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ELECTRONIC PROPERTIES OF TTF-TCNQ : AN NMR APPROACH ⁽¹⁾

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Résumé. — Cet article contient une étude de la dépendance en fréquence du temps de relaxation spin-réseau des protons dans TTF-TCNQ(D₄) et TTF(D₄)-TCNQ à plusieurs températures et pressions. Il est démontré que dans les conducteurs quasi unidimensionnels seules les diffusions en arrière ($q = 2k_F$) et en avant ($q = 0$) contribuent à la relaxation nucléaire induite par la modulation du champ hyperfin.

Aux champs intermédiaires, $H_0 \approx 30$ kOe, la dépendance en fréquence du T_1 , $T_1^{-1} \propto H_0^{-1/2}$, provient du caractère diffus des excitations de spin au voisinage de $q = 0$. Vers les champs faibles l'augmentation de T_1^{-1} est limitée par l'existence d'un couplage interchaîne de grandeur finie (du type tunnel). Au moyen d'une analyse basée sur l'approximation RPA, nous avons trouvé d'étroites corrélations entre dépendances en pression et température de la constante de diffusion des excitations de spin et du temps de collision électronique obtenu par la conductivité longitudinale. L'interprétation des résultats de RMN au moyen du modèle de Hubbard nous permet d'exclure l'éventualité de description *grand U* et *petit U*. Toutefois l'importance des interactions électron-électron sur la relaxation de TTF-TCNQ est démontrée. Nous déduisons une valeur de 0,9 pour le rapport $U/4 t_{||}$ de la chaîne TCNQ.

Nous pouvons aussi admettre que les interactions électron-électron contribuent à la dépendance en température de la susceptibilité de spin entre 300 et 53 K en plus de la contribution due aux fluctuations de charges. Enfin nous présentons une description unifiée pour les conducteurs quasi unidimensionnels dans laquelle les divers composés sont classés suivant leur couplage transverse *tunnel* et leur temps de collision électronique. Nous déduisons de cette description que les couplages tunnels et Coulombiens sont suffisamment forts dans TTF-TCNQ et les composés dérivés pour justifier l'utilisation de la théorie du champ moyen.

Abstract. — This paper presents the frequency dependence of the proton spin-lattice relaxation time T_1 at several temperatures and pressures in TTF-TCNQ(D₄) and TTF(D₄)-TCNQ. It is shown that only backward ($q = 2k_F$) and forward ($q = 0$) scatterings contribute to the nuclear relaxation induced by the modulation of the hyperfine field in these one-dimensional conductors.

At medium fields, $H_0 \approx 30$ kOe, the frequency dependence of T_1 originates from the diffuse character of the spin density wave excitations around $q = 0$, leading to $T_1^{-1} \propto H_0^{-1/2}$. The enhancement of T_1^{-1} , is at low fields, limited by the existence of a finite interchain coupling (tunnelling type). We find, within a RPA analysis, close correlations between the pressure and temperature dependences of the spin excitations diffusion constant and the collision time derived from the longitudinal conductivity. The interpretation of the NMR data in terms of a Hubbard model excludes both *big U* and *small U* pictures. However, we point out the importance of the electron-electron interactions on the relaxation rate of TTF-TCNQ. We derive a ratio $U/4 t_{||} \approx 0.9$ for the TCNQ chain.

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We also assume that besides charge density waves fluctuations existing between 300 K and the phase transition at 53 K, electron-electron interactions make an important contribution to the temperature dependence of the spin susceptibility. Finally, we give a unified description of quasi one dimensional conductors in which the various systems are classified according to the transverse tunnelling coupling and the electron lifetime. It follows from this description that for TTF-TCNQ and its derivatives, transverse couplings (tunnelling and Coulomb) are large enough to justify the use of a mean-field theory.

1. Introduction. — The proton nuclear spin relaxation rate T_1^{-1} in TTF-TCNQ, as function of temperature, at ambient pressure and low frequency, was reported by the Pennsylvania group [1]. It was claimed to obey the Korringa law [2] $[T_1 T\chi_s^2]^{-1} = \text{const.}$ approximately. However, the value of this product exceeds the Korringa contact-interaction value [2]

$$\left(\frac{\gamma_N \hbar A}{g\mu_B} \right)^2 \frac{4\pi k_B}{(g\mu_B)^2 \hbar},$$

where A is the hyperfine field in gauss, by a large amount. On the basis of these observations, the Pennsylvania group suggested that the conduction electrons should be regarded as a free-electron gas (thus accounting for the $[T_1 T\chi_s^2]^{-1} = \text{const.}$ law), while dipolar electron-nucleus interactions account for the enhancement of this product over the contact-interaction value. In a previous publication by the present group [3, 4, 5] it was pointed out that the magnetic field dependence of the relaxation rate invalidates this simple picture; the relaxation rate is proportional to $H_0^{-1/2}$ at medium fields (~ 30 kOe) and becomes field-independent at low fields. This field dependence was attributed to the one-dimensional (1-D) random walk of the electron spin along the chains, and the electronic Zeeman frequency ω_e at which the field-dependence changes from constant to $H_0^{-1/2}$ was shown to be given by the escape time $\tau_\perp \approx 1/2 \omega_e$ of an electron from a chain due to tunnelling. Thus the spin density wave (SDW) excitations along the chain have a diffusive character (at least for $|q| \approx 0$) and the relaxation rate is strongly enhanced in weak fields by the multiple electron-nucleus scattering in this quasi 1-D system. In addition to the contact interaction, the dipolar coupling between the electron and nucleus also contributes to the relaxation process. This interaction, possesses the matrix element $I^\pm s^z$ for which the change from field-independent T_1^{-1} to $T_1^{-1} \propto H_0^{-1/2}$ occurs at $\omega_N \tau_\perp = 1/2$ instead of $\omega_e \tau_\perp = 1/2$, i.e. at a magnetic field 660 times higher. Thus, for field that can be obtained in the laboratory, $\omega_N \tau_\perp \ll 1$ and the contribution of this mechanism to the relaxation rate is field independent.

In section 2 we present the basic concepts underlying the theory of T_1 in 1-D metals. The random-walk in 1-D is formally treated by describing $\chi(\mathbf{q}, \omega)$ as diffusive. This property is well known to hold for $q \approx 0$, but it is not certain that it applies at $q \approx 2k_F$

as well; even if it does, it is not clear whether the diffusion constant is the same as that for $q \approx 0$. For this reason, we present formulae for two limiting cases : (i) Diffusive behaviour for both $q \approx 0$ and $q \approx 2k_F$ components, with equal diffusion constants. (ii) Coherent behaviour for the $2k_F$ component. The susceptibility is approximated by the RPA, in which case $\chi(2k_F, \omega)$ is considerably enhanced by the electron-electron Coulomb interaction U . The magnetic field dependence of T_1^{-1} is arrested at low fields due to electron tunnelling between chains, and the T_1 data yield an unambiguous value of the escape time τ_\perp , which can thus be measured individually for the TTF and TCNQ chains. However the relationship between the escape time τ_\perp and the tunnelling matrix element t_\perp is complicated. The Golden Rule [3] $\tau_\perp^{-1} = 2\pi/\hbar t_\perp^2 n(E_F)$ need not apply when the motion along the chain is coherent ($E_F \tau_v/\hbar \gg 1$), where τ_v is the electron collision time along the chains, and $n(E_F)$ may have to be replaced by τ_v/\hbar in this expression. A somewhat similar approach has been adopted by Ong and Portis [5].

Finally, we express T_1^{-1} in terms of the diffusion constant, the escape time and the enhancement factor, for both contact and dipolar electron-nucleus interactions.

In section 3, we present the measured values of T_1^{-1} as function of magnetic field for various temperatures and pressures for TTF and TCNQ chains. The relaxation rate is given by

$$(T_1 T)^{-1} = C_1 \left\{ \frac{1 + \sqrt{1 + \omega_e^2 \tau_\perp^2}}{2(1 + \omega_e^2 \tau_\perp^2)} \right\}^{1/2} + C_2$$

where $\omega_e = \gamma_e H_0$, and C_1, C_2, τ_\perp are 3 parameters depending on temperature, pressure and the nature of the chain (TTF or TCNQ). We also present the values of T_1^{-1} of TMTTF-TCNQ, as function of H_0 , and show that they are similar to those of TTF-TCNQ.

C_1 and C_2 will be discussed in section 4. C_1 is proportional to the collision time $\tau_v^{-1/2}$; thus we compare τ_v derived from C_1 with the value derived from the longitudinal conductivity $\sigma_\parallel = n_0 e^2 \tau_v/m^*$ over a wide range of temperatures and pressures. The diffusion constant is given by the free electron value $D = v_F^2 \tau_v$ for small and moderate $U/4 t_\parallel$, and by the Hubbard Hamiltonian value $D = 2\pi/\hbar b^2 t_\parallel^2/U$ for large values of $U/4 t_\parallel$. From the value of the enhancement factor $K_{2k_F}(\alpha)$ we estimate $U/4 t_\parallel$ to be about 1, excluding therefore, both the big U ($U/4 t_\parallel \gg 1$) and

the *small* U ($U/4 t_{\parallel} \ll 1$) situations. τ_{\perp} follows closely the jump time derived from the transverse conductivity. In the present work we claim that the NMR properties of TTF-TCNQ are dominated by two parameters namely the interchain tunnelling matrix element t_{\perp} , and the intra-chain collision time τ_v .

In section 5, we demonstrate how the properties of quasi-1-D metals in general depend on the values of the dimensionless parameters, namely t_{\perp}/E_F , which gives the *One Dimensionality*, i.e. the extent to which the material is one-dimensional ($t_{\perp}/E_F \ll 1$) or three-dimensional ($t_{\perp}/E_F \approx 1$), and $\hbar/E_F \tau_v$, which gives the degree of *cleanliness*. For $\hbar/E_F \tau_v \ll 1$ the material is clean and its properties should be dominated by the coherence length ξ , while for $\hbar/E_F \tau_v \gtrsim 1$, it is dirty, and the mean free path $\Lambda = v_F \tau_v$ has a dominant effect on the electronic properties. We show how the various materials can be presented on a one-dimensionality vs. cleanliness diagram. We get an anisotropic 3-D metal for $\hbar/\tau_v \leq t_{\perp}$, a true one-dimensional metal (i.e. coherent electronic motion along the chains, and diffusive one perpendicular to the chains) for $t_{\perp} < \hbar/\tau_v < E_F$; and a low-mobility semiconductor (i.e. diffusive motion along the chains as well)

for $E_F < \hbar/\tau_v$. Temperature and pressure affect mainly τ_v , and in some materials, t_{\perp} , and this causes the material to move on this diagram. The changes in the properties of the material brought about by application of pressure, or change in temperature, are as big as the differences between different materials (such as KCP and TTF-TCNQ). In this way, the picture derived from the systematic measurement of the NMR relaxation times gives us an overall view of quasi-one-dimensional metals.

2. Nuclear spin relaxation in quasi-one dimensional conductors. — Let us consider the hyperfine $I.s$ contact interaction between the nucleus and electron. In addition to this interaction, an orbital $I.l$ interaction may also exist in principle, but it is expected to be weak due to the quenching of the orbital angular momentum. There is also a dipolar $(I.s)/r^3 - 3(I.r)(s.r)/r^5$ interaction which will be discussed briefly. The dominance of the $I.s$ contact interaction is demonstrated experimentally by the strong *positive* Overhauser effect, with enhancement factor 200, observed in TTF-TCNQ [6].

The nuclear spin relaxation rate T_1^{-1} for the contact hyperfine interaction is given by the summation of the SDW response function over all the momentum transfer components q [7]

$$T_1^{-1} = \frac{2 \gamma_N^2 k_B T}{(g\mu_B)^2} \sum_q |A_q|^2 \frac{\chi''_{\perp}(\mathbf{q}, \omega_N)}{\omega_N} \quad (1)$$

where

$$A_q = \frac{-8\pi}{3} (g\mu_B) |u_q(0)|^2 \quad \text{and} \quad \omega_N = \gamma_N H_0$$

is the nuclear resonance frequency. The SDW response function $\chi''_{\perp}(\mathbf{q}, \omega_N)$ is given by the imaginary part of

$$\chi_{0\perp}(\mathbf{q}, \omega_N) = \frac{1}{2} (g\mu_B)^2 \sum_{\mathbf{k}} \frac{f_{\mathbf{k}\downarrow} - f_{\mathbf{k}+\mathbf{q}\uparrow}}{\varepsilon_{\mathbf{k}+\mathbf{q}\uparrow} - \varepsilon_{\mathbf{k}\downarrow} - \hbar\omega_N + i\eta}, \quad \eta = 0^+ \quad (2)$$

i.e.

$$\chi''_{0\perp}(\mathbf{q}, \omega_N) = \frac{1}{2} (g\mu_B)^2 \pi \sum_{\mathbf{k}} (f_{\mathbf{k}\downarrow} - f_{\mathbf{k}+\mathbf{q}\uparrow}) \delta(\hbar\omega_N - \varepsilon_{\mathbf{k}+\mathbf{q}\uparrow} + \varepsilon_{\mathbf{k}\downarrow}) \quad (3)$$

where $f_{\mathbf{k}}$ is the Fermi occupation number, in the independent particle approximation. Since the electronic energy $\varepsilon_{\mathbf{k}\sigma}$ is the sum of the kinetic energy $\varepsilon_{\mathbf{k}}$ and the Zeeman energy $\sigma\mu_B H_0 = \frac{\sigma}{2} \hbar\omega_e$, the electron Larmor frequency ω_e enters into this expression in an essential way.

The electron-electron correlations enhance $\chi''_{\perp}(\mathbf{q}, \omega)$. This effect has been treated in the RPA for a 1-D system [8]. We shall follow this treatment, although fluctuations should play an important role in 1-D systems [9]. In the RPA, $\chi''_{\perp}(\mathbf{q}, \omega)$ is given by :

$$\chi''_{\perp}(\mathbf{q}, \omega) = \frac{\chi''_{0\perp}(\mathbf{q}, \omega)}{[1 - \alpha F(\mathbf{q})]^2} \quad (4)$$

where $\alpha = U\chi'_0(0, 0)$, U is the electron-electron Coulomb repulsion (for a Hubbard Hamiltonian), and $F(\mathbf{q})$ is the Lindhard function $F(\mathbf{q}) = \chi'_0(\mathbf{q}, 0)/\chi'_0(0, 0)$ [8].

Since the electron gas is degenerate

$$(k_B T \ll \varepsilon_F \approx 1\,000 \text{ K})$$

and the Zeeman energy is small ($\hbar\omega_e \ll \varepsilon_F$), the SDW excitation contributing to T_1^{-1} in this 1-D conductor consists only of the $|q| \approx 0$ and $|q| \approx 2 k_F$ compo-

nents [10]. For electrons with an infinite scattering lifetime τ_v , a coherent picture applies and eq. (1) reduces to the *ordinary* Korringa relation (see appendix)

$$(T_1 T)^{-1} = \frac{1}{S} \chi_s^2 \left(\frac{\hbar \gamma_N A}{g \mu_B} \right)^2 \langle K(\alpha) \rangle \quad (5)$$

$$S = \frac{(g \mu_B)^2 \hbar}{4 \pi k_B}$$

$$\langle K(\alpha) \rangle = \frac{1}{2} \{ K_0(\alpha) + K_{2k_F}(\alpha) \}$$

$$\chi_s = \frac{1}{1 - \alpha} \chi_0, \quad \chi_0 = \frac{1}{2} (g \mu_B)^2 n(E_F).$$

The enhancement factor $K_{2k_F}(\alpha)$ is larger than $K_0(\alpha)$ because of the divergence of the Lindhard function there for 1-D systems. The relaxation rate T_1^{-1} is seen to be independent of the magnetic field.

2.1 FIELD DEPENDENCE OF THE RELAXATION RATE DUE TO RANDOM WALK IN ONE DIMENSION. — As mentioned in the introduction, T_1^{-1} in TTF-TCNQ shows a strong frequency dependence; thus the Korringa relation is seen to break down, due to the finite scattering lifetime of the electrons, moving along the chains, which brings about a random walk motion in one dimension, which has the property that the sum of the probabilities for return to the initial position after n steps, $\sum_n p_n$, diverges [11]. This scattering lifetime is $\tau_v \approx 3 \times 10^{-15}$ s at room temperature (from the expression for the conductivity, $\sigma = ne^2 \tau_v / m^*$), yielding a mean free path $\Lambda \approx 6 \text{ \AA}$ for the Fermi velocity of 1.8×10^7 cm/s. Since $\omega_e^{-1} \approx 10^{-11}$ s $\gg \tau_v$, the SDW excitations of small q components ($q \ll \Lambda^{-1}$) become diffusive [12], i.e.

$$\chi(\mathbf{q}, \omega) = \chi_s \frac{D q^2}{D q^2 - i \omega} \quad (6)$$

$$\frac{\chi_\perp(\mathbf{q}, \omega)}{\omega} = \chi_s \frac{D q^2}{(D q^2)^2 + \omega^2}$$

where χ_s and D are the spin susceptibility and the diffusion constant respectively.

The contribution to T_1^{-1} coming from the small q components can be derived from eq. (1) and (6) :

$$(T_1 T)_{|q| \approx 0}^{-1} \approx A^2 \chi_s (D \omega_e)^{-1/2}. \quad (7)$$

The large q components ($|q| \sim 2 k_F$) lead however to a contribution :

$$(T_1 T)_{|q| \sim 2k_F}^{-1} \approx A^2 \chi_s^2 \quad (8)$$

which is frequency independent, provided the $q \sim 2 k_F$ spin excitations are non-diffusive.

When the RPA treatment is used, the diffusion constant becomes :

$$D = v_F^2 \tau_v (1 - \alpha). \quad (9)$$

Thus, in our case, $D \approx 1 \text{ cm}^2/\text{s}$, and the maximum of the SDW excitation is expected at

$$q \approx (\omega_e/D)^{1/2} \approx 3 \times 10^5 \text{ cm}^{-1} \ll \Lambda^{-1},$$

and the macroscopic diffusion equation should apply very well for the $q \approx 0$ component of $\chi_\perp(\mathbf{q}, \omega)$. The situation regarding the $|q| \approx 2 k_F$ component is less clear. Since $2 k_F > \Lambda^{-1}$, one might expect the diffusion equation not to be valid, and $\chi(\mathbf{q}, \omega)$ to be coherent. However, this is not necessarily the case. $\chi(\mathbf{q}, \omega)$ in this region may be given by $\Sigma(q - 2 k_F, \omega) \cdot \chi(2 k_F)$, where Σ is a modulating function slowly varying in space, which can be expanded like $\chi(\mathbf{q}, \omega)$ in the region $q \approx 0$, and thus obey a diffusion equation as well. However, this assumption has not yet been rigorously established.

Performing the summation over q , we get for the non-diffusive $2 k_F$ components case :

$$\left[T_1 T \chi_s^2 \left(\frac{\hbar \gamma_N A}{g \mu_B} \right)^2 \right]^{-1} = \frac{1}{2 S} \left[\sqrt{\frac{1}{2 \tau_v \omega_e}} K_0(\alpha) + K_{2k_F}(\alpha) \right]. \quad (10)$$

Here,

$$K_0(\alpha) = (1 - \alpha)^2 \langle [1 - \alpha F(\mathbf{q})]^{-1.5} \rangle_{q \approx 0} \simeq (1 - \alpha)^{0.5} \quad (10')$$

$$K_{2k_F}(\alpha) = (1 - \alpha)^2 \langle [1 - \alpha F(\mathbf{q})]^{-2} \rangle_{q \approx 2k_F}. \quad (10'')$$

If the $2 k_F$ component of the susceptibility is also diffusive with the same diffusion constant as the $q \approx 0$ components, the factor $\sqrt{\frac{1}{2 \tau_v \omega_e}}$ in (10) should be common to $K_0(\alpha)$ and $K_{2k_F}(\alpha)$, namely

$$\left[T_1 T \chi_s^2 \left(\frac{\hbar \gamma_N A}{g \mu_B} \right)^2 \right]^{-1} = \frac{1}{2 S} \sqrt{\frac{1}{2 \tau_v \omega_e}} [K_0(\alpha) + K_{2k_F}(\alpha)]. \quad (11)$$

2.2 EFFECT OF TUNNELLING BETWEEN CHAINS. — As has been discussed in previous publications [3, 4], the law $T_1 \propto \sqrt{H_0}$ breaks down in the low field region. This effect is associated with the inter-chain hopping of electrons. Let τ_\perp be the escape time from the chain. The auto correlation function of the spin density $\varphi_q(t)$, which gives the power spectrum of eq. (6),

$$\varphi_q(t) = \frac{1}{2} \chi_s \exp(-Dq^2 |t|)$$

should therefore be replaced by :

$$\varphi_q(t) = \frac{1}{2} \chi_s \exp(-Dq^2 |t|) \exp(-|t|/\tau_\perp) \quad (12)$$

assuming a single exponential decay for the interchain hopping process. Taking the Fourier transform of (12), and summing over q , we get the contribution to $(T_1 T)^{-1}$ coming from the $q \approx 0$ components

$$(T_1 T)_{q \approx 0}^{-1} \approx A^2 \chi_s \sqrt{\frac{\tau_\perp}{D}} g(\omega_e)$$

where

$$g(\omega_e) = \sqrt{\frac{1 + \sqrt{1 + \omega_e^2 \tau_\perp^2}}{2(1 + \omega_e^2 \tau_\perp^2)}}. \quad (13)$$

The interchain coupling does not lead to any change in $(T_1 T)_{q \approx 2k_F}^{-1}$ (for the coherent assumption) because the hopping rate τ_\perp^{-1} is much smaller than the Fermi energy.

If the RPA is used for the estimation of D as was done in section 2.1 the relaxation rate becomes :

$$\left[T_1 T \chi_s^2 \left(\frac{\hbar \gamma_N A}{g \mu_B} \right)^2 \right]^{-1} = \frac{1}{2S} \left[\sqrt{\frac{\tau_\perp}{\tau_v}} g(\omega_e) K_0(\alpha) + K_{2k_F}(\alpha) \right]. \quad (14)$$

For $\omega_e \tau_\perp \ll 1$, T_1^{-1} becomes independent of frequency, and for $\omega_e \tau_\perp \gg 1$, this expression reduces to (10).

Let us try to estimate the relationship between the escape time τ_\perp and the interchain matrix element t_\perp .

If the Golden rule applies,

$$\tau_\perp^{-1} = \frac{2\pi}{\hbar} t_\perp^2 n(E_F). \quad (15)$$

However, in the present case it is not obvious that the Golden rule applies, since we do not necessarily have a continuum of final states (accessible from a given initial state). Consider a situation where at $t = 0$ the electron is on chain 1 ($\psi = \psi_1$), but there is a matrix element t inducing tunnelling to chain 2. Then, $\psi(t) = \psi_1 \cos t_\perp t/\hbar + \psi_2 \sin t_\perp t/\hbar$. Assume that after time $t = \tau_v$ the coherence between ψ_1 and ψ_2 is lost, and that $\tau_v t_\perp/\hbar \ll 1$. Then, the probability of the electron to be on chain 2 at $t = \tau_v$ is given by $(t_\perp \tau_v/\hbar)^2$, and per unit time the hopping probability is given by $t_\perp^2 \tau_v/\hbar^2$.

Thus,

$$\tau_\perp^{-1} = \frac{2\pi}{\hbar} t_\perp^2 (\tau_v/\hbar) \quad (16)$$

i.e. $n(E_F)$ is replaced by τ_v/\hbar . Numerically, the difference between $n(E_F)$ and τ_v/\hbar at ambient, is not very large, but the temperature and pressure dependence of

these two quantities is radically different; $n(E_F)$ depends only weakly on these quantities, while τ_v increases rapidly with decreasing temperature and increasing pressure [13].

Note that τ_\perp^{-1} also affects the transverse conductivity. By Einstein's relation, $\sigma_\perp = n_0 D_\perp e^2/k_B T$. Here, $D_\perp = l^2 \tau_\perp^{-1}$, where l is the interchain distance in the appropriate direction, and $n_0 = n(E_F) k_B T$ for degenerate Fermi statistics ($k_B T \ll E_F$). Thus,

$$\sigma_\perp = n(E_F) l^2 e^2 \tau_\perp^{-1} = \frac{2\pi}{\hbar} n(E_F) l^2 e^2 t_\perp^2 \tau_v/\hbar \quad (17)$$

$$\sigma_\perp/\sigma_\parallel = (t_\perp/t_\parallel)^2 (a/b)^2 \quad (17')$$

nearly independent of temperature and pressure, for this limit in contrast with the situation when the Golden rule applies, and $\sigma_\perp/\sigma_\parallel \propto \tau_v^{-1}$, which is very strongly temperature and pressure dependent [14].

For the derivation of the relation $\tau_\perp^{-1} \propto \tau_v$, see the important note added in proof.

2.3 RELAXATION PROCESSES IN STRONG FIELDS. — According the formula (11), with the diffusive assumption for the $2k_F$ components, T_1 should increase with increasing H indefinitely. Clearly this is absurd. One limitation to the increase of T_1 at high fields follows from the breakdown of the diffusion equation when

the collision time τ_v is no longer short compared with the Larmor period $2\pi/\omega_e$. Clearly, a continuum formulation is no longer valid in that limit. In that case, even if the electron returns to its initial position immediately, after one backward scattering and time $2\tau_v$, its spin has precessed appreciably and its interaction with the nucleus is no longer coherent. In this limit we are back to the single-scattering situation of 3-D systems, and T_1 follows the Korringa relation and is field independent. Its value should be $\sqrt{\tau_\perp/2\tau_v}$ times longer than the low-field limit. For TTF-TCNQ, $\tau_\perp \approx 4 \times 10^{-12}$ s; $2\tau_v \approx 6 \times 10^{-15}$ s thus the high field T_1 should be about 25 times longer than the low-field value, and the field to attain this value should be $\gamma_e H_0 2\tau_v \approx 1$, i.e. several mega-gauss.

However, for the situation described by eq. (14) where the $q \approx 2k_F$ spin excitations are non-diffusive the increase of T_1 at high fields is limited by the existence of the $K_{2k}(\alpha)$ contribution.

Additional relaxation mechanisms may also stop the increase of T_1 at much lower fields. For example, relaxation by impurities (such as magnetic centres produced by broken chains). Another possibility is relaxation by the electron nucleus dipolar interaction.

In most metals this process is much weaker than relaxation by the contact interaction, and therefore neglected. However, in TTF-TCNQ this neglect is not justified. This follows from 2 reasons: (1) For protons attached directly to an aromatic (homocyclic or heterocyclic) ring, there is a considerable degree of cancellation (due to symmetry) of the contact interaction between p_z orbital and the proton, and the resulting core-polarization interaction is therefore relatively weak. On the other hand, since the p_z orbital does not surround the proton spherically, but is close and to one side of it, the dipolar interaction is relatively strong. (2) The dipolar interaction possesses a $I^\pm s^z$ term in the Hamiltonian. This term does not depend on the angle of precession of the electronic spin in the x - y plane. Therefore, it gives rise to coherent multiple scattering even after times large compared with $1/\omega_e$. Therefore, in fields such that $\omega_e \tau_v > 1$, $\omega_N \tau_\perp < 1$, multiple scattering by the contact interaction is attenuated, while that of the $I^\pm s^z$ term of the dipolar interaction is not. The dipolar interaction should cause a saturation in the increase of T_1 with H when it becomes dominant over the contact interaction. The contribution to T_1^{-1} can be calculated using eq. (1) by replacing $\chi_\perp''(\mathbf{q}, \omega)$ by $\chi_\parallel''(\mathbf{q}, \omega)$ which is given by the imaginary part of:

$$\chi_{0\parallel}(\mathbf{q}, \omega) = \frac{1}{4} g^2 \mu_B^2 \sum_{\mathbf{k}, \sigma} \frac{f_{\mathbf{k}\sigma} - f_{\mathbf{k}+\mathbf{q}, \sigma}}{\epsilon_{\mathbf{k}+\mathbf{q}, \sigma} - \epsilon_{\mathbf{k}\sigma} - \hbar\omega + i\eta}, \quad \eta = 0^+ \quad (18)$$

in the independent particle approximation.

The essential time scale *here* is the nuclear Larmor frequency ω_N in place of the electronic one ω_e for the scalar contribution. The relaxation rate due to the $I^\pm s^z$ term is:

$$\left[T_1 T \chi_s^2 \left(\frac{\hbar \gamma_N B}{g \mu_B} \right)^2 \right]^{-1} = \frac{1}{2S} \left[\sqrt{\frac{\tau_\perp}{\tau_v}} g(\omega_N) K_0(\alpha) + K_{2k_F}(\alpha) \right] \quad (19)$$

with $g(\omega_N)$ derived from eq. (13) where B is the dipolar coupling constant, $B = \langle g \mu_B / r^3 \rangle$ where r is (essentially) the proton-carbon distance. In the dipolar contribution, the beginning of the rise of T_1 with $\sqrt{H_0}$ occurs at fields 660 times higher than that for the scalar coupling, i.e. at fields of a few mega-gauss, and for fields attainable in the laboratory, T_1 is field independent. The characteristic features of the frequency dependence of $(T_1 T)^{-1}$ are the following:

I. Weak fields, $H_0^{-1/2} > (2\gamma_e \tau_\perp)^{1/2}$, T_1 is field independent, and due mainly to the contact interaction.

II. Intermediate fields,

$$(B/A)^2 (2\gamma_e \tau_\perp)^{1/2} < H_0^{-1/2} < (2\gamma_e \tau_\perp)^{1/2}.$$

T_1^{-1} is field dependent, following (approximately) a $H_0^{-1/2}$ law, and due (mainly) to the scalar interaction.

III. Strong fields,

$$(2\gamma_N \tau_\perp)^{1/2} < H_0^{-1/2} < (B/A)^2 (2\gamma_e \tau_\perp)^{1/2}.$$

The dependence of T_1 on H_0 becomes weaker than in region II, and the relaxation process becomes more and more dipolar.

IV. $H_0^{-1/2} < (2\gamma_N \tau_\perp)^{1/2}$. Fields that are so high that they are not accessible in the laboratory for (TTF-TCNQ). However, for other materials, with a much longer τ_\perp , this region may become accessible. In this region T_1^{-1} again follows a $H_0^{-1/2}$ law.

On a T_1^{-1} vs. $H_0^{-1/2}$ curve, there should not be a break between regions II and III, whereas on a T_1 vs. $H_0^{1/2}$, a break should be seen (ref. [4], Fig. 11).

For the coherent $q \approx 2k_F$ assumption, a break at high fields should be observable even in absence of dipolar contribution to the relaxation rate, namely $B/A \ll 1$. On a T_1 vs. $H_0^{1/2}$ plot the break occurs when the contribution coming from the $q = 0$ (diffusive) spin excitations equals that coming from the $q = 2k_F$ (non-diffusive) spin excitations. For this situation, the field dependence of $(T_1 T)^{-1}$ vs. $H_0^{-1/2}$ is sketched on figure 1.

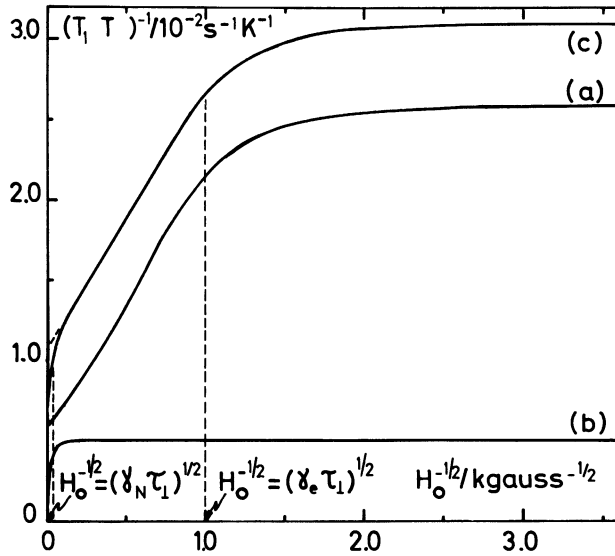


FIG. 1. — Schematic variation of $(T_1 T)^{-1}$ vs. $H_0^{-1/2}$, assuming non-diffusive $2 K_F$ components. a) Scalar coupling contribution, eq. (14). b) Dipolar coupling contribution, eq. (19). c) $(T_1 T)^{-1}_{\text{Total}} = (T_1 T)^{-1}_{\text{Scalar}} + (T_1 T)^{-1}_{\text{Dipolar}}$. The following values are used for the parameters (in arbitrary units), eq. (20); $C_1 = 2.0$, $C_2 = 0.6$; $C_1^d = 0.4$; $C_2^d = 0.1$.

3. Experimental results. — Powdered samples have been used in these experiments. The deuterated complexes have been prepared the same way as the non-deuterated ones [15]. TCNQ(D₄) has been obtained with a deuteration rate of 99.7 % (analysed by mass spectrometry) using the method of Dolphin *et al.* [16]. TTF deuteration of 96 % has been obtained with a method developed by Melby *et al.* [17]. The proton relaxation time T_1 was measured in the frequency range 10-90 MHz using a conventional pulsed NMR spectrometer and at 276 MHz using a high resolution NMR spectrometer. After a saturation of the magnetization by a comb of $\pi/2$ pulses its recovery was sampled by the free induction decay following a $\pi/2$ pulse. The free-induction decay was integrated in a box-car integrator while the magnetic field was swept through resonance. The recovery of the magnetization was found to be exponential over two decades of the maximum signal in all temperature and pressure ranges.

The pressure cell used was of a conventional copper-beryllium type working up to 10 kbar with compressed helium gas.

The frequency dependences of relaxation rates $(T_1 T)^{-1}$ at various temperatures and ambient pressure are summarized on figure 2. The frequency dependences at various pressures, at ambient temperature are displayed on figure 3. In the data analysis we shall take for the moment the point of view of non-diffusive $2 k_F$ components. We shall be able to show in the following section that this assumption leads to a consistent picture.

It is therefore more convenient to rewrite eq. (14)

$$(T_1 T)^{-1} = C_1 g(\omega_e) + C_2 \quad (20)$$

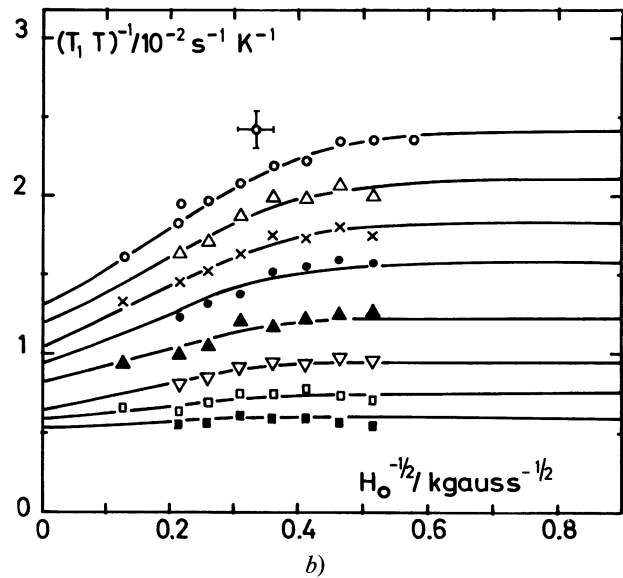
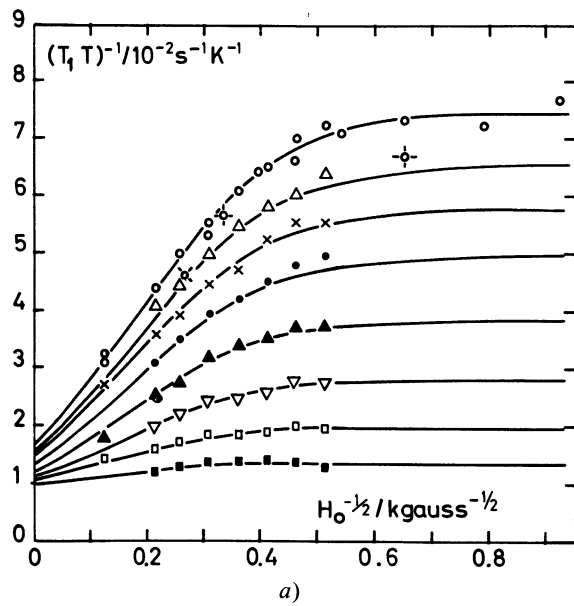


FIG. 2. — $(T_1 T)^{-1}$ vs. $H_0^{-1/2}$ under atmospheric pressure (a) for TTF-TCNQ(D₄) and (b) for TTF(D₄)-TCNQ at several temperatures ; ○ (296 K), △ (280 K) × (260 K), ● (240 K), ▲ (210 K), ▽ (180 K), □ (150 K), ■ (110 K). The solid lines are the theoretical curves (eq. (20)) drawn using the parameters of figures 4, 5 and 6. The data □, □ are taken from reference [1] and GULLEY, J. E. and WEIHER, J. F., *Bull. Am. Phys. Soc.* **19** (1974) 222, respectively.

where

$$C_1 = \frac{1}{2S} \sqrt{\frac{\tau_{\perp}}{\tau_v}} K_0(\alpha) \chi_s^2 \left(\frac{\gamma_N \hbar A}{g\mu_B} \right)^2 \quad (21)$$

$$C_2 = \frac{1}{2S} K_{2k_F}(\alpha) \chi_s^2 \left(\frac{\gamma_N \hbar A}{g\mu_B} \right)^2 \quad (21')$$

$(T_1 T)^{-1}$ depends now on the three parameters C_1 , C_2 , τ_{\perp} . The limiting values as $H_0 \rightarrow 0$ provide $C_1 + C_2$, and those as $H_0 \rightarrow \infty$ give C_2 . Instead of the approximate value of the escape time τ_{\perp} derived from the intersect of the high field dependences of T_1 with

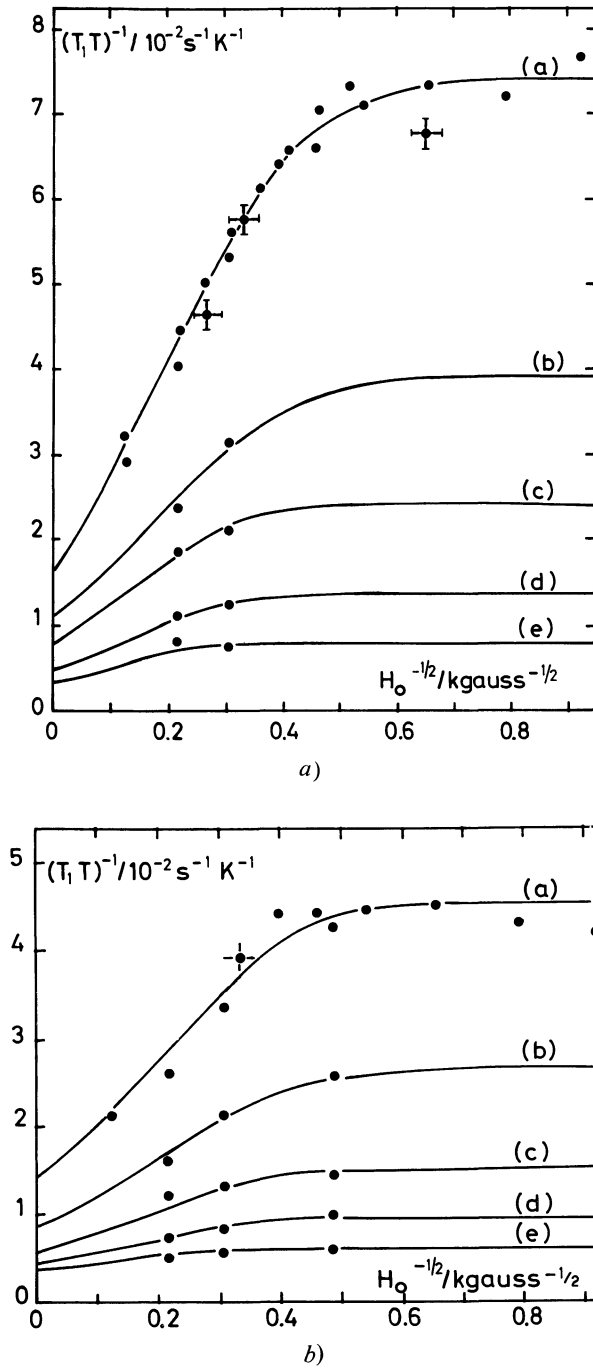


FIG. 3. — $(T_1 T)^{-1}$ vs. $H_0^{-1/2}$ at 296 K for : (a) TTF-TCNQ(D₄) and (b) TTF-TCNQ under various pressures ; (a) 1 atm, (b) 2 kbar, (c) 4 kbar, (d) 6 kbar and (e) 8 kbar. The solid lines are the theoretical curves (eq. (20)) drawn using the parameters of figures 4, 5 and 6. Data of reference [1] and Gulley and Weiher (see Fig. 2) are also included.

its low field value, namely $\tau_{\perp} \approx 1/2 \omega_e$, see section 1 and reference [3], we have performed here a fit of the experimental field dependence with the function $g(\omega_e)$. The temperature and pressure dependence of τ_{\perp} , C_1 and C_2 for all samples studied are reported in figures 4-6.

The procedure in the RPA to calculate τ_v and α in terms of the 3 experimental parameters C_1 , C_2 and α_{\perp}

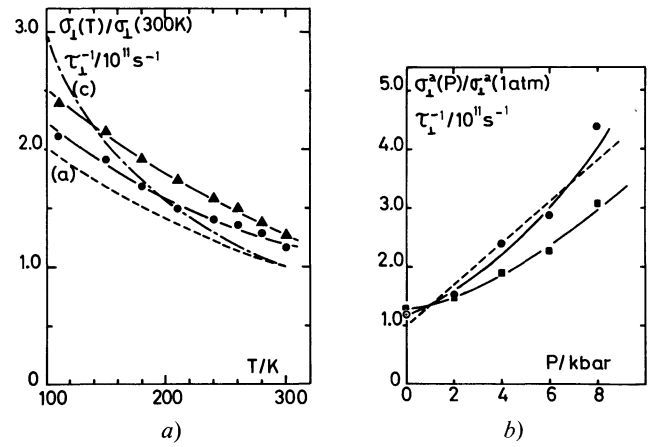


FIG. 4a. — Temperature dependence of the escape rate τ_{\perp}^{-1} in TTF-TCNQ(D₄) [●] and in TTF(D₄)-TCNQ [▲]. Normalized transverse conductivity, $\sigma_{\perp}(T)/\sigma_{\perp}(300 \text{ K})$, is also presented - - - (along a-axis) and - - - (along c-axis).

FIG. 4b. — Pressure dependence of the escape rate τ_{\perp}^{-1} at 296 K in TTF-TCNQ(D₄) [●] and in TTF-TCNQ [■]. Normalized transverse conductivity $\sigma_{\perp}(P)/\sigma_{\perp}(1 \text{ atm})$ is shown by broken lines (along a-axis), according to [14].

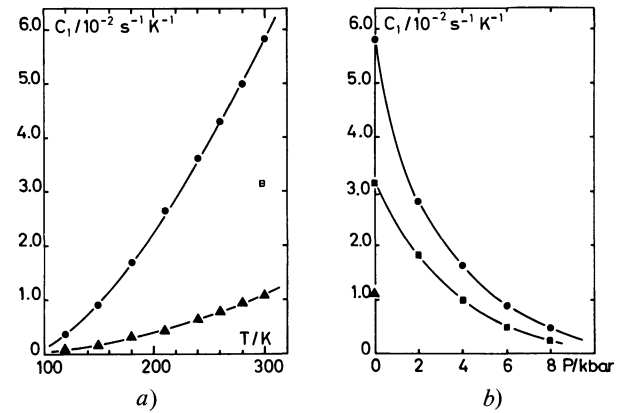


FIG. 5. — Temperature variation under atmospheric pressure (a) and pressure variation (b) of C_1 in TTF-TCNQ(D₄) [●], in TTF(D₄)-TCNQ [▲] and in TTF-TCNQ [□].

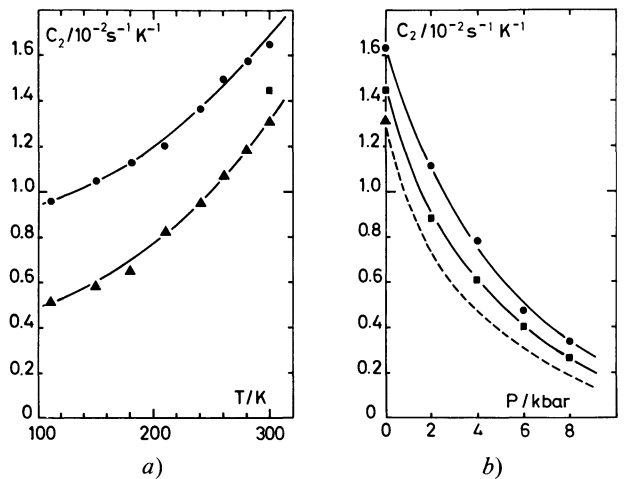


FIG. 6. — Temperature variation under atmospheric pressure (a) and pressure variation (b) of C_2 in TTF-TCNQ(D₄) [●], in TTF(D₄)-TCNQ [▲] and in TTF-TCNQ [■]. The broken line in (b) shows the pressure variation of C_2 in TTF(D₄)-TCNQ estimated assuming $C_2(\text{TTF-TCNQ}) = 1/2\{C_2(\text{TTF}) + C_2(\text{TCNQ})\}$.

is the following : $K_{2k_F}(\alpha)$ and thus $\alpha = U\chi'_0(00)$ are derived from (21') and (10''), τ_v is calculated then from (21).

The results of this analysis are shown in figures 7 and 8. We have taken the value of the spin susceptibility from reference [18] $\chi_s = 6 \times 10^{-4}$ uem/mole and have performed the analysis with susceptibility ratios $\chi_s^F/\chi_s^Q = 3/2$ or $7/3$ at room temperature according to references [19] and [20]. The hyperfine fields are $A = 1.26$ Oe and 1.5 Oe for TTF^+ and TCNQ^- respectively [21, 22].

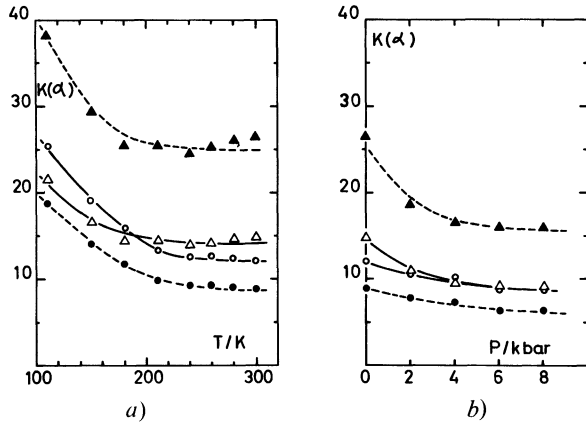


FIG. 7. — Temperature variation under atmospheric pressure (a) and pressure variation at 296 K (b) of the enhancement factor $K_{2k_F}(\alpha)$ in TTF-TCNQ(D_4) [O, ●] and in TTF(D_4)-TCNQ [Δ , \blacktriangle]. For solid lines, $K_{2k_F}(\alpha)$ was derived assuming $\chi_F/\chi_Q = 3/2$ (ref. [19]) and for broken lines $K_{2k_F}(\alpha)$ was derived assuming $\chi_F/\chi_Q = 7/3$ (ref. [20]).

Relaxation experiments have also been performed with the tetra methyl analog of TTF (TMTTF) compound with TCNQ, or TCNQ(D_4). The room temperature results are summarized in figure 9 for TMTTF-TCNQ and TMTTF-TCNQ(D_4). From the knowledge of the C_1 , C_2 , τ_\perp parameters of the non deuterated and of the TCNQ (deuterated) samples we can calculate the parameters of the TMTTF (deuterated) sample according to :

$$T_1^{-1} = 1/4 (3 T_{\text{TMTTF}}^{-1} + T_{\text{TCNQ}}^{-1}). \quad (22)$$

The results are reported in table I. We find, in particular that the behaviour of TCNQ is very similar in TMTTF-TCNQ and TTF-TCNQ. The low values for C_1 and C_2 in TMTTF-TCNQ(D_4) compared to those for TTF-TCNQ(D_4) figures 5, 6, can be ascribed to the weakness of the hyperfine coupling for the protons on the methyl groups. Otherwise, the T_1 frequency dependence on TMTTF-TCNQ does not exhibit a one-dimensional character significantly different from that of TTF-TCNQ.

Low temperature relaxation studies cannot be performed with confidence in TMTTF-TCNQ because of the additional contribution to T_1^{-1} provided by the methyl-groups rotation [23].

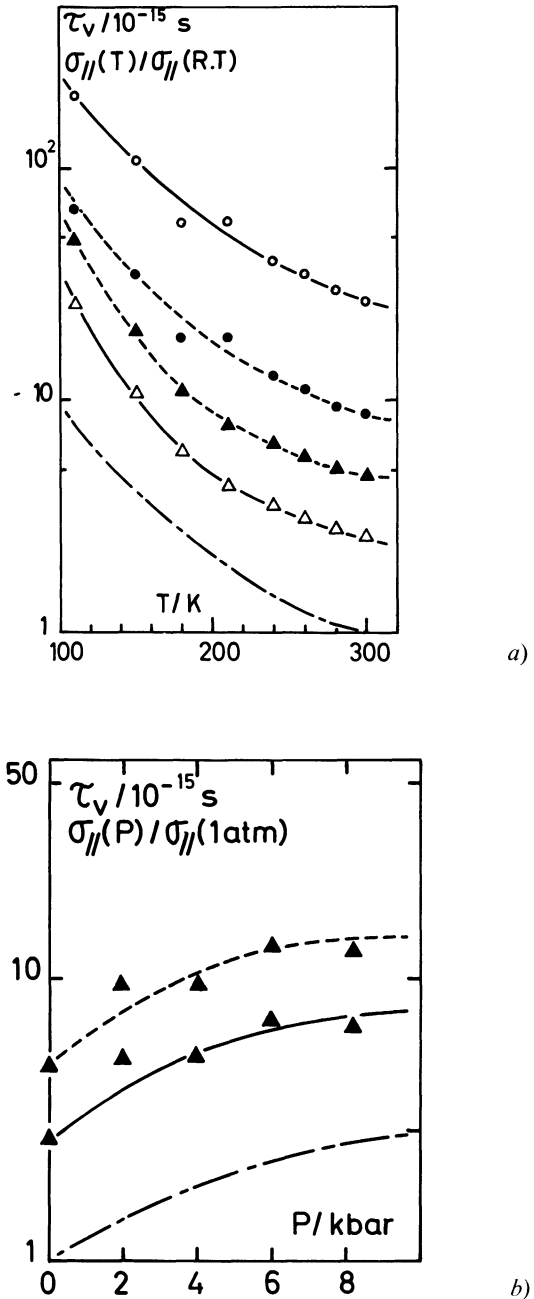


FIG. 8. — Temperature variation under atmospheric pressure (a) and pressure variation at 296 K (b) of the diffusion time τ_v in TTF-TCNQ(D_4) [O] and in TTF(D_4)-TCNQ [Δ]. For solid lines τ_v was derived using $\chi_F/\chi_Q = 3/2$ and for broken lines the ratio $7/3$ was used. Normalized longitudinal conductivities, $\sigma_{||}(T)/\sigma_{||}(300 \text{ K})$ and $\sigma_{||}(P)/\sigma_{||}(1 \text{ atm})$ are drawn by chain lines — — — — .

4. Discussion. — In section 3 we saw that the relaxation rate as function of frequency can be described by 3 parameters.

i) The escape time τ_\perp from the best fit with the function $g(\omega_e)$.

ii) The slope $C_1 = d(T_1 T)^{-1}/d(2 \omega_e \tau_\perp)^{-1/2}$ of the relaxation rate as function of field, which is due to the 1-D diffusion of electronic spins.

TABLE I

The three parameters C_1 , C_2 , τ_{\perp} , measured in TMTTF-TCNQ and TMTTF-TCNQ (D_4) at 300 K. C_1 and C_2 have been calculated for TMTTF(D_4)-TCNQ using the relation $T_1^{-1} = 1/4[3 T_{\text{TMTTF}}^{-1} + T_{\text{TCNQ}}^{-1}]$. The ambient pressure, room temperature parameters of TTF-TCNQ(D_4) and TTF(D_4)-TCNQ have also been given for reference.

	$C_1/10^{-2} \text{ s}^{-1} \text{ K}^{-1}$	$C_2/10^{-2} \text{ s}^{-1} \text{ K}^{-1}$	τ_{\perp}/s
TMTTF-TCNQ	1.5	0.8	5.5×10^{-12}
TMTTF-TCNQ(D_4)	1.4	0.45	4.4×10^{-12}
TMTTF(D_4)-TCNQ (calculated)	1.8	1.85	
TTF-TCNQ(D_4)	5.8	1.64	8×10^{-12}
TTF(D_4)-TCNQ	1.1	1.30	8×10^{-12}

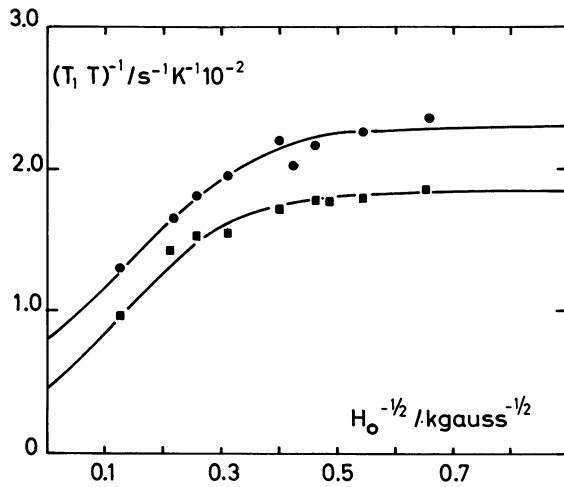


FIG. 9. — $(T_1 T)^{-1}$ vs. $H_0^{-1/2}$ at 296 K and atmospheric pressure in TMTTF-TCNQ [●] and in TMTTF-TCNQ(D_4) [■]. The solid lines are the theoretical curves, eq. (20), drawn with the parameters of table I.

iii) The limiting high-field relaxation rate

$$C_2 = (T_1 T)_{H \rightarrow \infty}^{-1},$$

attributed to the sum of the coherent scalar contribution of spin excitations at $q \approx 2 k_F$ and of the dipolar contribution (see sections 2.1, 2.3). However, the analysis of figures 7 and 8 we neglected the presumably small dipolar contribution to the relaxation rate.

4.1 THE ESCAPE TIME τ_{\perp} . — According to section 2.2, τ_{\perp} is the escape time from a given chain, and is related to the transverse electrical conductivity. Indeed figure 4 shows the closeness of the temperature and pressure dependences of these two quantities.

This is as expected, since in a diffusive transverse conductivity model [24] σ_{\perp} goes as :

$$\sigma_{\perp} = \frac{n_0 e^2 l^2}{k_B T} \tau_{\perp}^{-1}. \quad (23)$$

The number of carriers available for diffusion, n_0 , are restricted to the thermal layer at the Fermi level. Therefore, $n_0 \sim n(E_F) k_B T$ and the temperature and pressure dependences of σ_{\perp} and τ_{\perp}^{-1} should be identical ($\sigma_{\perp} \sim \tau_{\perp}^{-1}$) as shown in figures 4a, 4b.

The NMR escape time, and the conductivity jump time, are not completely identical, for the following reason : In the NMR experiments the escape time from TCNQ chains $\tau_{\perp}(Q)$ and from TTF chains $\tau_{\perp}(F)$ are measured independently (by the selective deuteration). These escape times are sums of contributions from jumps between similar chains (TCNQ \rightarrow TCNQ, denoted QQ and TTF \rightarrow TTF, denoted FF) and jumps between dissimilar chains (TCNQ \rightarrow TTF ; QF, TTF \rightarrow TCNQ ; FQ).

Thus (Fig. 10)

$$\begin{aligned} \tau_{\perp}^{-1}(Q) &= 2 \tau_{\perp}^{-1}(QQ) + 2 \tau_{\perp}^{-1}(QF) \\ \tau_{\perp}^{-1}(F) &= 2 \tau_{\perp}^{-1}(FQ) + 2 \tau_{\perp}^{-1}(FF) . \end{aligned} \quad (24)$$

On the other hand, the electrical conductivity in the c -direction is given by the sum of the conductivity of the arrays of TCNQ chains, and of TTF chains :

$$\begin{aligned} [n_Q(E_F) + n_F(E_F)] \tau_c^{-1} &= \\ &= n_Q(E_F) \tau_{\perp}^{-1}(QQ) + n_F(E_F) \tau_{\perp}^{-1}(FF) \end{aligned} \quad (25)$$

where $n_Q(E_F)$, $n_F(E_F)$ are the densities of states on the TCNQ, TTF chain. The electrical resistivity in the a -direction is the sum of the resistivities due to the TCNQ \rightarrow TTF and TTF \rightarrow TCNQ jumps :

$$\begin{aligned} [n_Q(E_F) + n_F(E_F)]^{-1} \tau_a &= \\ &= n_Q(E_F)^{-1} \tau_{\perp}(QF) + n_F(E_F)^{-1} \tau_{\perp}(FF) \end{aligned} \quad (26)$$

because the layers of TCNQ's and of TTF's alternate (Fig. 10). Since the a and c axes are not perpendicular, but at an angle $\beta = 104^\circ$, they are not principal axes of the conductivity tensor. But since the uncertainty in the conductivity is rather large, we shall ignore the deviation of β from $\pi/2$. By detailed balance we derive,

$$n_Q(E_F) \tau_{\perp}(QF)^{-1} = n_F(E_F) \tau_{\perp}(FQ)^{-1}. \quad (27)$$

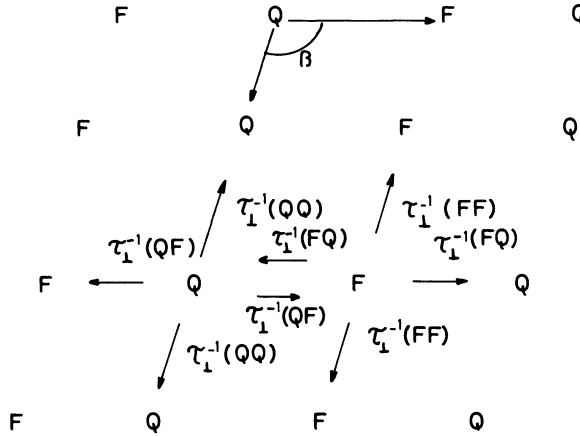


FIG. 10. — A schematic representation of the different escape times in the a - c plane.

Thus, in principle, if we know $n_Q(E_F)/n_F(E_F)$, $\tau_\perp(Q)$, $\tau_\perp(F)$, σ_{aa} , σ_{cc} we should be able to determine $\tau_\perp(QQ)$, $\tau_\perp(FF)$, $\tau_\perp(QF)$, $\tau_\perp(FQ)$, and check the consistency of eq. (24), (25), (26), (27) as well. However, due to the experimental errors of σ_{aa} , σ_{cc} which are quite large [25], the uncertainty in $n_Q(E_F)/n_F(E_F)$ and $\tau_\perp(Q)$, $\tau_\perp(F)$ (particularly at 150 K), we shall not attempt such a procedure.

Since $n_Q(E_F)/n_F(E_F) \approx 2/3$, [19] from (27) $\tau_\perp(QF)$ should be about 3/2 times shorter than $\tau_\perp(FQ)$. Experimentally (Fig. 4a) $\tau_\perp(Q)$ is only about 15 % shorter than $\tau_\perp(F)$. It is hard to account for this small discrepancy by a $\tau_\perp(FF)$ term, since from the structure and estimates of transfer integrals the direct coupling between TTF molecules in the c -direction should be very weak [26, 27].

The slightly stronger temperature dependence of σ_{cc} , compared with σ_{aa} , may be accounted for by slightly different values of τ_v . The coherence between ψ_1 and ψ_2 (section 2.2) is destroyed by scattering either on chain 1 or on chain 2, and therefore

$$\tau_v^{-1} = \tau_v^{-1}(1) + \tau_v^{-1}(2). \quad (28)$$

Thus the value of τ_v for TCNQ \rightarrow TTF tunnelling, $\tau_v^{-1}(Q) + \tau_v^{-1}(F)$ may be different from the value for TCNQ \rightarrow TCNQ tunnelling, $2 \tau_v^{-1}(Q)$. A better conductivity on the TCNQ chains [i.e. $\tau_v(Q)$ longer than $\tau_v(F)$], in accord with the thermoelectric power [28] and Hall effect [29], particularly at low temperatures, may account for this small deviation.

In conclusion we can say that the agreement between the temperature and pressure dependences of σ_{aa} , σ_{cc} and of $\tau_\perp^{-1}(Q)$, $\tau_\perp^{-1}(F)$ is indeed very good, bearing in mind all the complicating factors involved.

4.2 THE DIFFUSION CONSTANT AND ENHANCEMENT FACTOR. — The slope $C_1 = d(T_1 T)^{-1}/d(2 \omega_e \tau_\perp)^{-1/2}$ is shown in figure 5. According to section 2, C_1 is a product of 4 factors : the bare Korringa relaxation rate, the spin diffusion time $\tau_v^{-1/2}$, the escape time $\tau_\perp^{1/2}$

and the enhancement factor $K_0(\alpha)$. The Korringa relaxation rate can be determined from the measured hyperfine constant [21, 22] and spin susceptibility [18] and found to be $7 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1}$ for TTF-TCNQ(D_4) and $2 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1}$ for TTF(D_4)-TCNQ (at 300 K). Besides the temperature dependence of the Korringa product, $\chi_s^2 T_1 T$, the most striking feature of the experimental results is the strong temperature (and pressure) dependence of the product

$$\sqrt{\frac{\tau_\perp}{\tau_v}} K_0(\alpha).$$

Since in a 1-D model $K_0(\alpha)$ has no reason to be strongly temperature dependent we may try to account for the temperature dependence of

$$\sqrt{\frac{\tau_\perp}{\tau_v}}$$

in a number of ways. The diffusion time τ_v corresponds to a spin diffusion constant of the spin correlation function, eq. (6), namely $D \sim \tau_v/\chi_s^2$.

i) The *Big U* model. We can assume that there is strong electron-electron scattering due to the Coulomb interaction U , which however does not affect the resistivity since the total momentum of the electron system is conserved in these collisions. In this case, for $U \gg 4 t_\parallel$ [30], $D = 2 \pi / \hbar b^2$; t_\parallel^2/U with the Hubbard Hamiltonian, and D is nearly temperature independent in this limit, in contradiction with the factor ~ 40 increase seen at low temperature.

ii) Alternatively we may assume that $U \ll 4 t_\parallel$ in which case the electron-electron collision time is temperature dependent. In a 3-D system, this mechanism (Baber scattering) [31] follows a T^2 law, but in 1-D the temperature dependence is linear [32] also in contradiction with the experimental data of resistivity [13, 33, 35].

iii) The free electron model. Let us assume that D is given by the free-electron value $D = v_F^2 \tau_v$, where τ_v is the collision time for scattering by lattice vibrations [36] or spin fluctuations [37] and which determines the longitudinal conductivity $\sigma_\parallel = ne^2 \tau_v/m^*$. In this case the temperature and pressure dependence of τ_v follow that of σ_\parallel in agreement with the experiments, figures 8a, 8b. For this reason we favour iii).

The derivation of the enhancement factors $K_{2k_F}(\alpha)$ and electron scattering time τ_v of individual chains has been performed for two ratios of the susceptibility χ_F/χ_Q , 3/2 [19] and 7/3 [20]. This is summarized in figures 7 and 8.

Since $\tau_v(\text{TTF})/\tau_v(\text{TCNQ})$ is proportional to the fourth power of $n_Q(E_F)/n_F(E_F)$, and this ratio is not known with certainty, the uncertainty in the ratio of relaxation times is rather large, and figure 8 should be regarded as semi-quantitative only.

In order to get good agreement between the values

of τ_v derived from this NMR experiment and the conductivity [13], thermopower [28] and Hall effect [29] measurements we favour the ratio $\chi_F/\chi_Q = 7/3$.

With this assumption the enhancement factor is larger on the TCNQ chain than on TTF (Fig. 7a). On both chains they increase at low temperature. Assuming the temperature variation to be :

$$F(2 k_F, T) = \frac{1}{2} \ln \frac{4.56 T_F}{T} \quad (29)$$

and using for T_F a value of 1 000 K, the value of α varies from $\alpha = 0.70$ at 300 K to 0.54 at 150 K for the TCNQ chain, according to figure 7a (with 0.59 carriers/molecule) [38]. The latter value of T_F corresponds to a bandwidth $4 t_{\parallel}$ of 0.45 eV. This bandwidth value is in agreement with the molecular orbital calculations [27, 39], together with the optical data [40] and various experimental investigations for the TCNQ chain [41].

The TTF bandwidth value is not known with great accuracy from extended Hückel calculations [27]. It lies somewhere between 0.2 and 0.72 eV. Thus, not much can be said about this stack. If $T_F = 1\,000$ K is taken, the NMR analysis provides $\alpha = 0.66$ at 300 K (but may be $T_F < 1\,000$ K). Therefore, as far as correlations are concerned we believe that in TTF-TCNQ, electron-electron interactions play similar roles on both stacks.

Since the exact shape of the Lindhard function eq. (29) depends on the electron band description slightly, we cannot say more about the exact temperature dependence of α . But we can say conclusively that electron-electron correlations are significant on both chains with $\alpha \approx 0.7$ corresponding in the case of TTF-TCNQ to a ratio $U/4 t_{\parallel} \approx (0.8-1)$ under atmospheric pressure at 300 K. For TCNQ, $U/4 t_{\parallel}$ is equal to 0.9. With the choice $4 t_{\parallel} = 0.45$ eV for the TCNQ chain the enhancement of the spin susceptibility derived from [18] and a ratio $\chi_F/\chi_Q = 7/3$, becomes ≈ 3 . This enhancement is in good agreement with the one which can be derived from a correlation parameter $\alpha = 0.7$.

The enhancement factors decrease under pressure, figure 8, the decrease being slightly larger for the TCNQ chains than for the TTF chains.

Accordingly the electron correlation parameters decrease by $\approx 5\%$ under a pressure of 8 kbar.

As the pressure dependence of the band width, $4 t_{\parallel}$, is rather weak [42, 43] we can conclude from the NMR data that the electron-electron repulsion seems to be only weakly pressure dependent. This result is not in good agreement with the discussion of the pressure dependence of the spin susceptibility, in which it was concluded that U decreases substantially under pressure [37].

However, we should notice that the estimation of $K_{2k_F}(\alpha)$ under pressure depends appreciably on the pressure dependence of χ_s^2 through eq. (21). In parti-

cular we presume we may have overestimated the pressure dependence of χ_s at 8 kbar and therefore underestimated the pressure dependence of $K_{2k_F}(\alpha)$ since the analysis in this work has been performed using the pressure dependence of χ_s , which was actually only measured up to 4 kbar for TTF-TCNQ.

We may point out however, that the value $U/4 t_{\parallel} \approx 0.8-1$ found through NMR experiments here is in good agreement with the ratio 1.1 which has been derived independently from an analysis of the susceptibility based on the Shiba-Pincus model [44, 45] (see also the discussion section).

The values of τ_v at 300 K under atmospheric pressure (for $\chi_F/\chi_Q = 7/3$) $\tau_v(\text{TTF}) = 8.5 \times 10^{-15}$ s and $\tau_v(\text{TCNQ}) = 4.6 \times 10^{-15}$ s are in relatively good agreement with the electron scattering time

$$\tau = 3.1 \times 10^{-15} \text{ s}$$

derived from the optical reflectance measurements [46]. The thermopower [28] and Hall effect [29] measurements indicate that $\tau_v(\text{TCNQ}) > \tau_v(\text{TTF})$. Here, due to the large uncertainty in $n_Q(E_F)/n_F(E_F)$, the present values cannot be considered to be determined to better than a factor of two, and we do not claim here that from the NMR measurements,

$$\tau_v(\text{TTF}) > \tau_v(\text{TCNQ}).$$

4.3 THE DIPOLAR RELAXATION. — In the previous analysis the dipolar contribution to the relaxation rate was neglected. We shall now try and give some estimation of this contribution with the assumption of $2 k_F$ non-diffusive components (eq. (21), (21'))

$$C_1/C_2 = C_1^A/(C_2^A + C_1^B + C_2^B) \approx C_1^A/(C_2^A + C_1^B) \quad (30)$$

since $C_1^B \gg C_2^B$.

We derive therefore, at room temperature, from figures 5a, 6a and eq. (30) a ratio $(B/A)^2 \approx 0.3$ for TCNQ chains and $(B/A)^2 \approx 0.03$ for TTF chains.

The ratio 0.3 found for the protons belonging to the TCNQ chain is in very good agreement [47] with an Overhauser enhancement of +200 measured in TTF-TCNQ.

The weak temperature-dependence of the high-field relaxation rate is very evident in figure 2. Since theoretically the dipolar mechanism would be strongly temperature dependent (because of the strongly temperature dependent factor $(\tau_{\perp}/\tau_v)^{1/2}$), we see that we must reject it as the dominant high-field relaxation mechanism. Relaxation by magnetic impurities cannot account for the observed high-field relaxation rate either, first because the observed rate is considerably faster than the high-pressure relaxation rate, and second because its temperature dependence, down to helium temperatures, is too strong. Thus, unless we can find some alternative temperature and pressure dependent relaxation mechanism, such as relaxation by molecular motions, we must attribute the high-field relaxation to a non-diffusive $2 k_F$ component.

This assignment forces us to attribute the low-field relaxation rate to the $q \simeq 0$ component only, and this necessitates a high enhancement factor and thus a large value of $U/4 t_{\parallel}$.

So, we feel justified *a posteriori* in neglecting the dipolar contribution to the relaxation rate which represents at most for the TCNQ chain $\sim 1/3$ of the scalar contribution.

The temperature dependence of C_2 is much weaker than that of C_1 , figures 6a, 5a. This is in agreement with the ratio C_1/C_2 varying with temperature as

$$\sqrt{\frac{\tau_{\parallel}}{\tau_{\perp}}} \frac{K_0(\alpha)}{K_{2k_F}(\alpha)}.$$

If we now relax the assumption that the $2 k_F$ components are non diffusive (see section 2.1), the relationship $C_1/C_2 = (A/B)^2$ holds. Thus the temperature and pressure dependence of C_2 should reflect those of C_1 . It seems however that we must discard this possibility since between 300 K and 100 K, C_2 varies by a factor 2 whereas C_1 varies by a factor 15.

A salient feature of all the dipolar relaxation mechanisms, is an anisotropy of T_1 , which should depend on the orientation of the magnetic field with respect to the vector connecting the two spins. For a powder, some distribution in the values of T_1 should be observed. Experimentally, a perfectly exponential recovery of the magnetization was observed over 2 decades. Perhaps the orientation dependences due to the electron-proton interaction in TCNQ, electron-proton interaction in TTF; proton-proton interaction in TCNQ, and proton-proton interaction in TTF, cancel each other due to the rather different orientations of the respective vectors. Work on single crystals may be useful to check this point.

5. Conclusion. — **5.1 ELECTRON-PHONON INTERACTION VERSUS ELECTRON-ELECTRON INTERACTION IN TTF-TCNQ.** — One important consequence of the discussion in section 4.2 is the finding of a rather weak decrease of the parameter α with temperature. We observed a $\approx 20\%$ decrease between 300 K and 150 K. The parameter α is proportionnal to the real part of the uniform static susceptibility, $\chi'_0(0, 0)$. Actually, the decrease of the experimental spin susceptibility χ_s between 300 and 150 K amounts to 30 % [18] which is somewhat larger than the change of α . We can however reconcile both experimental results using the following interpretation : Assume that the *bare* susceptibility $\chi'_0(00)$ is temperature dependent, due to the existence of CDW fluctuation effects above the phase transition temperature or possibly other factors, then the effect of correlations can be treated by the RPA, namely,

$$\chi_s(T) = \frac{\chi'_0(00)}{1 - U\chi'_0(00)} \quad (31)$$

giving rise to a stronger temperature dependence for χ_s than for $\chi'_0(00)$.

If we use the results of section 4.2 for α we find, from (31) a temperature dependence of χ_s between 300 and 150 K, in very good agreement with the experiment [18].

This work indicates that CDW's might play a certain role above the Peierls transition (of the TCNQ chain at 53 K). But this role is much weaker than that claimed by the Pennsylvania group [18, 20] which attributed the whole temperature dependence to CDW fluctuations effects, with a mean-field temperature much higher ($T_P^{\text{MF}} \approx 300$ K) than the actual phase transition temperature. A salient result of our NMR investigation is that CDW fluctuations and electron correlation effects are nearly equally important in TTF-TCNQ. This is also an indication that the mean-field Peierls temperature may be only a few degrees above the actual phase transition [4, 48].

The discussion of the NMR results has been based on a model which neglects all electron-electron interactions except the *on site* interaction (Hubbard model). Through this model a value $U/4 t_{\parallel} \approx 0.9$ has been derived.

Admittedly, the deviation of the momentum distribution from the Fermi function to a one more consistent with Fermi liquid theory decreases the jump at E_F and thus the peak in the Lindhard function derived in RPA [49].

Thus, the use of the RPA to derive the value of $U/4 t_{\parallel}$ from the NMR data is somewhat uncertain and it is likely that due to the many-body effects, the RPA underestimates this parameter and in reality α could be somewhat larger than 0.7 in TTF-TCNQ (see also the discussion in section 4.2). The point of view we have taken in this work, that of a strong influence of the electron correlations on electron susceptibility is a better approach than the Shiba-Pincus model [37]. However, with the neglect of charge fluctuations and the use of a 1-D antiferromagnetic Hubbard calculation a parameter

$$U/4 t_{\parallel} = 1.1$$

was derived (for TMTTF-TCNQ). This value is indeed in good agreement with the ratio derived in the present work for TTF-TCNQ. It is a further confirmation for the role played by electron correlations in TTF-TCNQ.

An early understanding of the NMR properties attempted to discuss the low frequency T_1^{-1} enhancement in terms of the *big U* model and led to fairly large values of $U/4 t_{\parallel}$ [4]. However, the recent experimental data presented in this work (temperature and frequency dependence of T_1) have confirmed the inability of the Hubbard model [30] to describe the diffusion constant (see sect. 4.2).

Finally we emphasize that the present work is in good agreement with the recent development of the Peierls-parquet theory [50]. It was shown there that

the introduction of the Coulomb interaction U besides the phonon mediated electron-electron attraction V does not suppress the existence of a Peierls transition, provided that $V > U$. We can now say with some confidence that the inequalities $V > U > t_{\parallel}$ are satisfied in TTF-TCNQ.

However in other charge transfer salts the situation where the Coulomb interaction is dominant over the electron-electron attraction V may occur (for example NMP-TCNQ). In that case it is not obvious that the lattice Peierls transition will persist any longer. Therefore we shall try in the next subsection to present an experimental unified description of Quasi-One-Dimensional Conductors which includes both cases $U > V$ or $U < V$ of the theory [50].

5.2 UNIFIED DESCRIPTION OF QUASI-ONE-DIMENSIONAL CONDUCTORS. — Several quasi-1-D metals are known; the A-15's; (SN)_x; KCP and similar inorganic salts; organic charge transfer complexes like TTF-TCNQ, HMTSeF-TCNQ, NMP-TCNQ, and others. The question arises whether each such family should be regarded on its own, or whether a unified description for all these materials is possible. A preliminary attempt for a unified description, in form of a $t_{\perp}/t_{\parallel} - U/t_{\parallel}$ diagram (*Utopia*) was presented in ref. [4]. This presentation was motivated by the dramatic effect of hydrostatic pressure on the properties of KCP and TTF-TCNQ. The changes brought about by the application of pressure are so large that they may exceed the differences between the properties of the materials at ambient pressure. That description was somewhat oversimplified since it ignored scattering of the electrons by static defects, vibrations, etc...

The reason underlying such a picture is the following: the description of Q-1-D metals is dominated by two questions: (i) Can the electronic properties be described by Mean-Field theory (at least approximately), or are the fluctuations inherent to 1-D systems so strong, that such a description breaks down completely? (ii) Is the transverse motion of the electrons coherent or diffusive?

As for (i), some anomalies in the A-15's were associated with 1-D fluctuations quite some time ago [9, 5, 52] but t_{\perp}/t_{\parallel} is big enough there [53, 54] to make MF theory a rather good approximation [55]. In TTF-TCNQ, it was suggested at one time [56] that fluctuations depress T_p considerably below the MF value, however the coupling between chains in TTF-TCNQ seems to be sufficiently strong to prevent such a depression [3, 48, 57]. On the other hand, in KCP the 1-D fluctuations appear to be strong, and their effect is demonstrated in a dramatic way by the pressure experiment [58] where a transition from a fluctuating state ($P = 0$) to a state described by MF theory ($P > 35$ kbar) is induced. The dominant parameter here is [48] (t_{\perp}/t_{\parallel}) (ξ/b). When this number is large compared with unity, MFT is valid, while if it is small, fluctuations play a dominant role.

As for (ii), in the A-15's and (SN)_x the transverse motion is coherent [59]; in KCP and TTF-TCNQ it is diffusive [24, 60], and in HMTSeF-TCNQ it changes continuously from diffusive above 200 K to coherent below 60 K, as demonstrated by the Hall effect [61]. The dominant parameter here is $t_{\perp}\tau_v/\hbar$; if it is large compared with unity, the transverse motion is coherent, while if it is small, it is diffusive. The proof goes as follows:

Assume that at time $t = 0$, the electron is on chain (or chain family) 1, and that the donor-acceptor tunnelling matrix element is given by t_{\perp} . Then at time t the electron wave function is given by:

$$\psi(t) = \psi_1 \cos t_{\perp} t/\hbar + \psi_2 \sin t_{\perp} t/\hbar \quad (32)$$

and $\psi(t)$ builds up coherently on chain 2. One factor that arrests this coherent build up is the scattering of the electron, either on chain 1 or on chain 2, characterized by τ_v .

If $t_{\perp}\tau_v/\hbar > 2\pi$ the wave function $\psi(t)$ (32) oscillates back and forth several times between the chains, and we can consider it to be a coherent superposition of ψ_1 and ψ_2 .

However, if τ_v is short enough so that $t_{\perp}\tau_v/\hbar < 1$, $\psi(t)$ has no time to build up on chain 2 before its phase is destroyed, and we do not have a coherent superposition, but rather a diffusive motion between the two chains.

Thus, we can expect the change over from the diffusive to coherent motion to take place at a temperature at which $\tau_v \approx \hbar/t_{\perp}$. Thus, a natural description is one in t_{\perp}/E_F vs. $\hbar/E_F\tau_v$ plane; i.e. *one dimensionality vs. cleanliness* ($\hbar/E_F\tau_v \sim b/\Lambda$, very roughly, where b is the intermolecular distance). In this plane (Fig. 11), we have 5 regions: (a) Mean field coherent (left hand, top). Here we just have a very anisotropic (3-D or 2-D) metal, (A-15, (SN)_x, HMTSeF-TCNQ below 60 K). (b) Fluctuating coherent (left hand, near bottom). Here the electron must be described by a wavepacket extending over several chains, but fluctuations are very strong. (c) Mean field diffusive (centre top). Here we have a 1-D metal that can be described by MFT. The 3-D band structure plays no role since the phase relation between the electron wave function on different chains has no meaning here (TTF-TCNQ; HMTSeF-TCNQ above 200 K; KCP under pressures in excess of 30 kbar). (d) Fluctuating diffusive (centre bottom). Here the electrons are localised on their respective chains, and fluctuations are strong (KCP at $P = 0$). (e) Overall diffusive (right). Here the electrons move in a diffusive way along the chains as well. The Fermi energy and wave-vector of the electrons lose their meaning, and it is a question of semantics whether we denote this state as *metallic*.

NMP-TCNQ has been located in this region because of its poor room temperature conductivity and of the observed frequency dependence of T_1 very similar to that of TTF-TCNQ [62, 30].

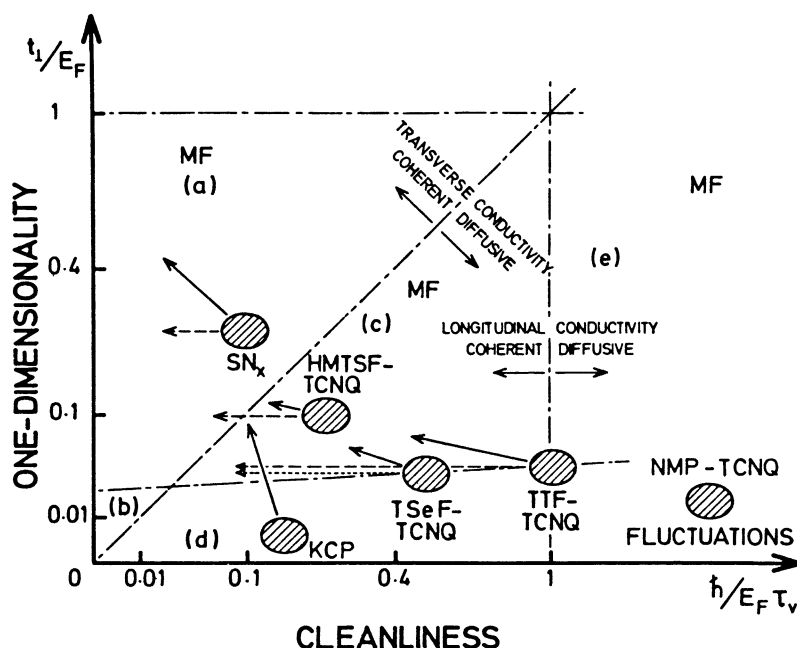


FIG. 11. — A *One-dimensionality vs. cleanliness* diagram for the description of quasi 1-D conductors. $\sqrt{t_{\perp}/E_F}$ and $\sqrt{\hbar/E_F \tau_v}$ representations have been used for both axis. While TTF-TCNQ appears in this diagram to be on the borderline between *mean field* and *fluctuating* regions, interchain Coulomb interactions ignored here place it well within the *mean field* region. The borderline between *mean field* and *fluctuations* regions hits the y-axis at $t_{\perp}/E_F \approx b/\xi$. Continuous arrows show the effect of pressure (10 kbar for the organics, 30 kbar for KCP and SN_x). Broken arrows show the effect of cooling to ~ 60 K.

Pressure reduces the *one dimensionality* by increasing t_{\perp} (mainly in KCP), and/or improves the cleanliness by increasing τ_v (in TTF-TCNQ, HMTSeF-TCNQ) and does so in a very *clean* and controlled way [4]. The complexity of the A-15's is well illustrated by this diagram. Various bands possess values of t_{\perp}/E_F from about 1/10 to much more than 1; values of E_F (i.e. the widths of peaks of the density of states) also vary widely between bands [54] as do the values of τ_v . Thus the various bands can cover practically every region on this graph.

This description takes into account electron spin fluctuations scattering by the Coulomb interactions (U) [37], fixed defects [63, 64] and librions [36], by their combined contribution to τ_v^{-1} , but ignores Coulomb coupling between chains [65, 66] as well as elastic coupling between chains [67] which also help to make the MF approximation valid, and play an important role in TTF-TCNQ [36] since $(t_{\perp}/t_{\parallel}) (\xi/b)$ is not quite large enough all by itself to make the MF approximation valid.

Such a description ignores many factors, such as the occupation of the band (a small occupation may play a role, as in the Labbe-Friedel-Barišić model of the A-15's [68]); the phonon frequency ω_0/E_F [69, 70]; the electron-phonon coupling constant λ (or T_p/E_F) [71]; the ratio of the electron-phonon coupling constants at $q = 0$ and $q = 2 k_F$ (*geology*; [72, 73]); effects of intrachain Coulomb coupling (in addition to reducing τ_v) [32, 74, 75]; the differences between the two chains (τ_v , as well as the other parameters, are different for the donor and acceptor chains);

some effects of fluctuations [76, 69]; anharmonicities and solitons [77, 78]; some effects of the disorder [79], etc. Still, we feel that this description is useful for an overall view of quasi-one dimensional metals. Obviously, much work remains to be done in the near future, especially on the magnetic properties of the conducting charge-transfer salts. In particular, it would be of interest to know more about the relative correlations of TTF and TCNQ chains. However, we hope that this work on NMR, together with its interpretation has clarified the question about the role of electron-electron interactions in TTF-TCNQ. This problem has been (and apparently is still) the subject of some controversy in the scientific community.

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Appendix : derivation of the Korringa relation in 1-D systems. Assuming A_q independent of q , the relaxation rate is given by

$$(T_1 T)^{-1} = \gamma_N^2 k_B |A|^2 \sum_{\mathbf{q}} K^0(\mathbf{q}) \frac{1}{\omega_N} \Gamma''(\mathbf{q}, \omega_N)$$

where

$$K^0(\mathbf{q}) = \frac{1}{|1 - \alpha F(q)|^2}, \quad \alpha = U\chi'_0(00)$$

and

$$\Gamma''(\mathbf{q}, \omega) = -\pi \sum_{\mathbf{k}} (f_{\mathbf{k}+\mathbf{q}\downarrow} - f_{\mathbf{k}\uparrow}) \delta(\hbar\omega + \varepsilon_{\mathbf{k}\uparrow} - \varepsilon_{\mathbf{k}+\mathbf{q}\downarrow})$$

$$\varepsilon_{\mathbf{k},\sigma} = \varepsilon_{\mathbf{k}} + \sigma \mu_B H_0$$

then

$$\sum_{\mathbf{q}} K^0(\mathbf{q}) \Gamma''(\mathbf{q}, \omega) = \pi \sum_{\mathbf{q}} \sum_{\mathbf{k}} \left\{ - \left[f\left(\varepsilon_{\mathbf{k}} + \frac{\hbar\omega_e}{2} + \hbar\omega\right) - f\left(\varepsilon_{\mathbf{k}} + \frac{\hbar\omega_e}{2}\right) \right] \right\} \times \delta(\hbar(\omega_N + \omega_e) + \varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}+\mathbf{q}}).$$

Changing \sum into integration and using $\varepsilon_{-\mathbf{k}} = \varepsilon_{\mathbf{k}}$ we get

$$\sum_{\mathbf{q}} K^0(\mathbf{q}) \Gamma''(\mathbf{q}, \omega) = \pi \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}_F}) \hbar\omega_N$$

$$= \frac{\pi \delta(k - k_F)}{\left| \frac{\partial \varepsilon_{\mathbf{k}}}{\partial k} \right|_{k_F}} \hbar\omega_N$$

which is valid in the limit of

$$\hbar\omega_e \ll E_F, k_B T.$$

Therefore

$$\sum_{\mathbf{q}} K(\mathbf{q}) \Gamma''(\mathbf{q}, \omega) = 2\pi \left(\frac{L}{2\pi} \right) \frac{\hbar\omega_N}{\left| \frac{\partial \varepsilon}{\partial k} \right|_{k_F}} \sum_{\mathbf{q}} K^0(\mathbf{q}) \delta \{ \hbar(\omega + \omega_e) + \varepsilon_{\mathbf{k}_F} - \varepsilon_{\mathbf{k}_F+\mathbf{q}} \}.$$

As $\hbar\omega_e \ll E_F$, energy conservation requirement $\hbar(\omega_N + \omega_e) + \varepsilon_{\mathbf{k}_F} - \varepsilon_{\mathbf{k}_F+\mathbf{q}} = 0$ imposes the solutions $\mathbf{q} = 0$ and $\mathbf{q} = -2\mathbf{k}_F$

$$\delta \{ \hbar(\omega_N + \omega_e) + \varepsilon_{\mathbf{k}_F} - \varepsilon_{\mathbf{k}_F+\mathbf{q}} \} = \frac{1}{\left| \frac{\partial \varepsilon}{\partial k} \right|_{k_F}} \{ \delta(\mathbf{q}) + \delta(\mathbf{q} + 2\mathbf{k}_F) \}.$$

Introducing the density of states at Fermi level

$$D(\varepsilon_k) = \left(\frac{L}{2\pi} \right) \frac{2}{\left| \frac{\partial \varepsilon}{\partial k} \right|_{k_F}}$$

the relaxation rate becomes

$$(T_1 T)^{-1} = \gamma_N k_B |A|^2 \hbar\pi [D(E_F)]^2 \frac{1}{2} [K_0^0 + K_{2k_F}^0] \quad (\text{A.1})$$

defining the enhancement factor $K_{\mathbf{q}}$ by

$$K_{\mathbf{q}} = (1 - \alpha)^2 K_{\mathbf{q}}^0.$$

Eq. (A.1) becomes equivalent to the eq. (5) of section 2.

Note added in proof by : S. Alexander, Racah Institute of Physics, Hebrew University, Jerusalem. After receiving the proofs, we found out that the argument and conditions given for the derivation of eqs. (16) and (17) were misleading and in part wrong. Since one is dealing with transitions between continuum states on both chains, the Golden Rule in fact always applies. The longitudinal scattering does however lead to a reduction in the matrix element between states of the continuum. The correct matrix element is $t_1^2/(n(E_F)/\tau_v)$ resulting from incoherent mixing of states over a width $1/\tau_v$ and not t_1^2 .

Substitution in the standard Golden Rule expression the matrix element squared times the density of final states $n(E_F)$ leads to eq. (16) for all temperatures.

Note also that this expression is independent of volume. Thus eqs. (16) and (17) are correct but the derivation eq. (15) should be disregarded.

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