An NMR study of the organic superconductor : \((\text{TMTSF})_2\text{ClO}_4\)

T. Takahashi (*), D. Jérome and K. Bechgaard (**)

Laboratoire de Physique des Solides (associé au CNRS), Université Paris-Sud, 91405 Orsay Cedex, France

(Reçu le 22 septembre 1983, révisé le 7 décembre, accepté le 9 janvier 1984)

Résumé. — Nous présentons les résultats de mesures RMN effectuées sur des monocristaux de \((\text{TMTSF})_2\text{ClO}_4\). Ces résultats prouvent le caractère magnétique de l'état fondamental semi-métallique stabilisé par un champ magnétique élevé. Un état fondamental magnétique peut aussi être stabilisé par la présence d'un désordre moléculaire non magnétique en l'absence de tout champ magnétique appliqué. Le taux de relaxation spin-réseau ne suit pas une loi de Korringa à basse température. De plus, la forte augmentation du taux de relaxation observée au-dessous de 12 K peut être reliée soit à l'existence d'une instabilité onde de densité de spin (lorsqu'elle existe) soit à l'apparition de fluctuations d'un ordre supraconducteur à courte portée.

Abstract. — We report \(^1\text{H}\) and \(^{77}\text{Se}\)-NMR data on oriented single crystals which establish the magnetic character of the semi-metallic ground state stabilized under high magnetic field in \((\text{TMTSF})_2\text{ClO}_4\). A similar magnetic state can be stabilized at low temperature in the absence of magnetic field by non-magnetic molecular disorder. At low temperature the spin-lattice relaxation rate does not follow the Korringa law. A large enhancement of the relaxation rate occurring below \(\approx 12\) K may be related to the onset of the SDW instability (whenever it exists) or to the development of short range superconducting fluctuations.

1. Introduction.

In this work, we present the results of NMR-studies on \((\text{TMTSF})_2\text{ClO}_4\) in the wide temperature range from 1.3 K to 200 K, concentrating on the NMR spin-lattice relaxation properties measured on \(^1\text{H}\) and \(^{77}\text{Se}\) nuclei [1]. NMR relaxation probes the spin dynamics of the system which we are interested in [2].

The measured temperature range is divided into three regions, where different types of dynamics are encountered: the low temperature range below \(\approx 5\) K, the intermediate range below \(\approx 15\) K and the high temperature range above \(\approx 15\) K.

In the low temperature range the spin dynamics is influenced by various kinds of electronic instabilities. It is shown in this article that two situations must be considered. First, a non-magnetic conducting state which is obtained at low temperature in the whole temperature domain down to the superconducting transition at 1.2 K when the sample is cooled slowly down to helium temperature. Secondly, a spin density wave (SDW) state can be stabilized at low temperature by two different ways: (i) introduction of molecular disorder by a rapid cooling of the sample or (ii) application of a large magnetic field on a slowly cooled sample.

In the intermediate temperature region, the relaxation in the metallic region is discussed. We show that a simple Korringa relation breaks down, revealing a large and temperature dependent enhancement of the relaxation.

In the high temperature range, \(^1\text{H}\) relaxation shows the effect of the methyl group rotation on TMTSF molecules. The anion order-disorder transition at 24 K is found to affect this mechanism. The analysis will demonstrate that the motional effects are not important above 200 K and below 10 K, where the dominant contribution to the \(^1\text{H}\) relaxation comes from the conduction electrons.

The next section is devoted to the description of experimental details. The experimental results are presented and analysed in the section 3.

2. Experimental.

The \(^1\text{H}\) and \(^{77}\text{Se}\)-NMR measurements were performed on single crystals and a powdered sample of \((\text{TMTSF})_2\text{ClO}_4\) prepared by the same method as
described before [3]. We have used three single crystals in total with a typical size of $0.5 \times 0.5 \times 3$ mm$^3$ in the present work (only one crystal for each measurement) and found no appreciable sample dependence. The powdered sample consists of many small crystals with a typical size of $\sim 0.1$ mm$^3$ of a total weight of $\sim 20$ mg.

A conventional pulsed-NMR spectrometer was operated at frequencies of 13, 45, 52 and 60 MHz. For the single crystal measurements, we made a receiver coil with a rectangular cross-section and a size of $0.7 \times 0.8 \times 3$ mm$^3$ in order to obtain a good filling factor. The sample holder and the NMR-probe were made of teflon in order to avoid signals of spurious protons. Both single coil and crossed-coil geometries were used. The axis of the receiver coil was parallel to the crystallographic $a$-axis, so that the external field $H_0$ was always applied perpendicular to the conductive axis. The measurements for $H_0 \parallel c^*$ (perpendicular to the $a$-$b$ plane) and for $H_0 \parallel b'$ (perpendicular to $a$- and $c^*$-axis) are presented in this report.

For the crossed-coil measurements with the axis of the transmitter coil parallel to the $c^*$-axis ($H_0 \parallel b'$), a remarkable reduction of RF amplitude was observed at low temperatures. This is clearly due to the Eddy current loss in the conductive $a$-$b$ plane. For the other orientation ($H_0 \parallel c^*$) and for the single coil probe, there was no difficulty of this kind. The powdered sample was put into a teflon cell with an inner diameter of 3 mm, and the receiver coil was wound around it.

For $^1$H-NMR measurements, the free induction signal following the $\pi/2$ pulse was sampled digitally by a transient recorder and accumulated in a microcomputer. The spin lattice relaxation time was measured by observing the recovery in time after a comb of saturating pulses. The free induction signal in the single crystal is not a simple decay curve but has an oscillating component due to the dipole structure. We used the integrated value of the free induction signal observed at the resonance field.

For the $^{77}$Se-NMR, the spin-echo signal following $\pi/2 - \pi$ pulse series was accumulated by an analog box-car integrator. The field sweep method was used to observe the absorption signal. At low temperatures, we also used the digital integration of the spin-echo and the storage in the microcomputer.

3. Results and analysis.

3.1 THE LOW TEMPERATURE REGION $T < 5$ K.

$^{77}$Se and $^1$H-NMR measurements on the single crystal have demonstrated that the low temperature state (TMTSF)$_2$ClO$_4$ changes drastically, depending on i) the rate of decreasing the sample temperature and on ii) the strength of the external magnetic field. We present experimental evidences for these effects.

3.1.1 Cooling rate effects. — When the sample is cooled very rapidly (typically at a rate of $\geq 2$ K/s below 40 K, this is the so-called quenched state, Q-state) a magnetic (SDW) state is found to be stabilized below $T_M \sim 3.7$ K [3, 4].

Figure 1 shows the temperature dependence of the $^{77}$Se signal intensity and the linewidth measured in the rapidly cooled sample at a field of 55.3 kOe. The observed $^{77}$Se absorption lineshape is symmetric and gaussian in the whole temperature region. The full width at the half-maximum, $\Delta H_{1/2}$, and the signal amplitude were measured. The relative intensity was calculated as the product of the width by the amplitude. At temperatures above 5 K, the intensity is proportional to the inverse of the temperature, following a Curie law. Below 5 K, the observed intensity decreases rapidly, the reduction of the amplitude is faster than the line broadening. The resonance field of the observed line does not change within the experimental error $\leq 5$ Oe. This means that most of the $^{77}$Se-nuclei should give a resonance with a linewidth too broad to be detected or far from the measured field region.

Since $^{77}$Se-nuclei have spin $I = 1/2$, such a large inhomogeneous broadening (or resonance shift) is an evidence for the onset of strong local fields of hyperfine origin at low temperatures. In the same region where the intensity drops, the spin lattice relaxation rate of $^{77}$Se displays a peak anomaly, as shown in figure 2. This is explained as a result of the enhancement of NMR relaxation due to the so-called « critical slowing down » of magnetic fluctuations around a magnetic transition [5, 6].

We define (rather arbitrarily) the transition temperature as the temperature where half of the total $^{77}$Se signal disappears : this definition is in good agreement with the position of the maximum of relaxation rate.

**Fig. 1. —** $^{77}$Se-signal amplitude times the temperature for Q-state of TMTSF$_2$ClO$_4$ and linewidth versus temperature.
The magnetic transition temperature changes depending on the heat cycle on the sample. Figure 3 shows the temperature dependence of the $^{77}$Se signal intensity below 4.2 K measured for different heat treatments on the same crystal. The highest transition temperature in the present work is $T_m \approx 3.7$ obtained by the fastest cooling rate of $\sim 2$ K/s below 40 K.

On the contrary, when the sample is cooled slowly enough below 40 K (a cooling rate $\lesssim 0.2$ K/min the so-called relaxed-state, R-state at low temperature) no magnetic anomaly is observed at least above 1.3 K.

Similar magnetic anomalies were also observed by the $^1$H-NMR measurements at lower fields. Since the hyperfine coupling of the $^1$H-nuclei with electron spins is expected to be much smaller than that of $^{77}$Se the $^1$H-NMR signal is not wiped out. However, a remarkable broadening of the absorption line clearly indicates the onset of the magnetic phase in the Q-state. The $^1$H absorption line in the single crystal has a dipolar structure with two satellites on both sides of the central line which is probably due to a dipolar interaction. The splitting between the satellites and the central line is $\pm 8.0$ Oe in the external field $H_0 \parallel c^*$ (the structure depends on the field orientation). The additional broadening occurring in the magnetic state ($\approx 20$ Oe) completely smears out these structures.

The $^1$H spin-lattice relaxation rate of the Q-state displays a sharp peaking below 4 K as shown in figure 4. If we attribute this peak of relaxation to the onset of the SDW state we realize that the transition temperature is nearly the same as that derived from $^{77}$Se-NMR at higher fields. Data of $^1$H and $^{77}$Se-NMR are summarized in figure 5a. They suggest that the transition towards a magnetic state is field independent. It is also important to notice that the $^1$H relaxation rate shows a monotonous decrease at low temperature in the R-state, figure 4.

3.1.2 Magnetic field effects. — The $^{77}$Se-NMR measurements on the slowly cooled single crystal (R-state) at high fields revealed the existence of an other type of magnetic transition. Figure 6 displays the temperature dependence of (a) the $^{77}$Se signal intensity and (b) the spin-lattice relaxation rate measured in the external fields of 64 kOe and 74 kOe along the $c^*$-axis.

At high temperatures, the signal intensity follows a Curie law as usual and the linewidth is almost constant. The linewidth (the full width at half-maxi-
Fig. 5. — Proposed phase diagram ($T$ versus $H_{//c^*}$) for the Q-state (a) and the R-state (b) of (TMTSF)$_2$ClO$_4$. The data of specific heat ($\nabla$, ref. [9]) and the onset of magnetoresistance oscillations ($\Delta$, ref. [7]) are included together with NMR data. The $\Delta$ point refers to data of Bando, H., Oshima, K., Suzuki, M., Kobayashi, H. and Saito, G., J. Phys. Soc. Japan 51 (1982) 2951.

Fig. 6. — (TMTSF)$_2$ClO$_4$, (R-state), (a) $^{77}$Se NMR signal intensity versus temperature for fields $H_0 = 73.9$ and 64 kOe $// c^*$, a magnetic transition arises at 2.15 and 1.55 K respectively. The dashed line indicates the Curie-law behaviour. (b) $^{77}$Se relaxation rate versus temperature for fields $H_0 = 73.9$ and 64 kOe $// c$ and 64 kOe $// b'$. The dashed lines are guides to the eye.

The R-state phase diagram derived from NMR data with $H_{//c^*}$ is shown in figure 5b. The transition temperature and the magnetic field orientation dependence agree fairly well with a large number of other experimental results showing the onset of a field-induced phase transition: magnetoresistance oscillations [7, 8], specific heat [9], $^1$H-relaxation rate [10], Hall effect [11]. We suggest that the phase transition detected by $^{77}$Se NMR is indeed the same as observed by other methods. Hence, the field induced semimetallic state is magnetic.

3.2 INTERMEDIATE TEMPERATURE REGION, $T < 15$ K. — $^1$H and $^{77}$Se relaxation measurements in the R-state were extended to the higher temperature region. Figure 7 shows the temperature dependence of the $^1$H spin-lattice relaxation rate at magnetic fields of 3.05, 10.5 and 14 kOe. Both field and orientation dependences are small in the measured range of temperatures. The difference of almost 20 $\%$ is only slightly larger than the experimental errors of typically about 10 $\%$.

Since the conductivity in the R-state is always metallic and the spin susceptibility is almost constant in temperature [12] below 30 K a simple approach would consist in a Korringa-like behaviour for the relaxation, i.e. $T_1 \tau = \text{const}$. As shown in figure 8, $(1/T_1 \tau)^{-1}$ is strongly temperature dependent: $(T_1 \tau)^{-1}$ for protons increases by a factor $\sim 5$ as the temperature decreases from 10 K to 1.3 K.

A similar behaviour was also observed for $^{77}$Se relaxation rate. The results at a field of 64 kOe along the same field (64 kOe) is applied in the $b'$-direction (perpendicular to the $c^*$-axis) no magnetic transition is observed in the measured temperature region. The $^{77}$Se relaxation rate in this case is plotted in figure 6b.

Fig. 7. — Temperature dependence of $^1$H spin-lattice relaxation rate for different magnetic fields and orientations.
the $b'$ direction when no magnetic state is observed at low temperature are plotted with a different scale on the same figure.

Since we do not know the hyperfine fields of $^1$H and $^{77}$Se-nuclei in TMTSF molecule, we cannot compare their relaxation rates quantitatively. The relaxation rate of $^{77}$Se is larger by three orders of magnitude than that of $^1$H. This ratio seems rather reasonable. We only claim here that a large enhancement of $(T_1 T)^{-1}$ is observed at low temperature for $^1$H and $^{77}$Se in the broad field region from 3.05 kOe up to 74 kOe.

One may worry about the effect of relaxation from paramagnetic impurities which could give rise to a residual contribution at low temperature.

However, first the amount of paramagnetic impurities or free radicals is particularly low in (TMTSF)$_2$ClO$_4$. Curie-tail measurements performed on samples of the same origin give a higher limit value of $\approx 3 \times 10^{-4}$ spin 1/2 per molecule [12]. Secondly, the nuclear relaxation induced by fixed paramagnetic impurities is field dependent [2], namely $(T_1)^{-1} \propto H^{-2}$. Therefore in case of relaxation via paramagnetic impurities we may expect some magnetic field dependence, especially at low fields. The data of figure 7 do not reveal any appreciable field dependence between 3 and $14$ kOe at 1.2 K for the relaxation rate of protons. Even if we make the assumption of an impurity induced contribution to the relaxation rate of $10^{-2}$ s$^{-1}$ for protons the contribution to $^{77}$Se relaxation in fields of 64 kOe should also amount to less than $10^{-2}$ s$^{-1}$ (taking into account the ratio between $^{77}$Se nuclei and protons (1/36) and the square of the ratio of magnetic fields (60/3)$^2 = 400$). The latter estimate is considerably smaller than the intrinsic $^{77}$Se relaxation rate. The behaviour at low temperature of the $^{77}$Se relaxation and probably also the $^1$H relaxation appears to be related to the properties of the electron gas. It is interesting to notice that the « Korringa dependence » of $T_1 T$ reported by Azvedo et al. [13] in $^{77}$Se-(T$_1 T)^{-1}$ powder data on (TMTSF)$_2$PF$_6$ ($P = 6.9$ kbar, $H = 105$ kOe) in the $T$-domain lower than 4.2 K is not followed for our present data of (TMTSF)$_2$ClO$_4$.

Maniv [6] has proposed several possibilities for the enhancement of the spin-lattice relaxation near the onset of a SDW transition. Fluctuations in the electron spin density lead to a strong divergence of $(T_1 T)^{-1}$ at the SDW transition. This is a possible interpretation for the sharp peaking of $(T_1 T)^{-1}$ at $3.7$ K in the Q-state of (TMTSF)$_2$ClO$_4$. However the divergence of $(T_1 T)^{-1}$ in the R-state of (TMTSF)$_2$ClO$_4$ is more puzzling since no SDW ground state has been detected with the experimental conditions of figure 8. The low-field data are particularly striking $(H_0 = 3.05$ kOe$/b')$ since for such an orientation of the magnetic field the external magnetic field is still much smaller than the critical field $H_{c1}(0) \approx 15$ kOe [1]. Therefore superconductivity should be observed at about 1 K or so. We wish to emphasize that in our picture of quasi $1-D$ superconducting precursor effects, fluctuations could exist in the $T$ and $H$ domain above $T_\nu(H = 0)$ or $H_0(T = 0)$. Therefore no disappearance of their influence on the relaxation is expected at values of magnetic fields larger than $H_{c1}(0) = 15$ kOe. Maniv and Alexander [14, 15] have suggested that fluctuations in the superconducting gap parameter could enhance significantly the relaxation rate close to $T_c$. Furthermore this relaxation rate enhancement is amplified by the strong anisotropic nature of the electron energy spectrum $(T_1^{-1} \sim (T - T_c)/T_c)$. The mean-field treatment of the fluctuations which has been used by the previous authors [14, 15] is probably not appropriate for quasi $1-D$ superconductors such as (TMTSF)$_2$X for which fluctuations above $T_\nu$ (and below $T_c$ mean field) are essentially fluctuations of the phase of the order parameter [16, 17]. Superconducting phase fluctuations may also be responsible for the enhancement of $(T_1 T)^{-1}$ at low temperature in (TMTSF)$_2$ClO$_4$ (R-state). Fluctuating superconducting triplet pairing could give rise to an enhancement quite analogous to the effect of SDW fluctuations [18]. In short, the behaviour of $(T_1 T)^{-1}$ in (TMTSF)$_2$ClO$_4$ R-state, is definitely far from a Korringa relation but more theoretical work is still needed in order to establish the origin of the relaxation rate enhancement.

3.3 Higher temperature region, $T > 15$ K. — At high temperature above 15 K, $^{77}$Se NMR measurements become very difficult on single crystals because of the smallness of the signal to noise ratio. Consequently most data at high temperature have been obtained from $^1$H spin-lattice relaxation of a powdered sample. We have checked with a few points performed at several temperatures on a single crystal the absence of...
of visible difference between powdered and single crystal data.

The experimental results are shown in figure 9, where the logarithm of $T_1^{-1}$ is plotted against the inverse temperature. Characteristic features of the $^1H$ relaxation rate are summarized as follows:

1. The relaxation rate has a strong temperature dependence, consisting of several broad peaks. This suggests that there are several different mechanisms of relaxation in (TMTSF)$_2$ClO$_4$.

2. The relaxation curves are not single exponential in this temperature region. Since this is also observed in the single crystal, it is not due to an anisotropy of the dipolar relaxation as expected in powder samples. The relaxation curves can be decomposed into two components, one with the longer $T_1$ and another with the shorter $T_1$. The shorter $T_1$ component corresponds to the smaller fraction ($1/3 \sim 1/4$) of the total intensity. This suggests an inhomogeneity depending on the crystallographic sites.

3. The shorter component becomes too short to be measured above $T \sim 25$ K. This may be associated to the anion order-disorder transition.

4. The frequency dependence of the relaxation rate is clearly observed, especially below $\approx 100$ K.

Since all protons in this material are on the methyl groups located on the four corners of TMTSF-molecules, the rotational motion degree of freedom contributes to the $^1H$-relaxation. This mechanism has been widely examined by taking into account quantum tunnelling motions together with the classical rotations.

Recently, Clough and co-workers [19] have presented a general description of the methyl rotations on the basis of their « methyl thermometer model ». This model has been found to apply to a wide variety of organic molecules containing methyl groups. According to their formalism, the $^1H$ relaxation rate due to this mechanism is written as:

$$T_1^{-1} = C_1 \left\{ \frac{\tau}{1 + \omega^2 \tau^2} + \frac{4 \tau}{1 + 4 \omega^2 \tau^2} \right\} +$$
$$+ C_2 \left\{ \frac{\tau}{1 + (\omega - \omega_0)^2 \tau^2} + \frac{4 \tau}{1 + (2 \omega - \omega_0)^2 \tau^2} \right\} +$$
$$\frac{4 \tau}{1 + (\omega + \omega_0)^2 \tau^2} + \frac{4 \tau}{1 + (2 \omega + \omega_0)^2 \tau^2} \right\}$$

where $\omega$, $\omega_0$, and $\tau^{-1}$ are the $^1H$ Zeeman frequency, the tunnelling frequency and the thermally activated reorientation rate. The $C_1$- and $C_2$-terms correspond to E-E transition and A-E transition respectively, between rotational modes with different symmetries (A and E$^\alpha$). $C_1$ and $C_2$ are coefficients describing the dipolar coupling but usually taken as fitting parameters. The tunnelling frequency $\omega_0$ is the separation between the levels with A- and E-symmetry (divided by the Planck constant $\hbar$) and is a function of the potential barrier height $V$. The methyl thermometer model claims that the temperature dependence of the reorientation rate $\tau^{-1}$ is universally determined at a given barrier height $V$. The usual Arrhenius-type relation between $\tau^{-1}$ and the temperature as $\tau^{-1} = v_\infty \exp(-\varepsilon/kT)$ breaks down but, even here, we can use this exponential dependence in a narrow temperature region by the proper choice of an « effective » activation energy $\varepsilon$.

i) $10$ K $< T < 25$ K.

The observed relaxation rate can be decomposed into an exponentially temperature dependent contribution and another contribution which is more weakly temperature dependent (see for example single-crystal data below 15 K in Fig 9). One can consider the former as the rotational component and the latter as the electronic contribution. At low temperature where $\omega \tau \gg 1$, the formula (1) is reduced as $T_1^{-1} \propto \tau^{-1}$. Thus we can estimate the effective activation energy as $\varepsilon \sim 120$ K. According to the calibration given by Clough et al. [19], this value corresponds to the potential barrier height of $\sim 300$ K in the temperature unit and to $\omega_0/2\pi \approx 1$ GHz. Thus, the low barrier height limit ($\omega_0 \gg \omega$) can be applied; one can say that the rotational relaxation comes from the $C_1$-term and it is « frozen » in the lower temperature region below 10 K.
The non-single exponential relaxation is originated from the motional component because it is pronounced only in the region where the motional effects are dominant. Moreover, in this temperature domain both components of the relaxation have almost the same temperature dependence (see Fig. 9).

The frequency dependence of $1/T_1$ between 13 and 45 MHz ($10 < T < 25$ K) is consistent with the model with $C_1$-terms dominant in equation (1).

ii) $25$ K < $T$ < $40$ K.

In this region, the relaxation rate at 45 MHz is larger than at 13 MHz. As far as considering the effects of methyl rotations, this occurs only when the tunnelling frequency $\omega_q$ is comparable to the nuclear Zeeman frequency $\omega$ ($\sim 45$ MHz). We have to assume a higher potential barrier $V$ of at least $700$ K than the lower temperature value of $\sim 300$ K. This may be related to the anion order-disorder transition observed at $T \sim 24$ K. Since the methyl groups on TMTSF-molecules are located very near the ClO$_4$ ions, it is likely that the electrostatic potential for the methyl groups changes drastically around the transition temperature. The shorter $T_1$ component has also an anomaly at this transition, as pointed out above.

In other words, the low barrier height of $\sim 300$ K may be the result of the structural transition (anion ordering). The case of the isostructural compound (TMTSF)$_2$PF$_6$ under pressure is worth comparing with the present results: the motional relaxation of $^1$H in (TMTSF)$_2$PF$_6$ under pressure ($\nu = 45$ MHz) has been found to decay exponentially below 40 K with no particular anomaly around 24 K.

iii) $40$ K < $T$ < $200$ K.

There is another broad peak of relaxation rate around $T \sim 80$ K. The temperature and frequency dependence may be described by those of the $C_1$-term of the equation given before, which is essentially the same as the Bloembergen-Purcell-Pound formula. At temperatures above the peak position, the relaxation rate $T^{-1}_1$ decreases exponentially again. Here $T^{-1}_1$ is simply proportional to $\tau (T^{-1}_1 \propto X v^{-1} \exp(v/T))$. The apparent activation energy $v$ is estimated as $\sim 750$ K.

According to the calculation of $\tau^{-1}$ by Clough et al. [19], we found that the corresponding barrier height is about 900-1 000 K. However the agreement between the calculation and the experimental data is only qualitative. This may suggest the possibility that this relaxation peak is due to another type of molecular motion.

McBrierty et al. [20] presented the data of $^1$H relaxation in this material at temperatures 300 K > $T$ > 80 K. Their results below 200 K are systematically larger by a factor $\approx 2$ than the present ones, but the apparent temperature dependence and the peak values agree well with each other. One of the probable reasons of this discrepancy is that they may have neglected the non-single exponential behaviours of $^1$H-relaxations; hence the data may be some averaged values of shorter and longer components.

iv) $T > 200$ K.

While our measurements are limited below 200 K, McBrierty et al. [20] have shown that the relaxation rate increases again as increasing the temperature above 200 K. We suggest that the electronic contribution becomes dominant again in this temperature region. The relaxation rate can be decomposed into a component $T_{1(e)}^{-1}$ due to the coupling to the conduction electrons and a molecular motion component exhibiting an exponential temperature dependence $T_{1(o)}^{-1} \propto \exp(v/T)$, thus $T^{-1}_1$ becomes:

$$T^{-1}_1 = T_{1(e)}^{-1} + T_{1(o)}^{-1}.$$ (2)

The interpretation of the electronic contribution in equation (2) is not straightforward since in low dimensional conductors only electron forward scatterings ($\Delta q \approx 0$) and backward scatterings ($\Delta q \approx 2k_F$) contribute to the spin lattice relaxation [21, 1]. Therefore $T_{1(e)}^{-1}$ becomes magnetic field dependent when the electron Larmor frequency $\omega_q$ is larger than the electron life time in a plane (2D spin dynamics behaviour, $T^{-1}_1 \propto X \log \omega_q$) or larger than the electron life time on a single chain (1D spin dynamics behaviour, $T^{-1}_1 \propto X_{0}^{-1/2}$). The methyl protons of (TMTSF)$_2$PF$_6$ do show such 3D to 2D spin dynamics cross-over at $H \approx 10$ kOe ($T = 4.2$ K, $P = 6.9$ kbar) [22]. We may expect similar field dependence to exist at high temperature in (TMTSF)$_2$ClO$_4$. In the absence of data at various frequencies we shall assume (very crudely) that both nuclear frequencies 13 or 45 MHz correspond to a low field regime ($\approx 3$D spin dynamics).

The relaxation rate thus reads:

$$(T_1 T)^{-1} = \frac{4 \pi k_v}{(\mu \mu_s)^2 h} \chi_k^2 \alpha_H^2 K$$ (3)

where $\chi_k$ and $\alpha_H$ are the spin susceptibility and the proton hyperfine coupling constant respectively. $K$ in equation (3) is an enhancement factor which contains contributions from $q = 0$ and $q = 2k_F$ scatterings [21]:

$$K = K_{2k_F} + \frac{1}{\tau_{1}} K_0$$ (4)

where $\tau_{1}$ is the electron hopping frequency between ($a$-$b$) planes, and $\tau_{1}$ is the intrachain electron scattering time ($\tau_{1} \approx 3 \times 10^{-15}$ s at room temperature) [23].

By using the measured values $(T_1 T)^{-1} \sim 4 \times 10^{-3} \text{s}^{-1} \text{K}^{-1}$ and $\chi_k \sim 2.4 \times 10^{-4}$ emu/mol [12] at 300 K we derive from equation (3) $\alpha_H^2 K \sim 5.6$ (Oe$^2$). We do not know any reliable estimate of $\alpha_H$, but it is generally of the order of 1-2 Oe. Thus the enhancement factor $K$ is $2 \sim 5$. This is significantly smaller than the enhancement observed at low temperature below 15 K. It is also smaller than the room temperature enhan-
cement of the relaxation in TTF-TCNQ or TMTTF-TCNQ (K ~ 20) [21]. This is probably due to the fact that the electron-electron interactions are weaker in the (TMTSF)$_2$X family than in the TTF-TCNQ series.

In conclusion, the single crystal NMR study of (TMTSF)$_2$ClO$_4$ performed on $^{77}$Se and $^1$H nuclei has conclusively established the magnetic character (SDW-state) of the R-state semimetallic ground state stabilized by a large magnetic field. It is also shown that a magnetic state can be stabilized below 3.7 K by frozen-in anion disorder (ClO$_4^-$) when the sample is rapidly cooled below 40 K (Q-state). A remarkable temperature dependent enhancement of $(T_1 T)^{-1}$ is evident in the R-state below 12 K from $^1$H and $^{77}$Se relaxation data in the field domain 3-64 kOe independent of the transverse orientation of the field.

SDW fluctuations close to the high-field induced SDW long range order could be responsible for the low temperature enhancement of the relaxation rate. However this enhancement is still large even when the superconducting ground state is not destroyed by a magnetic field ($H = 3$ kOe). This feature leads us to suggest that superconducting fluctuations may enhance the nuclear spin lattice relaxation rate in a broad temperature region up to 12 K or so. At higher temperature $^1$H relaxation is shown to be strongly dependent on the methyl group dynamics.

Acknowledgments.
We would like to acknowledge fruitfull discussions with F. Creuzet.

References