder than in single crystals). The transverse $b^* \parallel$ component $Q_b$ of the $Q$ vector is to some extent unexpected. We determine $Q_b = 0.2 \pm 0.05 b^*$ ($b^\parallel$ reciprocal lattice vector). Our results are in complete contradiction with the values usually found in the literature ($Q_b = 0.5 b^*$ as in Ref. [14] using best nesting conditions in a simple band structure, or $Q_b = 0$ as in Ref. [15] using exchange interaction). In fact, most theoretical models take a simplified orthorombic structure instead of the real triclinic one. As first pointed out by Yamaji [16], we show, in section 6, that our result of an incommensurate transverse best nesting vector is quite natural, if we take into account the two most important transverse transfer integrals between nearest neighbours, appearing in the simple tight-binding band calculation performed by Yamaji [16] and Grant [17]. Schematically, there are two dominant transverse transfer integrals in the respective directions $b$ and ($b - a/2$). Each of them, taken separately, favours a different nesting vector. When both are of the same order of magnitude, the resulting nesting vector is intermediate between these two vectors and depends on the ratio of the two competing integrals; we expect it to vary with pressure or the nature of the anion. Our results are in agreement with the best nesting conditions corresponding to the complex triclinic structure of the lattice. All models using best nesting conditions [14], but taking a simplified orthorombic structure leading to $Q_b = 0.5 b^*$, must be generalized to the real triclinic structure of the crystal before a quantitative comparison with the experiments.

Our results for the SDW on quenched (TMTSF)$_2$ClO$_4$ are quite different, definitely showing that the nesting vector depends experimentally on the nature of the anion. However, our data on ClO$_4$ are more difficult to interpret with the same accuracy as for PF$_6$ for experimental reasons (due to a smaller sample size, our signal to noise was less good); for this reason the magnetic field was taken sufficiently high (4.4 K) but unfortunately above the spin flop field; hence one part of the data corresponds to the spin flop phase and our theoretical fits are less accurate. Nevertheless we deduce that the order parameter
is of order of 0.1 and that the dipolar and contact terms are quite different from those corresponding to (TMTSF)$_2$PF$_6$. We are continuing further experiments at lower fields to obtain more precise informations.

2. Experimental methods.

The (TMTSF)$_2$ClO$_4$ and PF$_6$ crystals were synthesized by Bechgaard and Moradpour. Their size was respectively : $0.2 \times 0.4 \times 6$ mm and $1 \times 1 \times 5$ mm. The continuous N.M.R. absorption derivatives were observed using a home made wideband Robinson oscillator [18] associated with a lock-in and, in some cases, a multichannel signal averager, at the magnetic field values : $2.7$ kG, $4.4$ kG and $9.4$ kG. The magnetic field was rotated perpendicularly to the molecular stacking axis a of the single crystals. All measurements have been performed between $4.2$ K and $1.2$ K. For (TMTSF)$_2$ClO$_4$ the metallic relaxed state with ordered anions was obtained by slow cooling in one and a half hour from $60$ K to $10$ K in order to obtain the metallic state; we observed no change in the N.M.R. lines for slower cooling. The quenched state with SDW state was obtained by quenching in 5 seconds from $60$ K to $4.2$ K in liquid helium. The observed N.M.R. line was the same for different quenching in less than one minute. The measurement on (TMTSF)$_2$ClO$_4$ has been performed only at $4.4$ kG. This field was chosen sufficiently high, in order to compensate the low signal to noise ratio due to a small sample size, but near the spin flop field estimated by antiferromagnetic resonance [13]. More recent susceptibility measurements give a spin flop field of $3.1$ kG [19]. This last value is confirmed by our results. Hence one part of our data corresponds to the spin flop phase and their analysis is more difficult.

In (TMTSF)$_2$PF$_6$ the NMR measurements were made at the three preceding fields i.e. above and below the spin flop field (of order 6 kG from the values obtained from susceptibility anisotropy experiments [20]). To the best of our knowledge, no antiferromagnetic resonance seems to have been performed on (TMTSF)$_2$PF$_6$.

The quality of single crystals has been tested in the metallic state by our N.M.R. results. For example a twinned crystal of (TMTSF)$_2$PF$_6$ has been rejected by N.M.R. : simply the spectra in terms of field orientation were formed of the superposition of two spectra similar to that shown in figure 1, but shifted by the angle between the two crystals composing this twinned sample. This N.M.R. method is a way to test and orientate the bulk of a single crystal without any X ray irradiation, which in some cases can change the properties of the sample.

3. N.M.R. lineshapes in the metallic state.

3.1 General structure of the methyl lines. —

Figure 1 shows our experimental results for (TMTSF)$_2$ClO$_4$ in the relaxed state at $1.2$ K as a function of the magnetic field angle $\theta$ with long molecular axis $X$, in the plane perpendicular to the stacking axis a. The existence of this structure does not seem to have been pointed out in other N.M.R. experiments [9 to 11] performed on (TMTSF)$_2$X, essentially because most of them have been performed on powder samples [9 to 11], or by recording the free precession decay after one r.f. pulse, which needs for a useful Fourier transform very short recovery times of 1 or 2 $\mu$s (this is quite difficult technically at a low field like $2.7$ kG). In particular, the importance of single crystals, associated with the possibility to easily study the change of lineshape with the orientation of the magnetic field, had never been appreciated.

The experimental results for (TMTSF)$_2$ClO$_4$ [5] at $1.2$ K in the relaxed state are shown in figure 1. The theoretical spectrum of methyl protons undergoing tunnelling rotation has been calculated by Clough [7] and by Allen [8]. Figure 2 shows this spectrum for one isolated methyl group when the tunnelling rotation frequency is much larger than the magnetic dipolar interactions between proton spins. Two tunnelling states exist : the spatially symmetric ground state with total spin $3/2$ and the doubly degenerated excited state with total spin $1/2$. The dipolar interaction gives at large field a central line with relative transition probability 6 (one part with probability 4 comes from the $I = 3/2$ state and the other from $I = 1/2$ with a weight 2) and two symmetrical satellite lines with transition probability 3 coming from the transitions between the $I_s = 3/2$ and $I_s = 1/2$ substates of the fundamental $I = 3/2$ state. Hence the intensity ratio of the central line to one satellite is a factor 2. The satellite displacement is :

$$d = d_0(1 - 3 \cos^2 \psi)$$

with

$$d_0 = \frac{3}{4} \frac{(\gamma \hbar)^2}{R_{HH}}$$

where $\psi$ represents the angle between the external field and the C$_3$ axis of the methyl group and $R_{HH}$ is the shortest interproton distance.

As shown in figure 3, the molecule of TMTSF contains two pairs of symmetric methyl groups $P_1 = \{ C_{4}, C_{15} \}$ and $P_2 = \{ C_{5}, C_{14} \}$ (we take the notation of Ref. [21]) with the methyl C$_3$ axes respectively at about +35° and -35° of the molecular axis X in the molecular plane. Each pair gives two satellites with different displacements. The total line is composed of one central line and two pairs of symmetrical satellites. The theoretical satellite displacements $d_i$ are shown in figure 4 as a function of the angle $\theta$ of the external magnetic field with the molecular axis X, for each of the four methyl groups; they are obtained using in relation (2) : $\psi = \theta - W_i$ where $W_i$ are the precise angles of the methyl C$_3$ axes with molecular axis measured by X ray techniques [21-22]. These angles being close to the magic angle $\approx 35°$ all the
Fig. 1. — N.M.R. derivatives of methyl lines in the metallic paramagnetic state of relaxed $\text{(TMTSF)$_2$ClO}_4$. The full lines represent the experimental results and the dashed lines are the best least square fits. The numbers at the end of each line are the angles $\theta$ of magnetic field with the molecular axis as shown in figure 3. The curves have been normalized to the first moment of the absorption line obtained by double integration on a computer of the experimental derivatives.

Displacements at $\theta = 90^\circ$ nearly vanish giving a slightly broadened central line. At $\theta = 20^\circ$ one group is superposed with the central line and the other well separated. All these features are seen in the experimental results of figure 1.

3.2 THEORETICAL AND NUMERICAL ANALYSIS OF THE LINES IN THE METALLIC STATE. — For a complete interpretation of the lines observed in the SDW state, we need to extract the line-shape of one isolated methyl group from our results and to fit it correctly by a convenient simple analytic function. The simplest functions are Gaussian or Lorentzian form; after a comparison of the fit with these two types of functions, we found that a Gaussian line shape for each observed line was much better:

$$g(\omega, \Delta) = (\sqrt{2\pi} \Delta)^{-1} \exp\left(-\frac{\omega^2}{2\Delta^2}\right)$$

(3)
Fig. 2. — Energy levels of one methyl group undergoing fast tunnelling rotation. The tunnelling frequency is $3J$. The N.M.R. splitting is given by the averaged dipolar interaction: $d = \frac{3}{4} \left( \frac{2\hbar}{\mu_B} \right)^2 (1 - 3 \cos^2 \psi)$. The relative intensities of N.M.R. lines are indicated on the left.

Because there are 3 different transitions (2 for the central line and one for each satellite) for each of the four inequivalent methyl groups, a complete fit should include 12 Gaussians, with, in principle, 12 different widths. Since such a detailed fit is unrealistic for the precision of the experimental data, we take the following simplified model: we approximate the central line by a Gaussian of unique width $\Delta_c$ and take one Gaussian for the satellites of each pair $P_1 = \{ C_4, C_{13} \}$ and $P_2 = \{ C_5, C_{14} \}$ with respective parameters $\Delta_1$ and $\Delta_2$. Taking into account the transitions probabilities between the different levels, the line corresponding to one methyl group is fitted by

$$G(\omega) = 2 g(\omega, \Delta_c) + g(\omega - d, \Delta_2) + g(\omega + d, \Delta_1).$$

(4)

The theoretical lines giving the best fit are represented by the dashed lines in figure 1: the experimental N.M.R. derivatives have been integrated twice and all the curves are normalized to the first moment of the absorption line; for this reason there is no adjustable parameter for the intensity. The satellite displacements $d_i$ are calculated from relation (2) with the maximum shift $d_0$ as an adjustable parameter. For each field orientation the linewidth $\Delta_{CC}$, $\Delta_1$, $\Delta_2$ are adjusted to give the best least square fit to the data. The theoretical lines thus obtained are represented by the dashed lines of figure 1 and the corresponding widths are given in figure 5. The best fit for all angles $\theta$ is obtained for:

Fig. 3. — Structure of the molecule and relative disposition in the crystal. The molecular $X$ axis is in the left direction and the angle $\theta$ of field with the $X$ axis is measured in the reverse direction. The different orientations of the normal to the plane of methyl groups ($C_3$ axis) are indicated.
Fig. 4. — Dipolar shifts $d_i$ of methyl satellite lines as a function of the angle $\theta$ of field with molecular axis $X$. The shifts are indexed by the carbon numbers of the corresponding methyl groups.

Fig. 5. — Line width of individual methyl lines as a function of field orientation: a) $\Delta_c$ for the central line, b) $\Delta_1$ for the satellite line corresponding to methyl group of type P$_1$ (satellites associated to C$_4$ and C$_14$, methyl groups) as shown on figure 3, c) $\Delta_2$ for the methyl group P$_2$ (satellites due to C$_4$ and C$_14,$). The points with errors bars are the experimental widths obtained, at each angle, in the best least square fit shown as a dashed line in figure 1. The full line is an overall fit of these points by the most general functional form of $\theta$ obtained from the Van Vleck formula (Rel. (5)). The dotted line is the theoretical width obtained from an evaluation of the second moment by summing the dipolar interactions over the nearest methyl groups.

d$_0$ = 3.9 ± 0.1 G which corresponds to $R_{HH} = 1.76 + 0.02$ Å in good agreement with the usual inter proton distance measured by X rays in methyl groups [22].

Although this analysis is relatively simplified, the variations of the linewidths as a function of field orientation (Fig. 5) show interesting features. Empirically the lines broaden when several individual lines come close together ($\theta = 0$ or $\theta = 90^\circ$); this effect is maximum when all lines are superposed. The curves of satellite widths are different and not symmetric.
with respect to the molecular axis. This result is explained by the different environment for each methyl group. For example, it is clear, from the crystal structure, that the two methyls \( P_2 = \{ C_5, C_{14}\} \) have a larger number of nearest neighbours than the two others \( P_1 = \{ C_4, C_{15}\} \) as shown on figure 3. For this reason, for \( H_0 \) close to the direction of their nearest neighbours (\( \theta \approx -40^\circ \) to \( -50^\circ \)) their line width \( \Delta_2 \) is larger than \( \Delta_1 \).

We have performed a rough estimation of the line width of each methyl group as a function of field orientation using the Van Vleck [23] formula for the second moment:

\[
\Delta_i^2 = M_{2i} = \frac{3}{4} (\gamma \hbar)^2 \cdot I(I + 1) \times \\
\sum_k (1 - 3 \cos^2 \phi_{ik})/R^2_{ik}
\]

\( I = 3/2 \) and \( \phi_{ik} \) represents the angle between \( H_0 \) and the vector \( R_{ik} \) joining two methyl groups. We sum over the closest methyl-neighbours. The corresponding theoretical curves \( \Delta_4, \Delta_{15} \) for each methyl of the pair \( P_1 \) are quite close together. Hence we take the half sum \( \Delta' = (\Delta_4 + \Delta_{15})/2 \) as a reasonable estimate of the width \( \Delta_4 \) of the single line used in the fit of our experimental lineshape. In the same way, we take \( \Delta'_2 = (\Delta_4 + \Delta_{14})/2 \) as an estimate of \( \Delta_2 \). The results thus obtained are represented by the dotted lines of figures 5b and 5c. These variations of individual line width with magnetic field angle, are compared to a least square fit of the experimental data by the most general function of \( \theta \) obtained from relation (5) (full lines)

\[
\Delta_i(\theta) = \\
[A_i + B_i \cos(2 \theta + \alpha_i) + D_i \cos(4 \theta + \alpha'_i)]^{1/2}.
\]

The agreement is satisfactory between these two curves considering the approximations used to reduce the number of parameters.

From all this analysis we are able to separate the contributions of each pair \( P_1, P_2 \) of the different methyl groups within each line; figure 6 illustrates this remark for two particular field orientations. This possibility is very important for our analysis of the results obtained in the SDW state, because it gives the possibility to attribute each observed shift in the SDW to one particular methyl pair unambiguously.

4. The SDW state : determination of the local fields from the experimental N.M.R. lines.

4.1 Experimental results. — The experimental results, as a function of field orientation, are shown in figures 7, 8, 9b for \((\text{TMTSF})_2\text{PF}_6\) and on figures 9a for \((\text{TMTSF})_2\text{ClO}_4\) at 1.2 K. Figures 7 and 8 represent the raw data for \( \text{PF}_6 \) at \( H = 2.7 \text{ kG} \) and \( H = 9 \text{ kG} \), respectively. On figure 9b we have selected a restricted set of data from figure 7, that we compare to theoretical fits as explained below. The raw data for \((\text{TMTSF})_2\text{ClO}_4\) at 4.4 kG have been published in reference [5]. Figure 9a represents a part of these data chosen for the numerical fit. In figure 9a, b and c, all lines have been normalized to the first moment of the integrated curves by double numerical integration. For all figures 9a, b and c the \( X \) scale is half and the \( Y \) scale four times the scale of figure 1 (the line intensity of the derivatives decreases as the square of their width). We note a large broadening with respect to the metallic state and the presence of additional satellites. The results are qualitatively different for both compounds. An important experimental fact is particular to \( \text{PF}_6 \) : the line narrows drastically when \( H_0 \) is perpendicular to the plane \( (a, b') \). The width is nearly comparable to that corresponding to the metallic state for the same orientation as shown in figure 9c. This implies that all local fields are almost parallel to the \( b' \) direction. No such narrowing is observed with \((\text{TMTSF})_2\text{ClO}_4\) where the local fields have components perpendicular to \( b' \). Thus a simple qualitative study of the experimental results reveals that the SDW structures seen at the atomic level are quite different.

For \((\text{TMTSF})_2\text{PF}_6\) the high field data (Fig. 8) show the occurrence of a spin flop transition. When the external field direction is close to the \( c^* \) axis (i.e. perpendicular to the easy axis \( b' \), the lineshape are similar to that observed at low field (Fig. 7). For \( H_0 \) parallel to \( b' \) the lineshapes are completely different, they correspond to the spin-flop phase.
4.2 ORIGIN OF THE LOCAL FIELDS. — The local field $H_i$ created by the electronic spins on the proton site $i$ of the molecule $j$ is the sum of two contributions:

$$H_i = H_{Di} + H_{Ci}. \quad (7a)$$

The first term represents the dipolar interaction

$$H_{Di} = \sum_{l,k} \rho_i \left[ S_k \left( \frac{1}{R_{l,k}^3} - 3 \frac{R_{l,k}}{R_{l,k}^5} \right) \right] \quad (7b)$$

the sum is performed over all atoms $l_k$ of each molecule $k$, and $\rho_i$ represents the spin density on each atom of the TMTSF molecule ($\sum \rho_i = 1$). The second term represents the hyperfine contact field arising from the Dirac interaction:

$$H_{Ci} = \frac{8}{3} \pi \cdot \rho_i \cdot S_j. \quad (7c)$$

It is proportional to the electronic density $\rho_i$ of the conduction electrons on the nucleus $i$ considered.

Using the theoretical fit obtained in the metallic state (Sect. 3) the broadened lines of the SDW state are mathematically analysed in order to extract the experimental local fields $H_i$. The best fits are obtained for an incommensurate structure. At this stage, we do not need any explicit theoretical calculation of the dipolar or hyperfine contact fields. We only use the remark that the local field $H_i$ is linear with respect to the $S_p$, which is obvious in relations (7b) and (7c).

A comparison of the experimental fields with theoretical values from (7b, c) will be performed in section 5, in order to determine the wave vector $Q$ and order parameter $\delta$. 

Fig. 7. — Experimental results in the SDW state of (TMTSF)$_2$PF$_6$ as function of the angle $\theta$ of magnetic field with molecular axis at a magnetic field of 2.7 kG (raw data).

Fig. 8. — Experimental results in the SDW state of (TMTSF)$_2$PF$_6$ at 9.4 kG. When the external field $H_0$ is perpendicular to $b'$ (easy axis) the lines are comparable to that of figure 7. When $H_0$ is parallel to $b'$, they differ completely: this proves the occurrence of a spin flop transition.
Fig. 9. — Comparison of theoretical fits (dashed lines) to the NMR derivatives (full lines) in the SDW states of:
(a) (TMTSF)₂ClO₄; (b) (TMTSF)₂PF₆. For each compound, a restricted set of experimental curves has been selected from the raw data (Fig. 2 or Ref. [5] for (TMTSF)₂ClO₄ and Fig. 7 of this paper for (TMTSF)₂PF₆). The N.M.R. absorption derivatives have been integrated twice by computer and all curves are normalized to the first moment of the absorption line. The precision on the experimental angles is within ± 2°; to correct the corresponding experimental errors, the angles θ have been readjusted within ± 2° in the least square fit. For comparison we show on the right (c), at the same scales, the N.M.R. lines of (TMTSF)₂ClO₄, for θ = 15°, in the metallic state. The X and Y scales are the same for all curves of this figure. The X scale is half and the Y scale four times that of figure 1.
4.3 Commensurability of the SDW. — The local magnetization \( S_j \) on one molecule at site \( R_j \) in the SDW state can be described by relation (1)

\[
S_j = \mathbf{s} \cdot \mathbf{\mu}_B \cos(\mathbf{Q} \cdot \mathbf{R}_j + \varphi)
\]

where \( \mathbf{\mu}_B \) represents the Bohr magneton, \( \mathbf{s} \) the direction of the magnetization and \( 0 \leq \delta \leq 1 \) the order parameter (dimensionless).

4.3.1 Commensurate phases. — Usually \( \mathbf{Q} \) is supposed commensurate and equal to the simplest possible value: \( \mathbf{Q} = (1/2, 1/2, 1/2) \) (in coordinates based on the reciprocal lattice basis vectors: \( \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^* \)). As in reference [10], it seems natural that the two molecules of the unit cell have the same magnetization. Thus along the stacking axis \( \mathbf{a} \), the sequence is \( (+ + - - + - + - -) \) for the magnetization. This corresponds to the choice \( \varphi = \pi/4 \) in relation (1). However a commensurate structure where the magnetization is concentrated on one of the two molecules of the cell is possible, the other carrying no magnetization; this corresponds to \( \varphi = 0 \) in relation (1) and to the sequence \( (+ + - - + + - -) \). In the first case \( \varphi = \pi/4 \), due to the centrosymmetry of the crystal, the local fields from one molecule to the next are related by inversion. This case corresponds to four inequivalent methyl sites with four independent local fields. In the second case, the two molecules of the unit cell carry independent fields and there are eight inequivalent methyl sites with eight different fields.

In the preceding section the lines have been fitted with a sum of Gaussian functions, and we have been able to separate the contribution of each methyl group: \( G_i(\omega) \) (Rel. (4)). The new theoretical form of this line in the presence of a local field \( \mathbf{H}_i \) is simply given by

\[
G_i^c(\omega) = \frac{1}{2} \left[ G_i(\omega + h_i) + G_i(\omega - h_i) \right]
\]

(h\(_i\) denoting the projection of \( \mathbf{H}_i \) on the external field \( \mathbf{H}_0 \).

We assume that the intrinsic Gaussian widths are the same in the metallic and the SDW state. This assumption is certainly not exact, because when the local fields are large, the \( T_2 \) relaxation (or the homogeneous part of the linewidth) increases with a difference larger than their dipolar interaction. Thus \( T_2 \) is expected to increase in the SDW state as observed in pulsed N.M.R. experiments [24]. Nevertheless the overall linewidth, which includes the dipolar interaction between spins seeing different local fields, changes by much less than \( T_2 \); the maximum possible decrease is 2/3 for spins seeing completely different fields. In our case, we are far from this situation and a crude evaluation leads to a change of linewidth in the range 10\( \% \) to 20\( \% \); this change being relatively small, we neglect it and suppose that the width of Gaussians used in our fit are the same in the SDW as that found in the preceding chapter in \((\text{TMTSF})_2\text{ClO}_4\). We have not studied the lineshapes of \((\text{TMTSF})_2\text{PF}_6\) in the metallic state in detail. The difference might come from the dipolar interaction with the fluorine and phosphorus nuclear magnetic moments of the \( \text{PF}_6 \) anions. Using a crude evaluation (similar to Rel. (5)), we estimate this contribution to be less than 10\( \% \) of the linewidth. We shall neglect it and take for both compounds the same linewidth as that measured in the metallic state of \((\text{TMTSF})_2\text{ClO}_4\) (see Fig. 5).

The analytic expression of the total line in the commensurate states \( (++--++) \) and \( (++--++) \) is obtained by adding respectively the four (or eight) contributions of each methyl group (Rel. (7)) with four or eight fields \( h_i \) taken as adjustable parameters. These \( h_i \) are then adjusted by a computer program to obtain a least square fit to the experimental data.

4.3.2 Incommensurate phase. — We now suppose that \( \mathbf{Q} \) is incommensurate with the lattice (note that either \( \mathbf{Q}_a \) or \( \mathbf{Q}_b \) alone or both can be incommensurate). From relation (1) we see that there is a continuous sinusoidal distribution through the sample of the magnetization \( S_j \). The local field on one isolated site \( i \) is the sum of a dipolar contribution and a hyperfine contact term (see Rel. (7)). Both are linear with respect to the magnetization \( S_j \) carried by the molecule \( j \). Thus the distribution of local fields \( \mathbf{H}_i \) seen by each of the four inequivalent methyl sites is sinusoidally modulated through the sample. We remark that, due to the centrosymmetry, in this case only four methyl groups are inequivalent. Through the sample the sinusoidal field distributions for the local field projections on the external field \( \mathbf{H}_0 \) are given by:

\[
h_i \cos(\varphi + \alpha_i) \quad (i = 1 \text{ to } 4) .
\]

The number of methyls in the field \( h \) is proportional to:

\[
\mathcal{N}(h) = \frac{1}{\pi} [h^2 - h^2]^{-1/2}
\]

(similar to a one-dimensional density of state). The lineshape corresponding to one of the four methyl groups is the convolution product:

\[
(G_i \ast \mathcal{N}(\omega)) = \frac{1}{\pi} \int_{-h}^{h} G_i(\omega - h) \mathcal{N}(h) \, dh .
\]

The \( G_i \) given by relation (4) is the sum of four Gaussians \( g(\omega, \Delta) \) (Rel. (3)).

In figure 10 we compare, for one isolated Gaussian line \( g(\omega, \Delta) \) (see Rel. (3)), the shapes obtained respectively in the commensurate \( 1/2[ g(\omega + h, \Delta) + g(\omega - h, \Delta)] \) and incommensurate state \( (g \ast \mathcal{N}(\omega)) \) as a function of \( \omega^* = \omega/\Delta \) and \( h^* = h/\Delta \). For \( h^* > 1 \), the line splits into two well separated satellites. In the commensurate case, the maximum intensity of the satellites is independent of \( h^* \) whereas in the incommensurate case it decreases drastically as the total
width \( h^* \) increases. This remark is important to distinguish incommensurate and commensurate structures, as shown in the following paragraph.

To obtain the analytic expression of the total line we add the four contributions (Rel. (11)) of the four inequivalent methyl groups, with four adjustable parameters \( h_i \) (\( i = 1 \) to 4). Using a computer the four parameters \( h_i \) are adjusted in order to obtain the best least square fit to the data.

4.3.3 Comparison of the different fits. — In figure 11, for both compounds, the best numerical fits obtained by the methods explained in 4.3.1 and 4.3.2 are compared, for the commensurate and incommensurate cases.

For this comparison we choose the field orientation for which the ratio of the total broadening of the global line to the intrinsic Gaussian line-width is maximum. This corresponds to \( \theta \approx 30^\circ \) for both compounds. It is clearly impossible to fit the experimental line with four discrete fields \( h_i \) corresponding to the commensurate phase : (+ + + + + + + +) as shown in figure 11a. A much closer and better fit is obtained with eight discrete fields \( h_i \) corresponding to the (+ + - - + + - -) commensurate phase, although, for PF6 more structures are seen on the theoretical line (Fig. 11b). The best fit is obtained within the incommensurate hypothesis (four sinusoidal distributions of fields \( h_i \cos (\varphi + \alpha_j) \)) as shown in figure 11c.

We conclude that the structure is most probably incommensurate for both compounds. We must, however, emphasize that the ratio of the maximum field \( h_i \) to the intrinsic linewidth is too small to distinguish a strictly incommensurate phase from a commensurate phase with a nesting vector of high order \( \mathbf{Q} = \left( \frac{m}{n}, \frac{p}{q} \right) \) where \( m, p \) are relatively high-order rationals (more precisely \( m, n > 4 \)). We have just seen that the difference between a fit with eight discrete fields and a strictly incommensurate phase (with an infinite number of discrete fields) is small.

We emphasize that the qualitative difference between a fit with four discrete fields : (+ + + + + + + +) for the commensurate phase, and the incommensurate case has already been illustrated by figure 10 and related remarks (see 4.3.2). The incommensurate phase is characterized by small satellites for the largest local fields \( h_i \). Very small satellites appear clearly in the (TMTSF)2ClO4 lines. In a preliminary publication [5], owing to the large difference of line-shape in the SDW states of PF6 and ClO4, some of us had proposed a mixing of a large part of metallic domains with small SDW domains. With comparable quenching times, the metallic EPR line is completely suppressed [20]; similarly, susceptibility measurements [19] seem to indicate that the quenched state is homogeneous SDW state. Thus for all these reasons, we find that this preliminary hypothesis was irrelevant and that the presence of small satellites is the signature of an incommensurate state (or commensurate of high order with a large number of discrete fields).

4.4 Determination of the local fields for the incommensurate phase.

4.4.1 Determination of the projections \( h_i \) of the four local fields on the external field in the incommensurate case. — For each field orientation, we determine the amplitudes \( h_i \) of the four local field sinusoidal distributions corresponding to an incommensurate structure, as explained in section 4.3.2. The corresponding least square fits are represented by the dashed lines of figure 9b for (TMTSF)2PF6 and of figure 9a for (TMTSF)2ClO4; the corresponding fields are shown in figure 12a for (TMTSF)2PF6 and in figure 12b for (TMTSF)2ClO4. We emphasize that we can easily distinguish the fields corresponding to the pair \( P_1 = \{ C_4, C_{15} \} \) of methyl groups (full and open circles) from those coming from the other pair \( P_2 = \{ C_5, C_{14} \} \) (full and open squares). In the metallic state, within \( 10^\circ \) around the angle \( \theta_0 \approx 20^\circ \), the lines corresponding to each pair \( P_1 \) or \( P_2 \) respectively are very different even qualitatively (see Fig. 6) : for one pair \( P_2 \), the satellites are superposed to the central line, giving a unique line of high intensity; for the
Fig. 11. — Comparison of theoretical fit (dashed lines) to experimental lines (full curves) in (TMTSF)$_2$PF$_6$ and (TMTSF)$_2$ClO$_4$ at two particular angles: respectively $\theta = 30^\circ$ and $35^\circ$. The two upper curves are for the simplest commensurate phases: a) SDW phase (+ + -- ++ +++) with four local fields $h_i(Q_x = 1/2, Q_y = 1/2, \phi = \pi/4)$. b) SDW phase (0 --0 ++ 0 +) with eight local fields ($Q_x = 1/2, Q_y = 1/2, \phi = 0^\circ$). The lower curve (c) represents the best fit, obtained with an incommensurate SDW phase ($Q_x$ or $Q_y$ or both incommensurate).

Fig. 12. — Maximum amplitudes $h_i(\theta)$ of the sinusoidal local field distributions in the incommensurate SDW state: a) for (TMTSF)$_2$PF$_6$ at 2.7 kG; b) for (TMTSF)$_2$ClO$_4$ at 4.4 kG. For each angle the four fields $h_i(\theta)$, corresponding to the four methyl groups, are deduced from the least square fit of the experimental N.M.R. derivatives shown on figure 9. The sets of points thus obtained have been fitted by: $[A + B \cos 2(\theta - \phi)]^{1/2}$, which is the most general functional form expected for $h_i(\theta)$ (full and dashed lines). We are able to separate the fields corresponding to the pair $P_1 = \{C_5, C_{15}\}$ of methyls groups (full lines and open or full circles) from that corresponding to $P_2 = \{C_5, C_{14}\}$ (dashed lines and full or open squares). However two fields originating from the same pair are undistinguishable in our measurements. For (TMTSF)$_2$ClO$_4$ (Fig. b), the external field is above the spin flop threshold 3.1 kG. The spin flop domain is limited by the wavy lines around which a discontinuity in the curves $h_i(\theta)$ is observed.
other pair \( P \) the satellites are well separated and the total line is split into three lines of small intensity.
In the SDW state, for this angle \( \theta_0 \), there are two large and two small local fields \( h_i \). The overall line-shape is completely different depending upon whether the large fields correspond to one pair or the other. Around this angle, the qualitative difference between the experimental lines in \((\text{TMTSF})_2\text{PF}_6\) and in \((\text{TMTSF})_2\text{ClO}_4\) lines results from this fact.

Contrary to \((\text{TMTSF})_2\text{PF}_6\), the smallness of the satellites experimentally observed in \((\text{TMTSF})_2\text{ClO}_4\) is due to two reasons: i) the incommensurate structure (see 4.3.3) which exists also for \text{PF}_6; ii) the fact that the largest fields correspond to the pair \( P_1 \), which gives three small lines in the metallic state. In \((\text{TMTSF})_2\text{PF}_6\) the largest fields correspond to the pair \( P_2 \) (with a unique line of higher intensity); thus they lead to qualitatively different shapes.

4.4.2 Determination of the local fields \( H_i \) — As emphasized before, the contribution of the molecule \( j \) to the local field \( H_i \) calculated on the methyl site \( i \) is linear with respect to the magnetization \( S_j \) on molecule \( j \) (see Rel. (7)). As \( S_j = s \cdot \delta \cdot \mu_0 \cdot \cos (Q \cdot \mathbf{R}_j + \varphi) \) (Rel. (1)), the \( \varphi \) dependence of \( H_i \) can be expressed by the general relation:

\[
H_i(\varphi) = H_i(\varphi') = H_i(\varphi) \cos \varphi + H_i'(\varphi) \sin \varphi
\]  

From relation (1), it is obvious that a phase change is equivalent to a space translation:

\[
H_i(\varphi) = H_i(\varphi') \text{ if } (\mathbf{R}_i - \mathbf{R}_j) \cdot Q = \varphi - \varphi'
\]

and since \( Q \) is incommensurate, this translation always exists for any phase change. Hence there is a continuous sinusoidal field distribution throughout the sample:

\[
H_i(\varphi) \cdot \mathbf{h}_0 = h_i \cos (\varphi + \alpha_i)
\]

where \( H_i(\varphi) \cdot \mathbf{h}_0 \) denotes the projection of \( H_i \) on any arbitrary direction \( \mathbf{h}_0 \) (for example, in our case, the external field direction). This remark has already been emphasized in relation (9) of section 4.3.2. Comparing with relation (12), we have:

\[
h_i = \left[ (H_i'(Q) \cdot \mathbf{h}_0)^2 + (H_i''(Q) \cdot \mathbf{h}_0)^2 \right]^{1/2}.
\]  

The coefficients \( H_i'(Q) \) and \( H_i''(Q) \) defined in (12) are easily interpreted in terms of local fields for particular value of \( \varphi \). \( H_i(Q) \) is the local field on methyl site \( i \) of one particular molecule \( j \) taken as the origin \( \mathbf{R}_j = 0 \) for \( \varphi = 0 \) and \( H_i'(Q) \) the local field on the same molecule for \( \varphi = \pi/2 \) (in other terms \( H_i'(Q) \) corresponds to the maximum magnetization \( S_m = s \cdot \delta \cdot \mu_0 \) on the molecule and \( H_i'(Q) \) to zero magnetization).

\( H_i''(Q) \) corresponds to the local field on the methyl site of a molecule which carries no magnetization. The hyperfine contact term is zero and, as shown in figure 15, the dipolar fields are smaller (the largest contribution comes from the molecule itself) so that \( H_i'(Q) \) is generally smaller than \( H_i(Q) \).

The respective projections \( H_i' \cdot \mathbf{h}_0 \) and \( H_i'' \cdot \mathbf{h}_0 \) of the two fields \( H_i'(Q), H_i''(Q) \) along the external field direction are sinusoidal functions of the angle \( \theta \) of the external field with respect to the molecular axis. Thus from relation (13), we obtain the general variation of \( h_i \):

\[
h_i(\theta) = [U_i + V_i \cos 2(\theta - \varphi)]^{1/2}.
\]
Fig. 14. — a) View of the (TMTSF)_2X crystal along the stacking axis showing clearly the asymmetry between the left and right parts of the TMTSF molecule. b) A view of the (TMTSF)_2X crystal along a direction close to c. The arrows indicate the directions of the different transfer integrals used in the band structure for the calculation of the nesting vector. Each transverse hopping rate along b and b - a/2 favours a different nesting vector (a SDW with alternate magnetization along b or b - a/2). When both integrals are in the same range, an intermediate nesting vector is realized.

In principle, the curve $h_1(\theta)$ determined in section 4.4.1 depends on three independent parameters only and is sufficient to determine the two fields $H_1(Q)$ and $H_1'(Q)$ completely (4 independent parameters for the components perpendicular to the a axis). However if $H_1'(Q)$ is relatively small compared to $H_1(Q)$, the following remark can be used:

If $H_1'(Q)$ is less than $H_1(Q)$, within an approximation better than $\frac{1}{3} |H_1'(Q)|^2 / |H_1(Q)|^2$, the maximum of $h_1(\theta)$ is equal to $|H_1(Q)|$ and the corresponding angle gives the direction of $|H_1(Q)|$ (see Rel. (13)). An estimate of $|H_1'(Q)| / |H_1(Q)|$ is given by the ratio of the maximum to the minimum of $h_1(\theta)$. As for most curves $h_1(\theta)$ represented in figures 12a, b, $|H_1'(Q)| / |H_1(Q)|$ is smaller than $1/3$, we can easily deduce the corresponding field $H_1(Q)$, within an approximation better than $1/18 \approx 5\%$.

By comparing the experimental local fields $H_1(Q)$ such obtained with theoretical calculations (using the Rel. (7a, c) and Rel. (1) with $\varphi = 0$) we shall separate the dipolar contribution from the hyperfine contact term and deduce the wave vector $Q$ and order parameter $\delta$ as shown in section 5.

4.4.3 Local fields $H_i'$ for (TMTSF)_2PF_6. — We have fitted the experimental points of figure 12a by the general expression (14). The largest fields corresponding to the pair $P_2 = \{C_5, C_{14}\}$ are represented by the dashed lines. The fields corresponding to $P_1 = \{C_4, C_{15}\}$ are shown by the full lines. All fields have their maximum around b', the direction of the magnetization below the spin flop transition (see Ref. [13]). Using the remark emphasized at the end of the preceding paragraph, the three largest fields can be reasonably deduced from the maxima of $h_1(\theta)$:

$$
|H_1'(Q)| = 9.5 \pm 1 \text{ G; } \phi_1 = 77^\circ \pm 10^\circ
$$
$$
|H_2'(Q)| = 24.5 \pm 1 \text{ G; } \phi_2 = 70^\circ \pm 5^\circ
$$
$$
|H_3'(Q)| = 17.0 \pm 1 \text{ G; } \phi_3 = 65^\circ \pm 5^\circ
$$

The precision on the smallest field $H_4'$ is smaller; we can estimate $|H_4'(Q)| \approx 4 \text{ G with } \phi_4 \approx 50^\circ$. From the minimum of $h_4$ at $3^\circ$ we can deduce that $H_4'(Q)$ is of the same order as $H_4(Q)$, whereas the fields $H_1'(Q), H_2'(Q), H_3'(Q)$ defined above are much smaller than $H_1'(Q), H_2'(Q), H_3'(Q)$, respectively.

These results are presented on figure 13a. At this stage of our analysis, we do not know the sign of each field. Within one pair we can interchange the fields numbered 1 and 4, which come from pair $P_1$, or the fields 2 and 3, which come from $P_2$, but we recall that we distinguish the fields belonging to $P_1$ from that corresponding to $P_2$ without any ambiguity.

4.4.4 Local fields $H_i'$ for (TMTSF)_2ClO_4. — The data for (TMTSF)_2ClO_4 are more difficult to interpret because the magnetic field (4.4 kG) has been chosen slightly above the spin flop field. The antiferromagnetic resonance [13] has proved that the anisotropy of the susceptibility tensor is practically of a planar type : the energy difference between the easy and intermediate axes is much smaller than the energy corresponding to the hard axis. Thus for an arbitrary direction of the magnetic field, the direction $\hat{\delta}$ of the magnetization is always in the plane perpendicular to the hard axis. If the projection of the external field along the easy axis is smaller than $H_{SF}$ (spin flop field), $\hat{\delta}$ remains along the easy axis; if it is larger, the magnetization flips along the intermediate axis (with a first order transition).

The exact directions of the susceptibility tensor for (TMTSF)_2PF_6 are still controversial. The antiferromagnetic resonance [13] finds an easy axis at 60° from
Fig. 15. — Theoretical dipolar fields in (TMTSF)$_2$PF$_6$ with easy axis $s$ directed along $b'$. The upper figures (a, b, c) represent the fields $H_i'$ on a molecule carrying the maximum magnetization $S_M = \delta \cdot \mu_b (\phi = 0^\circ)$ for $Q_b = 0, 0.2$ and $0.5$ respectively. The lower figures (a', b', c') represent for the same $Q_b$ values the fields $H_i'$ on one molecule carrying zero magnetization ($\varphi = \pi/2$). The scale is given for $\delta = 1$. For all figures we have assumed $Q_a = Q_\varphi = 1/2$.

(- a) with a projection along $b'$ in the plane perpendicular to $a$. More recent susceptibility measurements [19] determine the easy axis at $48^\circ$ from (a) with a projection of $b'$ at $90^\circ$ toward the small axis of the molecule, in the plane perpendicular to $a$. The antiferromagnetic resonance and the susceptibility measurements agree with $H_{SF} \approx 3.1$ kG. In figure 12b based on our measurements a discontinuity appears in the fields $h_i(\theta)$ which corresponds to the spin-flop transition. Beside the individual fits represented by circles and squares, we have performed a global least square fit in the following way: we assume that the $h_i(\theta)$ vary according to relation (14); we adjust the twelve parameters $U_i, V_i, \phi_i$ in order to get the best least square fit of all data corresponding to all angles in the domain outside the spin flop region. They are represented on figure 12b by dashed lines for the pair $P_2$ and by a full line for the pair $P_1$. If we include more points to the left or to the right of the domain limited by the wavy lines, the least square fit is not correct. We thus determine roughly the spin flop region, which extends over a domain of about $70^\circ$ centred around $\theta \approx 80^\circ \pm 10^\circ$ (i.e. between $b'$ and the small molecular axis $Y$). Because the centre of this domain corresponds to the projection of the easy axis on the plane perpendicular to $a$, our results agree better with the anisotropy axis found by the susceptibility measurements [19]. From the width of the spin flop domain ($70^\circ$), we can deduce the value of the spin flop field. If $\beta$ represents the angle between the easy axis and its projection onto the plane perpendicular to $a$, we have:

$$H_{SF} = H_0 \cos \beta \cdot \cos (70^\circ/2) \quad (H_0 = 4.4 \text{ kG}).$$

If $\beta = 30^\circ$ (as found by antiferromagnetic resonance), we get $H_{SF} = 3.1$ kG. If $\beta = 42^\circ$ (as found by susceptibility measurements), we obtain $H_{SF} = 2.7$ kG. We conclude that the spin flop field is close to 3 kG in agreement with the susceptibility measurements.

The maximum fields $H_i'$ corresponding to our fit outside the spin flop region are:

$$|H'_1| \approx 17 \text{ G with } \phi \approx 70^\circ \quad \text{for the pair } P_1$$
$$|H'_2| \approx 13 \text{ G with } \phi \approx 77^\circ \quad \text{for the pair } P_1$$
$$|H'_3| \approx 12 \text{ G with } \phi \approx 115^\circ \quad \text{for the pair } P_2$$
$$|H'_4| \approx 6 \text{ G with undetermined } \phi_3 \quad \text{(the field } h_3(\theta) \text{ is almost constant. It corresponds to two orthogonal fields } H'_3 \text{ and } H'_4 \text{ of equal magnitude; the angle } \phi_3 \text{ is undetermined).}$$
These fields are shown on figure 14. The same remarks as those pointed out in the previous section are valid.

5. SDW amplitude and wave vector

5.1 Theoretical evaluation of the local fields as a function of $Q$.

As emphasized in section 4.2 (Rel. (7)) the field $H_i(Q)$ created by the conduction electrons on one methyl proton at site $i$ is the sum of a dipolar field $H_{Di}$ and a hyperfine contact term $H_{Ci}$:

$$H_i = H_{Di} + H_{Ci}.$$  

5.1.1 Dipolar field. — The electronic density is spread over the selenium (for the main part) and carbon atoms of the molecule. We take the electronic spin densities $\rho_i$ calculated by Metzger [25] (Table I of this paper) for the atom $l$ of the TMTSF ion (the sum of the $\rho_i$ for all atoms of the molecule is 1). Using the relation (1) which defines the SDW and relations (7a, b), the dipolar term can be written:

$$H_{Di} = \delta \cdot \mu_B \sum_{l,k} \rho_l \cos (Q \cdot R_{lk} + \phi) \left[ \frac{s}{R_{lk}^3} - 3 \frac{R_{lk}}{R_{lk}^5} \right]$$

where $i$ labels the hydrogen site at which the local field is calculated. $R_k$ denotes the position of the molecule centre in the crystal lattice and $R_{ilk}$ is the vector joining the hydrogen site $i$ to the atom $l$ of the molecule $k$. $s$ is the unit vector parallel to the direction of the magnetization.

Because the distances between molecules are relatively large with respect to their size, we obtain a good approximation of the fields $H_{Di}$ by summing on 125 unit cells in the direct lattice with the aid of a computer. We have calculated the dipolar fields for nesting vectors $Q = (Q_a, Q_b, Q_c)$ with $Q_a = a*/2$, $Q_b = b*/2$, $Q_c = c*/2$ for $a$ varying from -1 to 1 by steps of 0.1 (see part of these results on Figs. 15 and 17). The $Q_c$ component of $Q$ along $c*$ has a very small influence on the results. Only a few percent of variations are observed if $Q_c$ is changed from $c*/2$ to 0.

We must emphasize that the discrete summation in relation (15) supposes that the electronic orbitals are strongly localized on the Se and C atoms. Theoretical band calculations [17] show that this hypothesis is valid in (TMTSF)$_2X$. Nevertheless we have checked that, if we spread the electronic distribution along the chain, or if we slightly modify the densities $\rho_i$, the directions and magnitudes of the largest dipolar fields are not fundamentally changed.

5.1.2 Hyperfine contact term. — The hyperfine contact term can be written (see Rel. (7c)):

$$H_{Cl} = -\frac{8\pi}{3} \rho_i \cdot S_j$$

where $S_j$ (Rel. (1)) represents the magnetization of the molecule $j$. $H_{Cl}$ is calculated on the proton $i$ of the molecule $j$ and $\rho_i$ represents the electronic density on the proton $i$.

Because the electronic density is very small on the hydrogen atoms, the calculation of $H_{Cl}$ from first principles is extremely difficult. However, we can estimate an order of magnitude of this term from the Knight shifts measured in the metallic state.

In the metallic state, the magnetization carried by the electrons of the molecule is $S_j = \chi_p H_0$ where $\chi_p$ represents the electronic susceptibility. If we assume that the tails of the wave functions and consequently the electronic densities do not change appreciably...
from the metallic state to the SDW state, the hyperfine term can be written:

$$ H_{Cl} = -\frac{8\pi}{3} \rho_{p} \chi_{p} H_{0} = -K_{i} H_{0} $$

(17)

$K_{i}$ representing the «Knight shift». Comparing with (16), we can write

$$ H_{Ci} = -\frac{K_{i}}{\gamma_{p}} S_{j} . $$

(18)

From the definition of $S_{j}$ in relation (1), the maximum amplitude of the contact term $H_{Ci}$ is:

$$ H_{Ci} = K_{i} \delta \mu_{B}/\chi_{p} . $$

(19)

The Knight shifts have never been measured on protons, however they have been recently determined, in a magic angle spinning experiment, on the methyl carbons (12) of the methyl groups: the $K_{i}$ are of the order of 20 ppm and it seems that physically they will be within the same range on the hydrogens within a factor 10. Appendix 1 presents a more detailed analysis. The susceptibility is of the order 2 to 10 emu/mole [20] and using formula (19) we obtain: $H_{Ci} = \delta \times 560$ G for a Knight shift of 20 ppm on the methyl protons.

Thus we expect the contact term contribution to the local fields to be of the same order of magnitude as the dipolar term which is of order 100 $\times$ $\delta$ to 200 $\times$ $\delta$ G as shown in figure 15. We point out that the contact term is preponderant on the other atoms of the molecules.

The fields (maximum of order 25 G) quoted in the book of Carrington and McLachlan [26] are electronic fields which must be converted to nuclear field $\gamma_{e}/\gamma_{n} = 659$ times larger to obtain the preceding results as explained in Appendix 1.

5.2 Separation of the dipolar and contact term — SDW amplitude and wave vector.

5.2.1 Asymmetry of the contact terms on the molecule. — The four Knight shifts measured by Bernier et al. [12] for the methyl carbons are ($-25.2, -22.2, -10, -6.3$ ppm) on the carbons (4, 5, 14, 15); they are ($38, 44, 17, 21$ ppm) for the carbons (1, 2, 11, 12); they are ($207, 137$ ppm) for the central carbons (3, 13).
These shifts are due to the isotropic hyperfine field, because magic angle spinning used in these experiments averages to zero the dipolar interaction.

This experiment cannot, within one of these groups, attribute a definite Knight shift to a particular carbon. However it is quite obvious from these results and from figure 14a showing the molecules along the stacking axis, that there is, for the selenium orbitals, a large asymmetry between the left and right parts of the molecule. Consequently it seems natural to assume that all the largest Knight shifts correspond to the same molecule side and that, on one side, the Knight shifts are practically the same for atoms symmetric with respect to the long molecular X axis.

Hence we expect that:

i) on the same molecule side, the two contact fields are practically equal,

ii) from one side to the other they differ by a factor 2.

5.2.2 Dipolar and contact terms are experimentally of the same order of magnitude. — For (TMTSF)$_2$PF$_6$, the four fields $H_i$, experimentally determined on figure 13, are almost parallel to the direction of the magnetization $\mathbf{s}$ parallel to $b'$. For this reason, we could, at first sight, think that all local fields are essentially due to the hyperfine contact terms. This hypothesis cannot be realized for the three following reasons:

i) In (TMTSF)$_2$PF$_6$, the intermediate axis of the susceptibility tensor is directed along $a$. In the spin flop phase ($H_0 = 9$ kG and directed along $b'$) $\mathbf{s}$ is directed along $a$, the projection of the hyperfine contact term in the plane perpendicular to $a$ vanishes and the N.M.R. line would narrow drastically and become comparable to the line observed in the metallic state. Such a behaviour is not observed on figure 8.

ii) The N.M.R. lines in (TMTSF)$_2$ClO$_4$ would not look so different from those corresponding to (TMTSF)$_2$PF$_6$, with local fields almost parallel to $b'$. Only the common direction of the maximum fields could be slightly shifted.

iii) With only contact terms, on the same molecule side, one contact term would be four times smaller than the other (see Fig. 13a), which seems unrealistic, according to the remark of the preceding paragraph.

From these experimental facts, we conclude that both dipolar and contact fields are of the same magnitude.

5.2.3 Nesting vector for (TMTSF)$_2$PF$_6$. — For $s$ parallel to $b'$ (easy axis), we have calculated the dipolar fields $H_{Di}$ ($\varphi = 0$) and $H_{Di}$ ($\varphi = \pi/2$) corresponding respectively to the fields $H_{i}$ and $H_{i}^*$ defined in the preceding paragraph for two particular values $\varphi = 0$ and $\varphi = \pi/2$ of the SDW phase. Each of the three protons of one methyl group sees a different field. The resulting dipolar field is given by the tunnelling average of the three different fields seen by the protons; for this reason the dipolar field at methyl site $i$ is calculated as the vectorial mean value of the three fields corresponding to the three protons.

We take $Q_x = a \frac{\pi}{2}$, $Q_y = a \cdot b' \frac{\pi}{2}$, $Q_z = c \frac{\pi}{2}$ where $\alpha$ varies from $-1$ to $1$. The results for $\alpha = 0$, $0.4$, $1.0$ are shown in figure 17.

An important qualitative remark appears in these calculations: the fields corresponding to the pair $P_2$ are always much smaller than those corresponding to $P_1$ for all $\alpha$ values between $-1$ and $1$. Thus the two local fields $H_2$, $H_3$ experimentally determined on figure 13a, for $P_2$, essentially represent the hyperfine contact terms. In agreement with this remark they are directed close to the magnetization direction $s$ (i.e. parallel to $b'$). The Knight shifts measured on the methyl carbons by Bernier et al. are negative [12]. If we assume that the same sign occurs for the hydrogens, $H_2$ and $H_3$ are in the positive direction with respect to $s$ (parallel to $b'$), as shown by relation (19). This fact is taken into account in figure 13a.

According to remark 5.2.1 and figure 14, it is natural to attribute the larger contact field to the left side (i.e. C$_3$) and the smaller to C$_{14}$ as drawn on figure 13a presenting the experimental local fields. We suppose that the contact terms on C$_4$ and C$_5$ are practically the same and equal to the projection of $H_2$ on $b'$ and that the contact terms on C$_{14}$ and C$_{15}$ are essentially $H_3$. The fact that the local fields on C$_4$ and C$_5$ are small and directed near $b'$ proves that the dipolar fields on these sites are directed in the opposite direction to $s \parallel b'$, in order to cancel the contact terms partially.

When $Q_y$ is varied from 0.5 to 0, the dipolar fields on C$_4$ and C$_{15}$ start from a direction perpendicular to $b'$ (Fig. 15c), come close to $b'$ for $Q_y = 0.2 \pm 0.05$ (Fig. 15a) and are again far from $b'$ for $Q_y = 0$ (Fig. 15a). Thus, it is impossible to fit our experimental local fields (Fig. 13a which are all nearly parallel to $b'$) with $Q_y = 0$ or $Q_y = 1/2$ and these simple nesting vectors are ruled out.

The best fit, obtained for $Q_y = 0.2$, is illustrated by figure 16. The contact terms are $H_{C1}^* = 24$ G and $H_{C3} = 14$ G for the left and right side of the molecule respectively. The order parameter is $\delta = 0.085$ leading to dipolar fields $H_{D1} = 18$ G and $H_{D4} = 10$ G. The total local fields $H_i = H_{Di} + H_{Ci}$ correspond to the experimental local fields shown in figure 13a within the experimental errors.

From the magnitude of the contact fields, and using relation (19), we predict the Knight shifts of the protons: $-10$ ppm on the left side (C$_4$, C$_5$) and $-6$ ppm on the right side (C$_{14}$, C$_{15}$) of the molecule. We note that these shifts, although small, are measurable at very high fields (10 T). They are, within a factor 2, of the same sign and same order as those measured by Bernier et al. [12] on the methyl carbons, proving the consistency of our analysis.

5.2.4 Nesting vector for (TMTSF)$_2$ClO$_4$. — The experimental data concerning (TMTSF)$_2$ClO$_4$ are
more difficult to interpret. The largest field maxima shown on figure 12b are spread on a wider range extending from $-25^\circ$ to $25^\circ$ of the perpendicular to the molecular axis. In contrast to PF$_6$, the fields $H_3^i$, $H_4^j$ (of the methyl pair P$_j$), which, in (TMTSF)$_2$PF$_6$, represent essentially the hyperfine terms, are smaller than those corresponding to P$_i$ ($H_i^1$, $H_i^2$), as shown by a comparison of figures 12b and 12a. This might be due to one of the following reasons:

i) a different nesting Q vector,  
ii) different Knight shifts.

i) The hyperfine contact terms are comparable to those observed in (TMTSF)$_2$PF$_6$, but the Q vector is very different, leading to large dipolar fields in a direction perpendicular to b', and thus, in contrast to (TMTSF)$_2$PF$_6$, the dipolar fields on C$_4$, C$_{15}$ do not compensate any more the contact fields. We have calculated the dipolar fields for $Q_b$ varying from $-1/2$ to $1/2$ with $\delta$ at $30^\circ$ of b' towards $-a$ in the plane (a, b') (easy axis of Ref. [13, 20]). Part of the results is shown in figure 17. We have not been able to obtain a fit with any $Q_b$ value. The main reason is that, within this hypothesis of large contact terms on (C$_5$, C$_{14}$), the fields $H_2^i$, $H_3^i$ would still essentially arise from the contact terms and would be parallel to the projection of the easy axis on the plane perpendicular to a (i.e. around b' within $10^\circ$), which is not experimentally the case in figures 12b and 13b.

At this stage, we must point out that the order parameter $S_f = \delta \cdot \mu_B \cdot \cos (Q \cdot R_f + \phi)$ has been chosen with the simplest form. More intricate SDW phases including several Q vectors are not excluded, although on general grounds, their anisotropy structure, seen by antiferromagnetic resonance, could be expected to be more complex.

ii) It might happen that the ratio of the contact terms to the dipolar fields is smaller than in (TMTSF)$_2$PF$_6$. This implies that the Knight shifts in (TMTSF)$_2$CIO$_4$ could be smaller than in (TMTSF)$_2$PF$_6$ : the tails of the electronic charge distribution on the hydrogen atoms could be sufficiently changed by the nature of the counterions, modifying the Knight shifts on the methyls. Within this hypothesis, we can approximately fit the experimental fields illustrated in figures 12b and 13b. The best compromise is shown in figure 18 with $Q_b = 0.3$. The corresponding dipolar fields (shown in Figs. 17b, b' and represented by the dotted arrows) are 8 G for the left side of the molecule (C$_3$, C$_4$) and 4 G for the right side (C$_{14}$, C$_{15}$). As the easy axis is at $30^\circ$ from b', this corresponds to contact terms of 9.2 G and 4.6 G, i.e. $2.5$ times smaller than those observed in (TMTSF)$_2$PF$_6$. They would lead to Knight shifts of $4$ ppm and $2$ ppm, still in reasonable agreement with the values observed on the methyl carbons of (TMTSF)$_2$CIO$_4$ ($-20$ ppm to $-10$ ppm, Ref. [12]).

The order parameter is $\delta \approx 0.12$, slightly larger than that measured in (TMTSF)$_2$PF$_6$, but due to the large error bars in this evaluation of the ratio of dipolar terms to contact terms, the difference is not significant. We conclude that it is also of order 0.1.

Because the fields $H'_i = H_i'$ (Fig. 18b) are for two of them of the same order as the fields $H'_i = H_i' + H_i''$ (Fig. 18a), the maximum experimental fields shown by figures 12b and 13b do not correspond to the fields $H_i'$ (this simplification occurred approximately for (TMTSF)$_2$PF$_6$ because we had $H_i'' \ll H_i'$ for all $i$ (Figs. 15 b and 16b)). Using relation (13) we deduce from figures 18a, b the exact positions of the maxima of the curves $h_i(\theta)$, they are represented in figure 18c. This figure must be compared to figure 13b deduced from the experimental results of figure 12b. The agreement is satisfactory. However we must remark that the ratio of the maxima to the minima of the curves $h_i(\theta)$ corresponding to figure 12b appreciably differ with those obtained from the fields $H_i'$, $H''_i$ of figure 18 using relation (13); in particular, for $h_2$, we find $h_2^{\max}(\theta)/h_2^{\min}(\theta) \approx 1.4$ instead of 4 in the experiments (open squares of figure 12b).

There are at present too many unknown quantities (such as the precise directions of the susceptibility tensor which vary within more than $10^\circ$ from one reference [13] to another [19]), to give definite conclusions. We are undertaking further experiments at lower fields (below the spin flop threshold $H_{SF}$) and at much higher fields, including field orientations out of the plane perpendicular to a. At $H_0 \gg H_{SF}$ the magnetization flips along the intermediate axis nearly along a. The projection of the contact term on the plane perpendicular to a vanishes. In this case, the broadening of the line is essentially due to the dipolar contribution. This is a way to separate the dipolar and hyperfine contributions.

6. Theoretical proof that the nesting vector is incommensurate and variable with counterions.

The band structure for the real crystal structure has been calculated by Yamaji [16], and by Grant [17] who has also evaluated the transfer integrals as a function of the counterion. The band structure is essentially one-dimensional with two sheets perpendicular to the stacking axis a. The small transverse integrals determine the vector Q of the SDW. The best nesting vector Q connecting the two sheets of the Fermi surface minimizes the energy, as shown in figure 19. The exact tight-binding energy given by Grant and Yamaji [17-16] is :

$$E(k) = 2 \; t_{13} \; \cos(k \cdot b) \pm |T(k)|$$  

(20)

with

$$T(k) = t_{51} + t_{52} \; e^{-i \cdot k \cdot a} + t_{12} \; e^{-i \cdot k \cdot b} + t_{11} \; e^{-i \cdot k \cdot (a-b)}$$

where $t_{51}, t_{52}$ are the transfer integrals along the stacking axis a, $t_{13}, t_{11}, t_{12}$ are the transverse transfer integrals in the (a, b) plane along the two directions b and $b$ ($b$ - a/2) respectively, as shown in figure 14b. The calculations of Grant show that the two transverse integrals $t_{13}, (t_{11} + t_{12})/2$ are of the same order.
Fig. 18. — A possible interpretation of the data in (TMTSF)$_2$ClO$_4$. Figure (a) represents the local fields $H_i'$ (full arrows) as seen by a molecule carrying the maximum magnetization ($\varphi = 0\degree$). The dashed arrows represent the dipolar contributions $H_{6i}$, for $Q = 0.3$ and $\delta = 0.12$ the dotted arrows represent the contact terms $H_{ci}$. For any $Q$, the theoretical dipolar field components perpendicular to $b'$ on any carbon of pair $P_2$ are relatively small (see Fig. 17). If we keep the same contact terms as in PF$_6$, we are not able to fit the experimental field $H'$, which is at 500 away from $b'$. For this reason we need to assume that the contact terms are 2.5 times smaller than in (TMTSF)$_2$PF$_6$ but with the same hierarchy: $H_{C1}' = H_{C2}' = 2 H_{C3}' = 2 H_{C4}'$. The lower figure (b) shows the local fields $H_i''$ seen by a molecule carrying zero magnetization ($\varphi = \pi/2$). They correspond to the dipolar fields of figure 17b (the contact terms are zero). In contrast to (TMTSF)$_2$PF$_6$ they are not negligible with respect to the $H_i'$; the fact that the magnetization is directed out of the molecular plane increases the theoretical ratio $|H_i''|/|H_i'|$ (as shown on Fig. 17). In this case we must use the relation (13) without any simplification in order to determine the corresponding maxima of the curves $h_i(0)$ (experimentally shown on Fig. 12b and 13b). The theoretical results are shown on figure (c) and compared to the experimental results of figure 13b (dashed area). The agreement is only approximate. We need further experimental results before giving definite conclusions.

and their ratio depends on the nature of counterions. When the integral $t_{13}$ along $b$ is dominant ($t_{11} \approx t_{12} \approx 0$) the nesting vector is given by the simple and natural result $Q = (a^*/2, \pm b^*/2, c^*/2)$ as shown in figure 19. When the others along $b - a/2$ (i.e. $t_{11}$ and $t_{12}$) are preponderant, the nesting vector is given by the same method using $b - a/2$ instead of $b$: $Q = (a^*/2, 3/4 b^*, c^*/2)$. In the case of two integrals of same order $t_{13} \approx (t_{11} + t_{12})/2$, the nesting vector is naturally intermediate between these two limiting cases. If we develop the exact tight-binding electron energy [17] to first order in transfer integrals and in dimerization i.e. $t_{13}$, $(t_{12} + t_{11})/2$ and $t_{51} - t_{52}$ we obtain a Fermi surface composed of two sheets with a sinusoidal warping along $b$:

$$E_F = (t_{51} + t_{52}) \cos \frac{k \cdot a}{2} + \Delta E$$

with

$$\begin{align*}
\Delta E &= 2 t_{13} \cos k \cdot b + \\
&+ (t_{11} + t_{12}) \cos k \cdot \left( b - \frac{a}{2} \right) = A \cos (k \cdot b + \varphi')
\end{align*}$$

$$\varphi' = \arctg \left[ \frac{t_{11} + t_{12}}{t_{11} + t_{12} + 2 \sqrt{2} t_{13}} \right].$$

The phase $\varphi'$ has been neglected in the simplified formula given by Grant but, as first noted by Yamaji [17], this phase changes the nesting vector to:

$$Q = \frac{1}{2} a^* \frac{1}{2} \left( 1 + \frac{2 \varphi'}{\pi} b^* \right).$$

The nesting is perfect to first order in transverse integrals and dimerization, but higher order terms lead...
to incomplete nesting. The nesting vectors $Q$ obtained with this formula using the transfer integrals calculated by Grant for the different counterions are given in table I. For $(\text{TMTSF})_2\text{PF}_6$ the predicted value of the nesting vector $Q = (1/2, 0.25, ?)$ is in satisfactory agreement with that $Q = (1/2, 0.2, ?)$, obtained from the experimental N.M.R. results presented in this paper, taking into account the uncertainties in Grant’s calculations of the transfer integrals.

Table I. — Theoretical nesting vector $Q$ using transfer integrals calculated by Grant [17].

<table>
<thead>
<tr>
<th>Counterion</th>
<th>$Q$ (Å⁻¹)</th>
<th>$\alpha$ :</th>
<th>$\alpha$ :</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{TMTSF})_2\text{PF}_6$</td>
<td>0.504</td>
<td>(TMTTF)$_2\text{Br}$</td>
<td>0.314</td>
</tr>
<tr>
<td>$(\text{TMTSF})_2\text{ClO}_4$</td>
<td>0.441</td>
<td>(TMTTF)$_2\text{SCN}$</td>
<td>0.513</td>
</tr>
<tr>
<td>$(\text{TMTSF})_2\text{AsF}_6$</td>
<td>0.696</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**7. Conclusion.**

This paper presents the following new results: a) a detailed study of N.M.R. lineshape of methyl groups in single crystals of $(\text{TMTSF})_2\text{ClO}_4$ which accurately follows the theory of Allen and Clough [7, 8]; b) the measurement by N.M.R. of the local fields seen by the methyl groups in the SDW state of $(\text{TMTSF})_2\text{X}$ with $\text{X} = \text{ClO}_4$ and $\text{PF}_6$ and the indication that the SDW is incommensurate or high order commensurate. The theoretical interpretation of these fields leads to the determination of the wavevector $Q$ and amplitude $\delta$ of the SDW. For these two compounds they are different, as expected from simple but realistic theoretical considerations on the nesting vector and band structure. In particular the experimental results presented in this paper are in agreement with a theory using the best nesting conditions [14, 16], but taking into account the real triclinic structure [16].

To our knowledge, up to this date, nearly no detailed study of the lineshape of tunnelling methyl groups in single crystals had been performed. In particular our observation of the variation of the line width of the different methyl lines with the orientation of the magnetic field was strictly impossible on the powders used in typical experiments [7-8]. The observation of the methyl N.M.R. lineshape gives a way to orientate and test the bulk homogeneity of single crystals of $(\text{TMTSF})_2\text{X}$ without any X-ray radiation damage.

This preliminary study allowed us to interpret with accuracy the detailed N.M.R. lineshapes that we observed in the SDW state. The structures of the broadening observed are very different between the two compounds $\text{X} = \text{ClO}_4$ and $\text{X} = \text{PF}_6$ showing definitively that the corresponding SDW structures are not the same, contrary to simple theoretical models. In particular for $\text{X} = \text{PF}_6$ the SDW line becomes quite narrow when the magnetic field is perpendicular to the $(a, b)$ plane; for this reason the local field seen by the methyl groups are nearly in this plane $(a, b)$; this result imposes stringent conditions on the possible $Q$ vectors and our best fit of all lines for all angles gives $Q = (0.5, 0.2, ?)$ with an amplitude $\delta = 8.5\%$ for $\text{X} = \text{PF}_6$.

The results are different for $\text{X} = \text{ClO}_4$; such a narrowing is not observed for $H_0$ perpendicular to the $(a, b)$ plane. The determination of the SDW $Q$ vector is more difficult and less accurate because the experiments on $(\text{TMTSF})_2\text{ClO}_4$ have not been performed in the best conditions. We propose an approximate fit with $Q_0 = 0.3$ and $\delta$ of order 0.1, which give contact terms 2.5 times smaller than in $(\text{TMTSF})_2\text{PF}_6$, but we need further experimental results, at lower fields below the experimental threshold, to draw definite reliable conclusions. It is quite possible that the electronic densities and consequently the Knight shifts on the methyl sites vary with the nature of the counterion. In order to test this hypothesis, it would be worth while directly measuring these shifts on protons and carbons at high field, for various counterions $\text{X} = \text{PF}_6, \text{ClO}_4, \text{AsF}_6$ (and others) and comparing them. These shifts could also vary with temperature; the experiments must be made at room and helium temperatures.

In both cases the SDW vector is transversally incommensurate, in complete contradiction with oversimplified nesting theories [2, 14, 15] which do not take into account the real crystal structure, in particular the fact that the two transverse hopping frequencies along $b$ and $b - a/2$ are of the same order, as shown by Grant. This competition between two transverse directions in $(\text{TMTSF})_2\text{X}$ leads to the
conclusion that the nesting vector $Q$ is incommensurate and depends on: a) the nature of the molecule (sulfur or selenium), b) the nature of counterion $X$, and c) the pressure. We have verified case b) for $X = PF_6$ or $ClO_4$. It remains to study other counterions, sulfur compounds ($X = Br$) and pressure effects which are likely to be important. The same kind of study on BEDT compounds would be interesting, in particular the presence of methyls with slightly narrower lines could increase the accuracy of local field determination. Even if some day the neutron diffraction measurement of the SDW vector $Q$ becomes possible, these N.M.R. measurements will remain quite complementary. In particular the very small coupling along the $c$ axis prevents us from obtaining any information on the nature of ordering along this $c$ axis using N.M.R.; it could be disordered to some extent and thus increases the difficulty of the neutron diffraction experiments.

We must emphasize that we have not used all the possibilities of this experiment in the present work. The field has been varied in the plane perpendicular to $a$. More information could be obtained from a study with external field distributed in the whole space. The method used to separate the dipolar from the hyperfine interaction is somewhat empirical. It would be useful to separately determine the dipolar contribution with the following method: at field $H_0$ sufficiently high with respect to the spin flop threshold $H_{SF}$ the magnetization is directed along the intermediate axis $a$; for $H$ perpendicular to $a$, the N.M.R. broadening is only due to the dipolar field (the projection of the contact term along $H_0$ being zero).

The study of magnetic field effects is fascinating, in particular the different transitions between the semimetallic SDW states observed at high fields are likely to be associated with changes of the nesting vector that the N.M.R. can measure following the method described in this paper. This method, contrary to other thermodynamic or transport measurements, probes the SDW structure at the atomic level and thus can give more microscopic information than, for example, antiferromagnetic resonance. In the future we plan to measure the nesting vector at high magnetic fields. The theories of magnetic field effects are complex and thus have neglected the real density at molecular extremities to a factor 10, in agreement with our experimental results.

Appendix I.

The objections of one referee confusing nuclear and electronic hyperfine fields, and the fact that the hyperfine contact term has been neglected in several previous papers [9, 11] lead us to the following remarks.

As explained in the book of Carrington and McLachlan (chapter 6 of Ref. [26]), in aromatic radicals, the exchange coupling between the spins of the $\pi$ electrons in the C-H bonds with the delocalised $\pi$ electron leads to a negative hyperfine constant. The maximum splitting with one $\pi$ electron on the carbon is given by McConnell's relation: $a_{\pi} = Q p_{\pi}$, where $Q = -23$ G is measured in units of electronic field (i.e. $\gamma_e = 2.8$ Mc/s/G) which in units of nuclear proton spin field ($\gamma_n = 4.25$ kilocycles/s/G) is $\gamma_e / \gamma_n = 659$ times larger. Thus the maximum hyperfine field for a density $\rho = 1$ on the carbon atoms is $-23 \times 659 = -15159$ G for the N.M.R. splitting.

In the TMTSF ion, there is one electron molecular orbital spread over the molecule, mostly on the selenium atoms. The electron density $\rho^{\text{methyl}}$ on the methyl carbons is small but finite, and according to McConnell's relation, on the methyl protons, the hyperfine field is $Q \times \rho^{\text{methyl}} \times \delta$. If we take the value $\rho^{\text{methyl}} \approx 0.001$ roughly estimated by Metzger, we obtain $-15159 \times 0.001 \times 0.1 \approx -15$ G. The maximum splitting with one $\pi$ electron on the carbon is given by McConnell's relation: $a_{\pi} = Q p_{\pi}$, where $Q = -23$ G is measured in units of electronic field (i.e. $\gamma_e = 2.8$ Mc/s/G) which in units of nuclear proton spin field ($\gamma_n = 4.25$ kilocycles/s/G) is $\gamma_e / \gamma_n = 659$ times larger. Thus the maximum hyperfine field for a density $\rho = 1$ on the carbon atoms is $-23 \times 659 = -15159$ G for the N.M.R. splitting.

We emphasize that Metzger's calculation is valid for an isolated TMTSF$^+$ ion, but does not take into account polarization effects at the extremities of the molecule due to the proximity of the counterion. This calculation does not exhibit any asymmetry of the electronic spin densities on the molecule (contrary to the experiments [12]), associated with the zig-zag stacking of the chain of molecules. From these arguments, we expect an enhanced and asymmetric density at molecular extremities to a factor 10, i.e. $H_{CI}$, in the range of a few to 20 G. It will be sensitive to the nature of the counterion, as suggested by the difference between $ClO_4$ and $PF_6$ in our experimental results.

Taking into account the poor accuracy of the theoretical calculations, in particular for the tails of the wave functions, in the regions where $\rho$ is particularly small, we consider that theoretical estimates give an order of magnitude within a factor 10, in agreement with our experimental results.
References