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High-resolution NMR in bistetramethyltetraselenafulvalenium salts [$(TMTSF)_2X$, $X = ClO_4$, ReO_4, and PF_6]

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The resonance position and spin-lattice relaxation rate of well-resolved ^{13}C sites of the tetramethyltetraselenafulvalene (TMTSF) molecule in the organic conductors $(TMTSF)_2ClO_4$, $(TMTSF)_2ReO_4$, and $(TMTSF)_2PF_6$ have been measured as a function of temperature between 340 and 220 K. Comparison with neutral TMTSF and the use of Korringa's law has permitted determination of the electronic contribution to the relaxation rate and the resonance position. A change in slope in the resonance position as a function of temperature is an indication of a possible redistribution of the spin density over the molecule.

I. INTRODUCTION

Organic conductors—for example, salts of the $(TMTSF)_2X$ series (TMTSF is tetramethyltetraselenafulvalene)—are very anisotropic in reciprocal space: they are (quasi-) one-dimensional (1D) conductors, and very heterogeneous in direct space. The density of conduction electrons varies strongly from site to site. For the understanding of these materials it is of fundamental interest to know the behavior of the conduction electrons in real space. Previous studies[1-3] have shown that high-resolution nuclear magnetic resonance (NMR), in the solid state is a very powerful tool to study the local properties of the electron gas. However, a major problem that arises with this technique is that it is often difficult to separate the different contributions to the spin-lattice relaxation rate ($1/T_1$) and position of the NMR resonance (δ). The reonance position, for instance, is the sum of two contributions: the chemical shift (δ_0), which finds its origin in the local chemical environment, and the Knight shift (K), which depends on the local density of conduction electrons.

The physical properties of the organic conductors depend strongly on their structure. The structure of the $(TMTSF)_2X$ salts[4] is shown in Fig. 1. The organic molecules form stacks in the a direction, which form planes in the b direction; these planes are separated from each other by planes of anions in the c direction. Inspection of the structure indicates that the conduction-electron density should be very inhomogeneous over the molecule. We expect that the inner carbon atoms (that is, the carbon atoms labeled 1,2,3,4,5) should have the largest density of conduction electrons, and indeed, this is in agreement with the calculations of Metzger.[5]

We present in this paper the first systematic study of the metallic state of $(TMTSF)_2ClO_4$, $(TMTSF)_2ReO_4$, and $(TMTSF)_2PF_6$ using high-resolution NMR in the solid state. These three salts were chosen as they—although isostructural at high temperatures—are very different at low temperatures. The CLO_4^- salt becomes superconducting at ambient pressure, whereas in the PF_6^- salt superconductivity is only established for pressures higher then ~10 kbar; the transition temperature for both materials is close to 1 K. The latter showing a spin-density wave (SDW) ground state at ambient pressure below 10 K or so. On the other hand, $(TMTSF)_2ReO_4$ does not exhibit any of the usual 1D ground states, but shows a metal-semiconductor transition around 182 K instead, due to the structural ordering of the anions.[6]

We have determined the ^{13}C resonance position of the corner and methyl-group carbon atoms (the center carbon atoms are not easily observable with the present technique, and will not be discussed in this paper) as a function of temperature between 340 and 220 K. We have measured ^{13}C spin-lattice relaxation times in the same range of temperatures.

II. EXPERIMENTAL TECHNIQUES AND EQUIPMENT

TMTSF,[7] $(TMTSF)_2ClO_4$, $(TMTSF)_2ReO_4$, and $(TMTSF)_2PF_6$ (Ref. 8) were obtained by the usual procedures. The experiments were carried out on powdered samples (40–80 mg) using Bruker CXP spectrometers, operating at 50.3 or 75.4 MHz.

Magic-angle spinning (MAS) at a frequency larger than 2 kHz, cross polarization (CP), and proton decoupling were necessary to achieve good sensitivity and high resolution. Chemical shifts were determined with respect to TMS (tetramethylsilane) via adamantane as a secondary reference.

FIG. 1. High-temperature structure of $(TMTSF)_2X$ salts.

Variable-temperature measurements were carried out by passing a flow of chilled nitrogen gas through the NMR probe. Stability of the temperature was estimated to be better than 0.5 K during the accumulation of one spectrum ($\sim \frac{1}{2}$ h) and better than 1 K during a T_1 measurement ($\sim 5-12$ h).

Handling of the rotors, which consist of an alumina container and a Kel-F cap, was problematic. The cap wears out during thermal cycling, resulting in its separation from the container and often in the "explosion" of the container and subsequent loss of the sample. The samples of $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ were lost in this way.

The pulse sequences used to determine the different relaxation rates have been discussed elsewhere.[2] It should be stressed that, unless otherwise stated, no proton decoupling occurs during an evolution period.

III. RESULTS

A. Neutral TMTSF

In order to investigate the effect of delocalization of the conduction electrons on the NMR properties we first focus our attention on the neutral TMTSF molecule, which forms the basis for the conducting salts.

1. Identification

The different resonances (see Fig. 2) can be attributed to the different sites considering the relative intensities and relaxation rates,[2,3,9] this will be discussed in some more detail below. The line at 100 ppm is thus attributed to the center carbon atom, the doublet around 130 ppm to the corner carbon atoms, and the line at 18 ppm to the methyl-group carbon atoms.

2. Chemical shift

The NMR spectra of neutral TMTSF in a solution of $CHCl_3$ and in the crystalline state are given in Fig. 2. The spectra show, respectively, 3 and 5 lines; the line at 18 ppm showing a small but significant splitting at lower temperature and higher magnetic field. Unmarked lines are spinning sidebands; the envelope of the spinning sidebands reproduces the powder spectrum (with proton decoupling) for each site.

In solution there exists only three different types of carbon atoms: two methyl-group carbon atoms (M), two corner carbon atoms (Co), and one center carbon atom (Ce). We therefore expect three lines in the NMR spectra with relative intensities 2:2:1; in agreement with the spectra shown in Fig. 2. Solid TMTSF crystalizes in space group $P_{\bar{1}}$ (Ref. 10) with one molecule per unit cell. The crystal symmetry (inversion with respect to the origin) increases the number of different carbon sites to five. In Fig. 3 we show the temperature dependence of the chemical shift of these carbon sites. This temperature dependence is negligible for all but the corner carbon atoms; the parameters of a least-squares fit to a linear function of temperature are given in Table I.

3. Relaxation times ($T_1, T_{1\rho}, T_2$)

We have measured the different relaxation times at ambient temperature; the results are given in Table II. The spin-lattice relaxation for the methyl-group carbon atoms could not be described by a single exponential, and the T_1 given is a mean value. We have not measured the proton relaxation time direction, but it could be estimated as $T_1(^1H) \sim 15$ s; this is in reasonable agreement with the methyl-group contribution to $T_1(^1H)$ in the metallic salt, which amounts to ~ 3 s.[11]

The spin-spin relaxation time (T_2) and the relaxation time in the rotating frame ($T_{1\rho}$) are of the same order of magnitude in the metallic salts and in neutral TMTSF. However, the spin-lattice relaxation time is an order of magnitude smaller in the metallic state. This is explained by the fact that T_2 and $T_{1\rho}$ are mainly determined by slow molecular motions (rotation of the methyl groups in our case) which are not an effective source of relaxation at the T_1 time scale. All relaxation times in the neutral molecule increase with the distance between the considered site and the methyl groups, as expected. In the metallic salt T_1 increases with the distance to the center

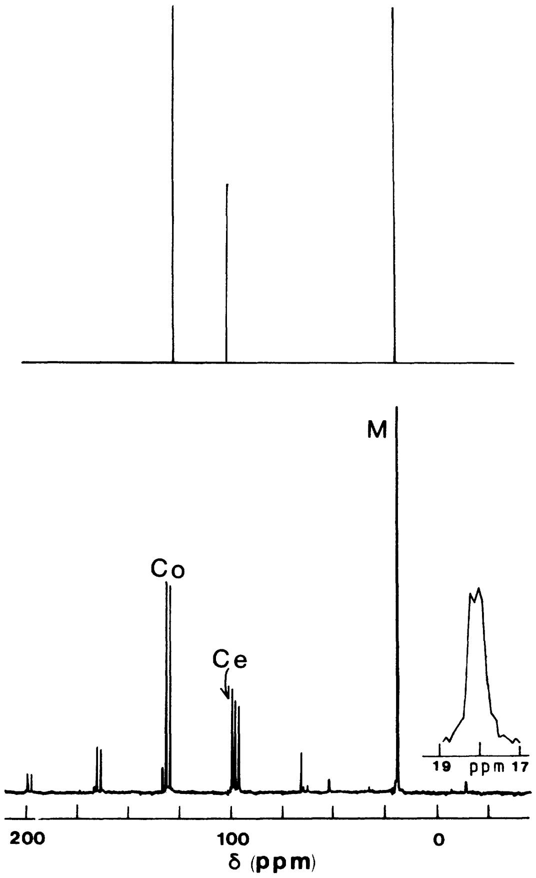

FIG. 2. NMR spectra of neutral TMTSF, both in solution (top, $f = 50.3$ MHz ambient temperature), and in the solid state (below, $f = 75.4$ MHz ambient temperature). The inset shows the line at 18 ppm at $T = 210$ K. Unmarked lines are spinning side bands, the envelope of these spinning sidebands reproduces the powder line shape for each site.

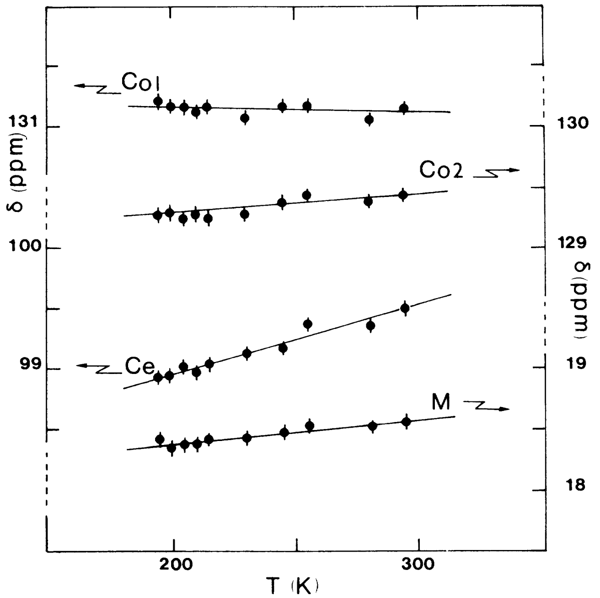

FIG. 3. Temperature dependence of the chemical shift (δ) of the TMTSF carbon atoms; this temperature dependence is extremely small in comparison with those in the metallic salt (see Fig. 5).

of the molecule, and the dominant contribution to $1/T_1$ is thus provided by the interactions with the conduction electrons.

B. The metallic state at ambient temperature

1. Spectra

The NMR spectra of $(TMTSF)_2ClO_4$, $(TMTSF)_2ReO_4$, and $(TMTSF)_2PF_6$ are given in Fig. 4. The differences between these spectra are rather small. These salts have the same overall structure, and therefore the $\mathbf{q}=\mathbf{0}$ component of the susceptibility should be more or less independent of the anion, as should be the quantities—such as the conductivity and the resonance position—which depend on this part of the susceptibility.

There are two organic molecules per unit cell, but the symmetry reduces the number of crystallographically different carbon sites to ten and therefore we expect two quartets and one doublet in each spectrum. Considering relaxation times and multiplicity, we attribute the group of four lines at 0 ppm to the methyl groups, the group of four resonances at 150 ppm to the corner carbon atoms, and the lines at 250 and 300 ppm to the center carbon atoms.

TABLE I. Derivative of the chemical shift with respect to the temperature (A, $\pm 1.0\times 10^{-3}$ ppm/K) and extrapolation of the chemical shift to $T=0$ K (B, ± 0.2 ppm).

Site	Ce	Co1	Co2	M	Units
A	5.9	−0.5	1.4	2.1	10^{-3} ppm/K
B	97.5	131.3	129.0	18.0	ppm

TABLE II. Spin-lattice relaxation time (T_1), relaxation time in the rotating frame ($T_{1\rho}$) and spin-spin relaxation time (T_2) for the carbon atoms in neutral TMTSF (ambient temperature, $f=50.3$ MHz).

Site	T_1 (s)	$T_{1\rho}$ (ms)	T_2 (ms)
Ce	146±40	220±50	1.50±0.50
Co1	182±55	70±15	0.22±0.02
Co2	184±50	70±15	0.22±0.02
M	35±5	8±2	0.11±0.02

2. Spin-spin relaxation time

The spin-spin relaxation time in these materials is determined by the dipolar coupling with the protons. The T_2 of the methyl groups is site independent and amounts to 60±5 μs in $(TMTSF)_2PF_6$ and

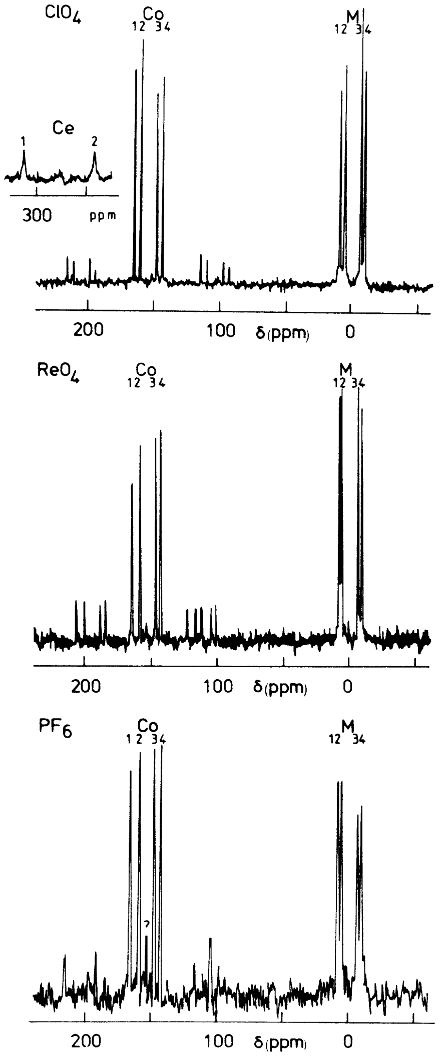

FIG. 4. Spectra of $(TMTSF)_2ClO_4$, $(TMTSF)_2ReO_4$, and $(TMTSF)_2PF_6$ at ambient temperature ($f=50.3$ MHz). Two different systems for numbering the carbon atoms are used: the first is based on the crystal structure (Fig. 1), C1 to C5 and C11 to C15, the second on the spectra Ce1 to Ce2, Co1 to Co4, and M1 to M4.

$(TMTSF)_2ClO_4$, and to 95±10 μs in $(TMTSF)_2ReO_4$. With proton decoupling during the variable delay, T_2 increases to over 5000 μs. No relaxation effects due to coupling with the fluorine atoms could be detected in $(TMTSF)_2PF_6$: T_2 of this salt was, even with proton decoupling, not significantly different from T_2 in the other salts.

3. *Spin-lattice relaxation time*

The spin-lattice relaxation times for the corner and methyl-group carbon atoms are given in Table III. For the corner carbon atoms, T_1 varies by a factor of 2 over the different sites, but is almost independent of the anion. For the methyl-group carbon atoms, T_1 is independent of both the site and the salt. Our results for $(TMTSF)_2ClO_4$ reproduce those previously published[2] in global behavior over the molecule, but not in absolute value.

C. The metallic state, variable temperature

1. *Resonance position*

The resonance position of the corner and methyl-group carbon atoms in $(TMTSF)_2PF_6$ and $(TMTSF)_2ReO_4$ is given as a function of temperature between 340 and 220 K in Fig. 5. The variation of the resonance position with temperature exhibits a gradual change in slope (Table IV) around different temperatures for the different sites. The effect on the methyl-group carbon atoms is less pronounced than on the corner carbon atoms. Despite this change in slope, the linewidths remain constant, and therefore the effect is homogeneous over the entire sample. Furthermore, the change in slope cannot be explained as an artifact of the experimental technique.

A similar behavior of the resonance position has been observed for the corner carbon atoms of the TTF molecule in ^{13}C-enriched tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) by Takahashi *et al.*[12]

In $(TMTSF)_2PF_6$ we observe a, as yet unidentified, line with a very strong temperature dependence close to 150 ppm.

2. *Relaxation time*

The spin-lattice relaxation time has been measured over the same temperature range as the resonance position.

TABLE III. ^{13}C spin-lattice relaxation time [T_1 (s)] at ambient temperature and at $f=50.3$ MHz.

Site	ClO_4	T_1 (s) ReO_4	PF_6
Co1	0.53±0.05	0.38±0.09	0.53±0.07
Co2	0.62±0.05	0.59±0.09	0.70±0.09
Co3	0.81±0.08	0.59±0.09	0.77±0.09
Co4	0.93±0.10	0.85±0.10	1.01±0.10
M1	4.4±0.4	3.2±0.5	
M2	3.6±0.3	3.8±0.5	
M3	3.5±0.3	3.4±0.4	
M4	4.1±0.3	2.6±0.3	

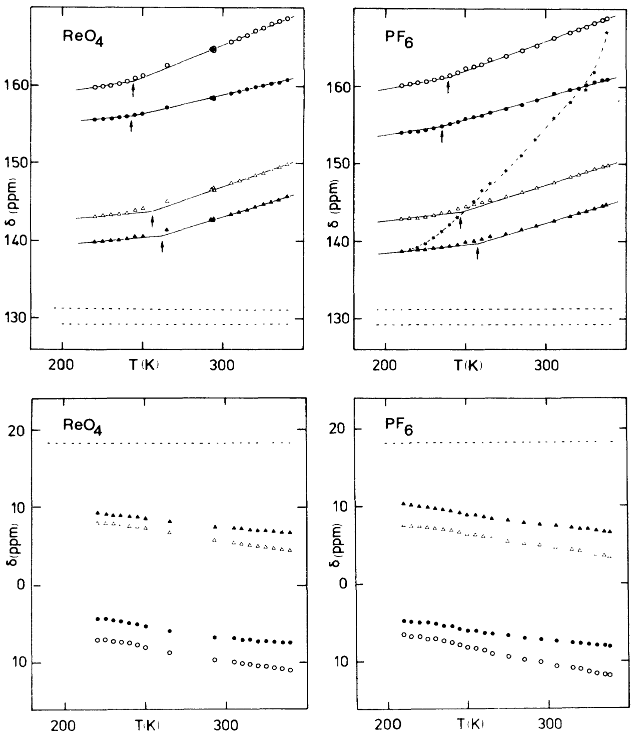

FIG. 5. Resonance position of the corner (top) and methyl-group carbon atoms (bottom) in $(TMTSF)_2ReO_4$ (left) and $(TMTSF)_2PF_6$ (right) as a function of temperature. In $(TMTSF)_2PF_6$ an unidentified line with a strong temperature dependence is observed. The dashed lines give the temperature dependence of the equivalent sites in neutral TMTSF.

The T_1 measurements were optimized for the corner carbon atoms and the accuracy for the methyl-group carbon atoms is therefore limited. However, the measurements indicate that T_1 for the methyl groups decreases with increasing temperature: an indication that this T_1 is mainly determined by methyl-group rotation.[11]

IV. DISCUSSION

A. Frequency dependence

The spin-lattice relaxation rate in low-dimensional conductors is frequency dependent, due to the finite lifetime of an electron on a given chain (τ_b) or plane (τ_c). When the electronic Larmor frequency (ω_e) is short with respect to the interplane hopping rate, we expect a three-

TABLE IV. Slope (A) of the ^{13}C resonance position vs temperature (T) in $(TMTSF)_2ReO_4$ and $(TMTSF)_2PF_6$.

	A (10^{-3} ppm/K)			
	$T<240$ K		$T>290$ K	
Site	ReO_4	PF_6	ReO_4	PF_6
Co1	32±4	38±3	84±2	76±2
Co2	19±4	29±3	49±2	59±2
Co3	17±4	22±2	72±2	67±2
Co4	19±4	19±2	64±2	64±2

dimensional (3D) behavior of the relaxation rate and when the frequency is large with respect to the interchain hopping rate a 1D behavior. The crossover between the different regimes will occur when $\omega_e \tau_b \approx 1$ and $\omega_e \tau_c \approx 1$, respectively.

The spin-lattice relaxation rate is related to the imaginary part of the spin susceptibility (χ'') through[13]

$$\frac{1}{T_1} = \frac{2\gamma_n^2}{\hbar\omega_n} \sum_{\mathbf{q}} | A_{\mathbf{q}} |^2 \chi''(\mathbf{q},\omega_n) \ ,$$

where $A_{\mathbf{q}}$ is the hyperfine coupling constant, generally assumed independent of $\mathbf{q}$ ($A_{\mathbf{q}} = A$), and ω_n is the nuclear Larmor frequency. The spin susceptibility in (quasi-) 1D materials is principally determined by its components at $\mathbf{q}=0$ and $\mathbf{q}=2\mathbf{k}_F$. The component at $\mathbf{q}=2\mathbf{k}_F$ is less important at ambient temperature, but becomes dominant below ~ 30 K.[14,15] For the values of $\mathbf{q}$ such that $|\mathbf{q}| \ll 1/L$, with L the mean-free path, $\chi(\mathbf{q},\omega_n)$ becomes diffusive;[16] i.e.,

$$\chi(\mathbf{q},\omega_n) = \chi_s \frac{\sum_j D_j q_j^2}{\sum_j D_j q_j^2 - i\omega} \ , \tag{1}$$

where D_j is the spin-diffusion constant in the j direction and χ_s is the Pauli susceptibility. The relaxation rate becomes frequency dependent, and can be written as

$$\frac{1}{T_1 T} = C_1 f(\omega) + C_2 \ ,$$

where C_1 and C_2 describe the interactions, but are frequency independent, and $f(\omega)$ describes the frequency dependence (see below). This function was derived by Soda *et al.*[17] neglecting the transverse anisotropies: i.e., assuming $D_a, \omega_e \gg D_b, D_c$. This approach is not very satisfactory as only a 3D-1D crossover can be described in this way. We have expanded expression (1) to a more general case; assuming $D_a \gg \omega_e, D_b, D_c$ and an orthogonal crystal, we obtained $[f(\omega) = F(\omega)/F(0)]$

$$F(\omega) = \frac{abc}{(D_a D_b D_c)^{1/2}} \frac{1}{2\pi} \left[z \ln \left[\frac{y^2 + R^2 + \sqrt{2} y (r^2 + R^2)^{1/2}}{y^2 + R^2 - \sqrt{2} y (r^2 + R^2)^{1/2}} \right] + y \ln \left[\frac{z^2 + R^2 + \sqrt{2} z (r^2 + R^2)^{1/2}}{z^2 + R^2 - \sqrt{2} z (r^2 + R^2)^{1/2}} \right] \right.$$
$$\left. - \left[\frac{\omega}{2} \right]^{1/2} \ln \left[\frac{y^2 z^2 + R^2 + \sqrt{2\omega} yz (\omega + R^2)^{1/2}}{y^2 z^2 + R^2 - \sqrt{2\omega} yz (\omega + R^2)^{1/2}} \right] - \sqrt{2\omega} \arctan \left[\frac{yz\sqrt{2\omega}(-\omega + R^2)^{1/2}}{\omega R^2 - y^2 z^2} \right] \right] ,$$

where $y^2 = \pi^2 D_b / b^2$, $z^2 = \pi^2 D_c / c^2$, $r^2 = y^2 + z^2$, and $R^4 = r^4 + \omega^2$. The arctangent gives an angle between 0 and π radians. Note that this expression reproduces the limiting cases: (i) the expression of Soda *et al.*[17] when $\omega_e \gg D_b, D_c$; (ii) the expressions of Devreux *et al.*[18] in the 1D, 2D, or 3D limit. (iii) the expression of Ehrenfreund and Ron[19] in the limit $D_b \gg \omega_e, D_c$.

It is possible to introduce a unique transverse escape time ($\tau_\perp$), as defined by Soda *et al.* For anisotropies of the transverse conductivity, which are currently found in (TMTSF)$_2X$ salts [$\sigma_b / \sigma_c \sim 30$ (Ref. 20)], we find $\tau_\perp \approx D_b / b^2$. The crossover frequency is proportional to $1/\tau_b \sim \sigma_b$. Reanalyzing the ^{1}H data of Stein *et al.*[21] we find $\tau_\perp = 0.4 \times 10^{-12}$ s (instead of 1.3×10^{-12} s) and $t_\parallel = 26$ meV (instead of 13 meV, see Table V). This new value of $t_\parallel$ is much closer to the value given by Grant[22] (25 meV).

B. Korringa's law

As long as in a conductor the relaxation rate and the Knight shift find their origin in the same interaction, there exists a relationship (called Korringa's law) between the two.[23]

$$K^2 T_1 T = k_K = \frac{\hbar}{4\pi k_B} \left[\frac{\gamma_e}{\gamma_n} \right]^2 ,$$

where k_K is Korringa's constant for the considered nucleus (3.96×10^{-6} K s for ^{13}C) and γ_e and γ_n are, respectively, the electronic and nuclear gyromagnetic ratios ($\gamma_e = g\mu_B / \hbar = 17.6 \times 10^6$ s^{-1}G^{-1} and $\gamma_n = 6.73 \times 10^3$ s^{-1}G^{-1} for ^{13}C). Deviations from Korringa's constant are usually expressed through the Korringa enhancement factor (η) defined as

$$\eta = \frac{k_K}{(K^2 T_1 T)_{\text{expt}}} = \frac{k_K}{K^2} [C_1 f(\omega_e) + C_2] \ .$$

The theoretical expression for η in terms of electronic pa-

TABLE V. Parameters of the TTF chain in TTF-TCNQ and of (TMTSF)$_2X$ at ambient temperature; the temperature dependence of the relevant parameters can be found in the given references.

Parameter	TTF-TCNQ	(TMTSF)$_2X$	Units
χ_s	0.21[a]	0.1[b]	10^{-3} emu/mol
C_2	16.4[c]	0.4–0.7[d]	10^{-3} (K s)$^{-1}$
$F(2k_F)$	38[a]		
T_F		3000[e]	K
$\tau_\parallel$	2.3,[f] 3[g]	3[g]	10^{-15} s
$\tau_\perp$	8[c]	0.4[i]	10^{-12} s
t_a		0.4[e]	eV
t_b		25,[e] 27	meV
U		0.5–0.6	eV

[a] Reference 12.
[b] Reference 26.
[c] Reference 17.
[d] Reference 21.
[e] Reference 22.
[f] Reference 33.
[g] Reference 8.
[h] Reference 34.
[i] Reference 9.

rameters is rather complicated; taking into account the dipolar contributions (D, through $\epsilon = D^2/A^2$) to the hyperfine interactions and dimensionality effects, we find for a (quasi-) 1D conductor.[12,17,24]

$$\eta = K(0)[\tfrac{3}{5}\epsilon f(\omega_n) + (1+\tfrac{7}{5}\epsilon) f(\omega_e)] + K(2k_F) , \qquad (2)$$

where

$$K(0) = \tfrac{1}{2}\left[\frac{\tau_\perp}{\tau_\parallel}\right]^{1/2}(1-\alpha)$$

and

$$K(2k_F) = \tfrac{1}{2}(1+2\epsilon)\left[\frac{1-\alpha}{1-\alpha F_L(2k_F)}\right]^2 ,$$

$$F_L(2k_F) = \tfrac{1}{2}\ln\left[4.56\frac{T_F}{T}\right] .$$

The function $f(\omega)$ describes the frequency dependence [$f(\omega) = F(\omega)/F(0)$; $f(\omega_n) \approx 1$ at the experimental frequency], F_L is the Lindhard function evaluated here at $\mathbf{q} = 2\mathbf{k}_F$, T_F the Fermi temperature (Grant[22] gives $T_F \sim 3000$ K), and $\alpha = U/4t_\parallel$ (i.e., the Coulomb interactions of the Hubbard Hamiltonian over the bandwidth). The expression for η does contain only one site-dependent parameter, ϵ; therefore η should—contrary to our previous results[2,3]—not vary much over the molecule. Most of the parameters of expression (2) can be estimated as a function of temperature.

The temperature dependence of the transverse hopping rate (τ_b or $\tau_\perp$) and the electron lifetime ($\tau_\parallel$) can be derived from the conductivities as

$$\tau_\perp \sim 1/\sigma_\perp , \quad \tau_\parallel \sim \sigma_\parallel .$$

Using the resistivity measurements of Forrŏ *et al.*[25] we find

$$\frac{\sigma_\perp(200\text{ K})}{\sigma_\perp(300\text{ K})} \sim 1.13 , \quad \frac{\sigma_\parallel(200\text{ K})}{\sigma_\parallel(300\text{ K})} \sim 1.58 .$$

Notice that the transverse conductivity, and thus the transvrese hopping rate, is largely temperature independent, implying that $f(\omega_e)$ is temperature independent: $f(\omega_e;T) \approx f(\omega) \approx 0.67$.

The dipolar contribution to the hyperfine coupling in the metallic state should vary with temperature as the isotropic contribution, and therefore ϵ should be more or less temperature independent.

The temperature dependence of α is more difficult to obtain. However, we can obtain an estimation by comparing the ^{1}H data on TTF-TCNQ (Refs. 12 and 17) with those on (TMTSF)$_2X$ (Ref. 21). C_2 varies as

$$C_2 \sim K^2 K(2K_F) \sim (A_{\rm H}\chi_s)^2 K(2k_F) ,$$

where we supposed $\epsilon \ll 1$. Using $(A_{\rm H})_{\rm TTF}/(A_{\rm H})_{\rm TMTSF} \approx \frac{1}{2}$ (Ref. 21) and the parameters given in Table V we can calculate α as a function of temperature and ϵ. Depending on the exact value of C_2 (subtracting methyl-group contributions from the total relaxation rate is not straightforward[11]) and the exact value of ϵ we find $\alpha \approx 0.39-0.47$ at $T = 300$ K; the decrease with temperature is small, of the order of 10%. For η we find $\eta \approx 22-34$ at $T = 300$ K, the variation with temperature being also in the order of 10%. The temperature dependence of η is thus equal to, or less then, the experimental errors.

This value of α gives the following values of U [$t_a \approx 0.4$ eV (Ref. 22)]: $U \sim 0.5-0.6$ eV.

C. Knight shift

The origin of the Knight shift lies in the hyperfine coupling of the nuclear spin to the conduction electrons. The Knight shift is thus proportional to the local spin density (ρ_j); one finds[23]

$$K_j = \chi_s \frac{A_j \rho_j}{\hbar \gamma_e \gamma_n}$$

where the index j denotes the site. The isotropic part of the hyperfine coupling (A_j) now can be written as a function of the spin density on the considered site and the spin density on the neighboring sites:[27]

$$A_j = \rho_j + \sum_k a_{jk}\rho_k ,$$

where the a_j are positive and the a_{jk} are negative. Mehring *et al.*[24] have used $a_j \approx 85-100$ Hz and $a_{jk} \approx -39$ Hz for their analysis of (Fa)$_2$SbF$_6$ (Fa denotes fluoranthene) Knight shifts. Small, negative Knight shifts are then explained by the fact that the spin density on the considered site is small whereas it is large on a neighboring site. In the (TMTSF)$_2X$ salts, this means that the Knight shift of the methyl-group carbon atoms is—with a change in sign—determined by the spin density on the corner carbon atoms.[2]

D. Reference position

We have seen above that knowledge of the Knight shift is of fundamental importance when we want to evaluate local spin densities. The major problem in measuring K is to find a reliable reference position. The ideal would be an insulating salt of the same series, which has the same structure as the metallic salt: however, such an insulating salt does not exist. There are several other possibilities, each having its own limitations.

(i) The equivalent position in neutral TMTSF. It is *a priori* not clear in which way the difference in structure between the metallic salt and the neutral molecule on one hand, and the charge transfer to the anion on the other hand, affects the chemical shift. Furthermore, this reference position yields enhancement factors which are very heterogeneous over the molecule,[2,3] and this is not permitted since the Korringa enhancement should be independent of the considered site.

(ii) The equivalent position in semiconducting (TMTSF)$_2$ReO$_4$. The structure of the anion ordered ground state is different from the one in the metallic state; this should influence the chemical shifts. A practical problem is that the observed linewidth is larger then the expected Knight shifts.[12] The transition to the anion ordered ground state is first order and it is thus not possible to follow a given carbon resonance continuously through the transition. Furthermore, the Knight shift of the corner carbon atoms becomes negative at temperatures as high as 200 K when we use these lines as a reference.

(iii) The resonance position at $T=0$ K. It might be argued that the correct reference position is the extrapolation of the resonance position towards $T=0$ K. The problem is, of course, that the resonance position is only known to 200 K. The extrapolation is very uncertain as is shown by the change in slope around 240 K. For the corner carbon atoms in TTF-TCNQ it is not possible to correlate such an extrapolation to a property of the electron gas.

A possible determination of the reference position can be obtained from Korringa's law, rewritten in the following way:

$$\frac{1}{(T_1 T)^{1/2}} = \left[\frac{\eta}{k_K} \right]^{1/2} (\delta - \delta_0) \; . \tag{3}$$

This analysis is only valid for the sites for which T_1 is due to the hyperfine coupling with the electron gas: thus not for the methyl-group carbon atoms. The results are shown in Fig. 6. In Table VI we give δ_0 for the different corner carbon atoms. Note first the similarity between these values and the extrapolation of the high-temperature ($T \gtrsim 290$ K) resonance positions for all carbon atoms but Co1.

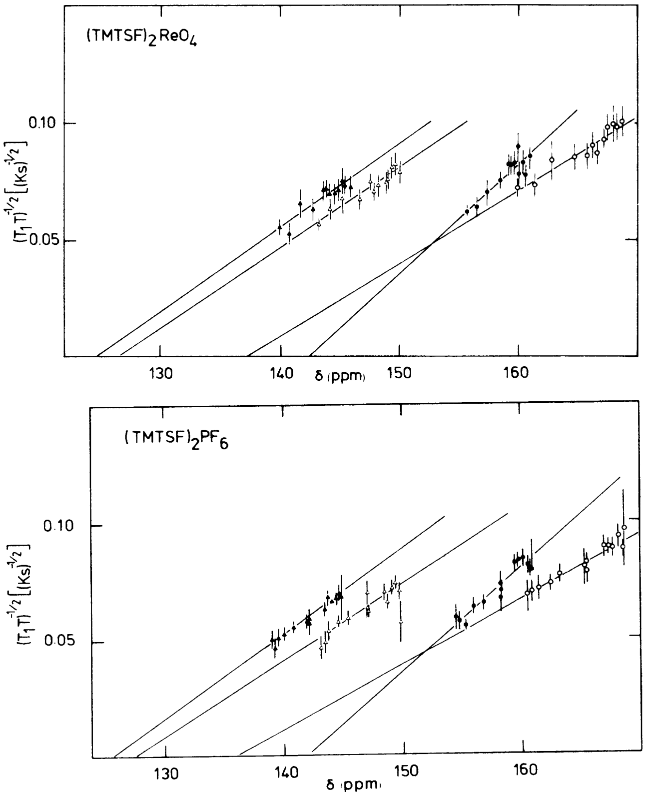

FIG. 6. $(T_1 T)^{1/2}$ as a function of the resonance position; the slope yields Korringa's enhancement and the intersection with the position axis, the reference position for the Knight shift.

TABLE VI. Reference position (δ_0) and resulting Korringa enhancement factor (η) of the corner carbon atoms in (TMTSF)$_2$ReO$_4$ and (TMTSF)$_2$PF$_6$

	δ_0 (ppm)		η	
Site	ReO$_4$	PF$_6$	ReO$_4$	PF$_6$
Co1	137±5	136±5	38±13	31±10
Co2	142±3	142±2	86±26	78±18
Co3	126±3	128±3	47±16	42±11
Co4	125±3	126±2	51±19	52±13

This determination of δ_0 is limited by the accessible temperature range, but we should also take care that there are no other contributions to its temperature dependence. We have seen above that η is almost temperature independent in the range of temperatures of the experiment, and the use of expression (3) is therefore justified.

The reference position for two out of four sites is larger than the equivalent position in neutral TMTSF, while for the two others it is less. This can be understood in the following way.

(i) The electron density that contributes to the chemical shift decreases when the salt is formed from the neutral molecule; this is due to the transfer of one electron per two organic molecules to the anion and the delocalization of three others. This decrease should affect all the sites in (more or less) the same way; the sign of the change in chemical shift depending on the sign of the electronic wave function.

(ii) The delocalized electrons do not have the same density on both ends of the molecule. These electrons will have a tendency to redistribute the core electrons, thus changing the chemical shift. This efefct reproduces the asymmetry of the conduction-electron density.

The values of η obtained from the above analysis are reported in Table VI. Inspection reveals that for three sites η is constant within the experimental uncertainty ($\eta \sim 30-50$), and in fact only slightly greater than the value calculated above ($\eta \sim 22-34$). The reason for the larger slope, and therefore larger enhancement factor, for one of the carbon atoms is not yet understood.

E. Change in slope

We finally focus attention on the change in slope of the Knight shift versus temperature. The origin of this change in slope is not very clear, but we can make the following observations.

(i) It occurs at the same temperature where microcracks are observed during resistivity measurements.[28]

(ii) It occurs at the onset temperature of the anion ordering in (TMTSF)$_2$ReO$_4$,[29] but is also observed in (TMTSF)$_2$PF$_6$.

(iii) The effect is due to the conduction electrons: a similar change in slope is observed on the TTF molecule in TTF-TCNQ (Ref. 12) at a slightly lower temperature, but not on the TCNQ molecule.[30]

(iv) The effect is homogeneous over the sample.

A possible interpretation comes from the logarithmic derivative of the Knight shift [$d\ln(K)/dT$]. To a first-order approximation this derivative should be site independent, and in fact vary as $d\ln(V)/dT$ [given as 0.3×10^{-3} K^{-1} (Ref. 31)]. When we calculate this derivative we notice that it is constant [$\sim(3.5\pm0.5)\times10^{-3}$ K^{-1}] for temperatures above the temperature at which the change of slope occurs, and passes through a maximum at this temperature to fall to half its high-temperature value [$\sim(1.5\pm0.5)\times10^{-3}$ K^{-1}]. Note firstly that $d\ln(K)/dT$ is much larger than $d\ln(V)/dT$, particularly for $T \gtrsim 250$ K, implying that the spin density varies more rapidly than can be expected from volume effects alone. Secondly, the value of $d\ln(K)/dT$ is very large for a metallic system. We therefore envisage a picture wherein the spin density is gradually redistributed over the molecule at temperatures above ~250 K; this redistribution being probably of structural origin.[32] It is tempting to speculate that such a redistribution of the spin density might trigger the anion ordering in $(\text{TMTSF})_2\text{ReO}_4$, though it is more probable that both events are a consequence of a common underlying mechanism.

It should be stressed that the analysis given above is based on the assumption that the spin susceptibility changes continuously with temperature. A direct measurement of this susceptibility with a good resolution in temperature is thus necessary to test this hypothesis.

V. CONCLUSION

We have presented here the first variable-temperature studies of the metallic state in organic conductors. We have measured ^{13}C spin-lattice relaxation rates and resonance position of the corner and methyl-group carbon atoms in $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTSF})_2\text{PF}_6$ as a function of temperature between 340 and 220 K. For the corner carbon atoms, T_1 is determined by the hyperfine interaction between the nucleus and the electron gas. The resonance position is of the sum of the Knight shift and the chemical shift. There is *a priori* no adequate reference position available for the determination of K, but Korringa's law has permitted us to determine such a position. We obtain in this way a coherent picture for three out of four corner carbon atoms. A further theoretical support will be necessary to achieve a complete analysis of all the presented data.

The Knight shift exhibits a gradual change in slope around different temperatures for the different carbon sites. This change in slope can be connected to a redistribution of the electron density over the molecule, which in turn might trigger the anion ordering in $(\text{TMTSF})_2\text{ReO}_4$. A more detailed analysis would require direct measurement of the spin susceptibility.

The results are almost independent of the anion, which is a consequence of the fact that the quantities we measure (T_1 and δ) are mainly determined by the $\mathbf{q}=0$ component of the susceptibility at these temperatures. This part of the susceptibility is almost independent of the anion, as is the overall structure of these materials at these temperatures.

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