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Nuclear relaxation in tetramethyltetraselenafulvalene salts (TMTSF)₂X, (X = PF₆, ClO₄)

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Résumé. — Le temps de relaxation des protons des groupements méthyl du (TMTSF)₂ClO₄ est mesuré de 330 à 40 K. On observe que la relaxation nucléaire *via* le couplage hyperfin avec les électrons itinérants est le processus dominant au-dessus de 200 K. Les mêmes considérations s'appliquent à (TMTSF)₂PF₆. A la température de 300 K on peut identifier deux régimes de variation de la relaxation en fonction du champ magnétique : (i) un régime de bas champ (2-25) kOe où $1/T_1$ est indépendant du champ et (ii) un régime de champs supérieurs à 25 kOe où une loi de diffusion unidimensionnelle conduit à des valeurs constantes pour les fréquences de saut suivant les directions *a* et *b*. On conclut que le couplage transverse de (TMTSF)₂X est intermédiaire entre les valeurs précédemment mesurées par RMN pour TTF-TCNQ et HMTSF-TCNQ.

Abstract. — The nuclear spin-lattice relaxation of methyl-protons in (TMTSF)₂ClO₄ is measured *versus* temperature between 330 and 40 K. The relaxation from the hyperfine coupling to the itinerant electrons is found to be dominant above 200 K. Similar conclusions apply to (TMTSF)₂PF₆. At 300 K two regimes of relaxation are identified *versus* magnetic field : (i) a low-field regime (2-25) kOe where $1/T_1$ is field independent and (ii) a field regime above 25 kOe where fitting the data with a 1-D diffusion law leads to consistent values of hopping rates along *a* and *b* directions. By comparison with earlier measurements on TTF-TCNQ and HMTSF-TCNQ it is concluded that the transverse coupling of (TMTSF)₂X is intermediate between that of the two-chain conductors.

1. Introduction.

The discovery of superconductivity in the (TMTSF)₂X series [1] of organic conductors has stimulated an intense investigation of their electronic properties.

However, the main problem which is still under discussion is the question related to the one-dimensional (1-D) character; in particular the impact of 1-D physics in the establishment at low temperature of the different long-range orders (magnetism or superconductivity). As far as superconductivity is concerned the relevant interchain coupling is the single-particle tunnelling coupling $t_{\perp}$. Several authors [2] have pointed out that the band structure anisotropy of the (TMTSF)₂X series is low enough to warrant the applicability of the mean-field approximation

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to the onset of superconductivity and to rule out the existence of 1-D precursor effects at temperatures larger than the 3-D ordering temperature. Alternatively, from the beginning of the existence of organic superconductivity the Orsay group [3] has emphasized that a careful and exhaustive interpretation of all possible experimental data requires the 1-D electron gas model as a starting point. Moreover, Bourbonnais *et al.* [4] have recently explained the behaviour of the nuclear spin-lattice relaxation rate $1/T_1$ of $(\text{TMTSF})_2\text{ClO}_4$ in terms of a quasi 1-D model down to 8 K. Within the context of the discussion about the 1-D character of the $(\text{TMTSF})_2\text{X}$ series any experiment leading to an estimate of $t_\perp$ is therefore of major importance. The determination of $1/T_1$ versus magnetic field represents precisely such an experiment since the existence of a field dependence is related to a low dimensional spin dynamics and allows consequently an estimate of the $t_\perp$ value.

2. Experimental.

Details concerning the preparation and the structure of the $(\text{TMTSF})_2\text{X}$ compounds can be found elsewhere [5]. NMR experiments have been performed on 50-75 mg powdered samples. Various phase-coherent spectrometers operating up to 276 MHz have been used for this study. At all frequencies but 276 MHz $1/T_1$ has been measured using a $\pi - \pi/2$ pulse sequence. At 276 MHz a saturation comb of $\pi/2$ pulses has been used, watching the subsequent recovery of the nuclear magnetization versus time. We have noticed that the recovery follows an exponential law over more than one decade of time at all frequencies.

Two possible sources of relaxation exist for the protons belonging to the CH_3 groups; (i) the methyl-group reorientation and (ii) the modulation of the hyperfine interaction by the electron motion. As already emphasized in early NMR studies of CH_3 groups in tetramethylated molecules [6] the reorientation mechanism is dominant at low temperature, say $T < 200$ or 150 K.

As we were primarily interested in this work by the hyperfine induced relaxation our first task with $(\text{TMTSF})_2\text{ClO}_4$ has consisted in the study of the temperature dependence of $^1\text{H} - 1/T_1$ in order to separate the various relaxation processes. The data of $1/T_1$ temperature dependence obtained at a nuclear Larmor frequency of 26 MHz for $(\text{TMTSF})_2\text{ClO}_4$ between 330 and 40 K are displayed in figure 1. These results are in fairly good agreement with recent measurements of Takahashi *et al.* [7] performed at 13 and 45 MHz. $1/T_1$ exhibits a well-defined maximum at 75 K and a weak shoulder around 55 K. Figures 2 and 3 show the field dependence of $1/T_1$ between 2 and 64 kOe at 300 K for $(\text{TMTSF})_2\text{ClO}_4$ and $(\text{TMTSF})_2\text{PF}_6$. We feel confident that the amplitude of the field dependence which is observed at high fields is clearly beyond the uncertainty of the measurements.

3. Interpretation.

According to figure 1, CH_3 reorientation is the dominant relaxation mechanism below 150 K. Four inequivalent CH_3 sites exist within each TMTSF molecule. However recent solid state high resolution ^{13}C NMR spectra suggest that only two CH_3 sites per molecule exhibit different local environments [8]. Hence, we have decided to fit the raw data of $1/T_1$ versus temperature by a model which takes into account two inequivalent CH_3 sites, using the model proposed by Clough *et al.* [9]. In the relevant temperature domain the relaxation is attributed to the classical reorientation of CH_3 groups in a three-nodal potential (i.e. we neglect quantum effects). $1/T_1$ for each site reads :

$$1/T_1 = C \left\{ \frac{\tau}{1 + \omega_n^2 \tau^2} + \frac{4\tau}{1 + 4\omega_n^2 \tau^2} \right\}, \tau = \tau_0 e^{E/T} \quad (1)$$

where C is a constant and E is the activation energy for the classical rotation.

Fig. 1. — Proton spin-lattice relaxation rate as a function of temperature for $(\text{TMTSF})_2\text{ClO}_4$. The dashed line gives the contribution of each methyl site using equation (1) and the values of table I, the full line the total CH_3 contribution.

Fig. 2. — $(\text{TMTSF})_2\text{ClO}_4$ proton spin-lattice relaxation rate as a function of field. The full curve is the theoretical expression using equation (4) and the values of table II. The dashed line gives the estimated CH_3 contribution at 300 K.

Fig. 3. — (TMTSF)₂PF₆ proton spin-lattice relaxation rate as a function of field. The full curve is a fitted using equation (4).

Table I. — Parameters of the fit of equation (1) to the data of figure 1.

Site	I	II	Units
<i>T</i> (of maximum)	55	74	K
<i>E</i>	345	675	K
<i>C</i>	1.3	2.3	10 ⁹ /s ²
τ_0	7.3	0.43	10 ⁻¹² s

Both CH₃ sites have been fitted in figure 1 using the parameters listed in table I. The excess of relaxation which is observed below 45 K may be related to the CH₃ quantum tunnelling. Above 200 K the hyperfine relaxation is clearly dominant. At room temperature the relaxation induced by the CH₃ reorientation amounts to $1/T_1 = 0.2 \text{ s}^{-1}$ (this is only 20 % of the total relaxation rate and it is field independent as long as $\omega_n \tau \ll 1$, i.e. up to 10³ kOe or so). As far as (TMTSF)₂PF₆ is concerned we find similarly according to the data of Scott *et al.* [10] a CH₃ reorientation contribution of 0.2-0.3 s⁻¹ at room temperature. The preliminary study of the $1/T_1$ temperature dependence enables us to attribute the field dependence of $1/T_1$ which is observed below 64 kOe to the hyperfine relaxation.

4. Discussion.

The spin-lattice relaxation produced by the contact hyperfine interaction is given in terms of the imaginary part of the dynamic electron susceptibility by [11] :

$$(T_1 T)^{-1} = \frac{2 k_B a^2}{\hbar^2} \sum_{\mathbf{q}} \frac{\chi''_{\perp}(\mathbf{q}, \omega_n)}{\omega_n} \tag{2}$$

where *a* is the hyperfine coupling constant, supposed to be *q*-independent.

In the case of a Q -1-D electron gas the q -summation in equation (2) is restricted to $\mathbf{q}$ -vectors close to $|\mathbf{q}| = 0$ and $|\mathbf{q}| = 2k_F$ [1]. For electrons with finite intra-chain scattering time τ_v and inverse Larmor frequency ω_e^{-1} such as $\omega_e^{-1} \gg \tau_v$ the SDW excitations of small $\mathbf{q}$ components become diffusive [12], hence

$$\frac{\chi''(\mathbf{q}, \omega)}{\omega} = \chi_s \frac{Dq^2}{(Dq^2)^2 + \omega^2} \quad (3)$$

where χ_s and D are the spin susceptibility and the diffusion constant respectively. According to equations (2) and (3) the $q \approx 0$ components lead to a field dependent $1/T_1$, namely $(T_1 T)^{-1} \propto H_0^{-1/2}$ [13, 14].

This remarkable behaviour is due to the well known slow decay ($\propto t^{-1/2}$) of the spin autocorrelation function at long times for 1-D spin dynamics. The influence of 1-D diffusion is not important for the $2k_F$ components since $2k_F$ is larger than the inverse mean-free path. On the other hand these components are likely to be enhanced by the $2k_F$ divergence of the SDW response function. The 1-D behaviour, $1/T_1 \propto H_0^{-1/2}$ holds as long as the relation $\omega_e \tau_\perp > 1$ is satisfied, $\tau_\perp$ being the life time of an electron on a given chain. Going to low fields, a cross-over towards a spin dynamic of larger dimensionality is observed when $\omega_e \tau_\perp \approx 1$. The relaxation rate can thus be written in terms of a three parameter law as follows [13] :

$$(T_1 T)^{-1} = C_1 g(\omega_e) + C_2 \quad (4)$$

where

$$g(\omega) = \left\{ \frac{1 + (1 + \omega^2 \tau_\perp^2)^{1/2}}{2(1 + \omega^2 \tau_\perp^2)} \right\}^{1/2}$$

$$C_1 = (2S)^{-1} \chi_s^2 a^2 (\tau_\perp / \tau_v)^{1/2} K_0, \quad C_2 = (2S)^{-1} \chi_s^2 a^2 K_{2k_F}$$

and $2S = (g\mu_B)^2 \hbar / 2 \pi k_B$.

K_0 and K_{2k_F} are the enhancement factors of the $q = 0, 2k_F$ response functions.

Fitting the (TMTSF)₂ClO₄ data by the relation (4) leads to the theoretical curve shown in figure 2 using the set of parameters listed in table II.

Table II. — Parameters of the fit of equation (4) to the data of figure 2.

$C_1 + C_2 = 3.67 \pm 0.07$	$/10^{-3} \text{ s}^{-1} \text{ K}^{-1}$
$C_2 = 1.1 \pm 0.5$	$/10^{-3} \text{ s}^{-1} \text{ K}^{-1}$
$\tau_\perp = 1.3 \pm 0.3$	$/10^{-12} \text{ s}$

A similar set of parameters is derived from the (TMTSF)₂PF₆ data. Equation (4) implies a 1-D diffusion as long as $\omega_e \tau_\perp > 1$ is satisfied. It is therefore important to check that the parameters of table II allow such an interpretation. In the 1-D regime, the relation $D_a > \omega_e > D_b$ must be satisfied [14] where $D_{a(b)}$ are the spin diffusion rates along the $a(b)$ directions. D_a is derived from the knowledge of C_1 by the following relation

$$D_a = [k_B / \hbar a^2 \chi_s / C_1]^2 \tau_\perp. \quad (5)$$

The hyperfine coupling constant of the methyl-protons in TMTSF is not known, but TTF-TCNQ(D₄), TMTTF-TCNQ(D₄) relaxation data [13] and the recent analysis of the TTF-TCNQ susceptibility [15] lead to an estimate of D_a relative to the diffusion rate in the TTF-

chain of TTF-TCNQ. Thus we get $D_a = 2 \times 10^{13} \text{ s}^{-1}$. D_b can then be derived from the conductivity anisotropy, since the relation $D_a/D_b = \sigma_a/\sigma_b$ holds in the transverse-diffusive regime of the conductivity [13]. With σ_a/σ_b in the range of 25-100 [1], one gets $D_b < 0.8 \times 10^{+12} \text{ s}^{-1}$, which is in fair agreement with the value of $1/\tau_\perp$ from table II. At $H_0 = 45 \text{ kOe}$, $\omega_e = 0.8 \times 10^{12} \text{ s}^{-1}$. Thus, we feel confident that a 1-D spin diffusion is an appropriate description for the range of magnetic fields in which $1/T_1$ has been found field dependent at room temperature. Consequently, the escape time ($\omega_e \tau_\perp \approx 1$) is limited by the hopping of an electron off a given chain along the direction of intermediate coupling (i.e. the b -axis). The transverse hopping rate is thus related to $t_\perp^b$ as follows [13] :

$$1/\tau_\perp \approx |t_\perp^b|^2 \tau_v. \quad (6)$$

The derived escape time is shorter for $(\text{TMTSF})_2\text{X}$ (see Table I) than those measured in both $\text{TMTTF-TCNQ}(\text{D}_4)$, ($\tau_\perp \approx 4.4 \times 10^{-12} \text{ s}$) and $\text{TTF-TCNQ}(\text{D}_4)$, ($\tau_\perp \approx 8 \times 10^{-12} \text{ s}$) [13]. This fact is not surprising on account of the significant Se...Se interchain coupling which characterizes the $(\text{TMTSF})_2\text{X}$ structure [16, 17].

The present NMR study, together with those performed in TTF-TCNQ [13] and HMTSF-TCNQ [18] hint that the transverse coupling of $(\text{TMTSF})_2\text{X}$ is probably intermediate between those of TTF-TCNQ and HMTSF-TCNQ. No field dependence of $1/T_1$ has been detected up to 60 kOe in the latter compound [18]. From the NMR data alone, we cannot tell much about the absolute value of the transverse coupling. A rough estimate can be derived from a comparison with TTF-TCNQ data [13]. Assuming similar τ_v for $(\text{TMTSF})_2\text{ClO}_4$ and TTF-TCNQ we obtain from equation (6) and the data of reference [19]

$$(t_\perp^b)_{\text{TMTSF}} \approx 2.5 (t_\perp)_{\text{TTF}} \quad \text{and} \quad (t_\perp^b)_{\text{TMTSF}} \approx 10\text{-}15 \text{ meV}.$$

Such a value for $t_\perp^b$ is admittedly smaller than the computation of the mean effective transfer integral ($t_1 = 23 \text{ meV}$) for the $(\text{TMTSF})_2\text{X}$ series [20] but it is within the range acceptable of conductivity anisotropy data [1].

5. Conclusion.

We have shown in the present study that the nuclear spin-lattice relaxation in $(\text{TMTSF})_2\text{ClO}_4$ and $(\text{TMTSF})_2\text{PF}_6$ above 250 K is dominated by the 1-D diffusion of the spins along the molecular stacking axis. As far as the transverse tunnelling coupling is concerned $(\text{TMTSF})_2\text{X}$ compounds lie in between TTF-TCNQ and HMTSF-TCNQ.

An other important question is to understand how the field dependence of $1/T_1$ is affected by the dramatic increase of the longitudinal conductivity (by a factor $\approx 10^3$) at 4.2 K. A field dependence of $1/T_1$ for various nuclei (^1H , ^{77}Se , ^{13}C) has been reported in the vicinity of the helium temperature in $(\text{TMTSF})_2\text{PF}_6$ at 6.9 kbar [21]. Undoubtedly such a field dependence observed with nuclei of very different gyromagnetic ratios must be related to some special properties of the electron gas. Azevedo [21] has fitted the field dependence above 20 kOe to a $\log \omega_e^{-1}$ law, suggesting a 2-D diffusion of the carriers in the $(a-b)$ planes. The recent measurements of Bourbonnais *et al.* [4] are in agreement with those of Azevedo [21] but they show that the field dependence is restricted at low temperature to the temperature domain 4 to 20 K. Bourbonnais *et al.* [4] have attributed the decrease of $1/T_1$ at high fields to a field induced reduction of the $2 k_F$ -SDW response function. The thorough interpretation of the field dependence of $1/T_1$ in the conducting state at low temperature requires more complete studies at various temperatures between 4.2 and 300 K which are now under completion with ^{13}C enriched $(\text{TMTSF})_2\text{X}$ samples.

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