1. Introduction. — High pressure measurements [1] have had a strong impact on the experimental study of the electronic properties of the conducting charge transfer salts of the TTF-TCNQ family. In particular, the very large pressure coefficients found in a variety of physical properties suggested the inability of the one-electron theories to provide a proper understanding of the static susceptibility and resistivity [2]. On one hand, the importance of the intra-chain Coulomb interactions in explaining the magnetic properties of TTF-TCNQ has been emphasized by several authors [3, 4, 5]. Moreover, inclusion of inter-chain Coulomb coupling is compatible with charge density (CD) phase transitions [6, 7, 8]. However, the important room temperature effects observed in the NMR relaxation rate of TTF-TCNQ, which will be discussed in the next section, are difficult to understand with just these Coulomb interactions. On the other hand, conventional Peierls treatments using a phonon mediated electron-electron interaction happen to be fairly consistent with the existence of structural phase transitions, but have been unable so far to provide a satisfactory explanation of the magnetic properties.

The purpose of this paper is to propose a theoretical support, combining both electron-electron and electron-phonon interactions, to the structural properties and the reinterpretation of the magnetic properties of TTF-TCNQ. In section 2 we develop the experimental background required for the theoretical model.
treated in section 3. The results are discussed and limits set to the validity of the model in the following sections.

2. Experimental determination of $\text{Im } \chi(2 k_F)$. — Cooper [9] has recently drawn attention to the fact that, when corrected for the effect of thermal expansion, the temperature dependence of the constant $b$-axis resistivity is strongly reduced from the observed $T^{2.3}$ law at atmospheric pressure. The actual constant volume resistivity along the $b$-axis has been derived in some detail by Friend et al. [10]. It is characterized by a linear power law, particularly above 150 K. In fact, similar constant volume corrections must be applied for all strongly pressure dependent quantities.

In this article we wish to draw attention to the constant volume behaviour of physical quantities derived from the NMR experiments. The relaxation rate of protons in selectively deuterated samples of TTF-TCNQ has been studied as a function of temperature, pressure and applied magnetic field [11]. It was thus shown that only backward ($q = 2 k_F$) and forward ($q = 0$) scatterings contribute to the nuclear relaxation induced by the modulation of the hyperfine field in one-dimensional conductors. The diffusive character of the $q \sim 0$ spins excitations of finite lifetime electrons ($\text{Im } \chi(q \sim 0) \approx Dq^2$) leads in one dimension to a magnetic field dependence of the relaxation rate, $T_1^{-1} \sim H_0^{1/2}$. The effect of the $q = 0$ spin excitations is dominant upon the effect of the $q = 2 k_F$ excitations in low fields, namely $H_0 \lesssim 30 \text{ kOe}$. However, the non-diffusive $q = 2 k_F$ spin excitations have been shown by experiment to dominate the relaxation at high fields. A very careful field dependence study has therefore allowed a direct experimental access to the determination of the imaginary part of the spin density (SD) response function at $q = 2 k_F$, $\text{Im } \chi(2 k_F)$, which is in turn proportional to the coefficient $C_2$ of reference [11]. The main experimental feature of this article is a non-trivial constant volume temperature dependence of $\text{Im } \chi(2 k_F)$ since, as shown in [11], $C_2$ is strongly pressure dependent.

We shall now develop the procedure we have used to achieve the constant volume reduction. Reproduced on figure 1 is the constant pressure dependence of the experimental quantity

$$C_2/A^2 \approx \frac{\text{Im } \chi(2 k_F)}{(g\mu_B)^2 \hbar \omega},$$

where $A$ is the hyperfine interaction constant. Thus $\text{Im } \chi(2 k_F)$ depends only on the electronic properties of either chain considered. The striking features are the large value and the strong temperature dependence of $\text{Im } \chi(2 k_F)$, both behaviours not usually observed in normal metals [12]. Below 110 K we have used in figure 1 the temperature dependence of the $^{13}$C relaxation rate for the TCNQ chain [13] and the temperature dependence of the proton relaxation rate in TTF-TCNQ ($D_A$) samples for the TTF chain [14]. This is justified since it has been demonstrated [11] that at low temperature the dominant relaxation mechanism is that coming from the $q = 2 k_F$ spin excitations. We have drawn on figures the temperature dependence of $\text{Im } \chi(2 k_F)$ for two volume that of 300 K and that of 60 K. The $b$-axis parameter decreases by 2.3% between 300 K and 60 K. Therefore, the constant volume curves for the volume of 300 K (....) and for the volume of 60 K (-----). Plot of the constant pressure dependence of $\rho/T$ normalized at room temperature with the value of $\text{Im } \chi(2 k_F)$ for both chains (---). Data of reference [10] have been used in this figure, $\sigma (60 \text{ K})/\sigma (300 \text{ K}) = 25$. A typical value of $\text{Im } \chi(q)/(g\mu_B)^2 \hbar \omega$ in a normal metal should lie around 5 eV$^{-1}$. On figure 1, we notice that the temperature dependence of $\rho/T$ follows closely that of $\text{Im } \chi(2 k_F)$ even though a
decrease of the resistivity by a factor of 25 is now currently observed on good quality crystals. Actually the agreement is especially good for the TCNQ chain. This fact may not be entirely fortuitous since first, the conductivity in TTF-TCNQ is known to be electron-like above 60 K from thermopower [15]. Hall effect [16] and NMR [17] determinations, and secondly, because it has been suggested [18] that the resistivity could be of magnetic origin in these 1-D conductors, leading precisely to \( \rho/T \sim \text{Im} \chi(2k_F) \). Explanation of the resistivity is still controversial. We only make use of the analogy between pressure and temperature dependence of the resistivity and \( C_2 \), setting

\[
\frac{\partial \ln \sigma}{\partial P} \approx -\frac{\partial \ln 1/C_2}{\partial P},
\]

and otherwise following the procedure already used for the derivation of the constant-volume temperature dependence of the resistivity [10].

We now wish to comment on the curves of figure 1. There is no doubt that \( \text{Im} \chi(2k_F) \) exhibits a maximum in its intrinsic temperature dependence, the maximum on the 300 K volume curve being probably slightly below ambient temperature. We are reasonably confident in the constant volume profiles of the TCNQ chains and to a lesser extent in those of the TTF chains. But the message still remains the same, that is the existence of shallow maxima at constant volume for both chains.

3. Theory. — The task at hand is to develop a theoretical model which can explain the large values of \( \text{Im} \chi(2k_F) \), the occurrence of a maximum in the constant volume curves of figure 1, and the observed structural transition of TTF-TCNQ. The large values of \( \text{Im} \chi(2k_F) \) can easily be explained by invoking important intra-chain Coulomb interactions. Mean field [6], Parquet [19, 20, 21], or renormalization group [22, 7, 8] treatments indeed yield considerable spin density response enhancement in such cases. These are, however, divergent at low temperatures. This divergence can conceivably be prevented by the appearance of a pseudo-gap. We eliminate the possibility of a SD pseudo-gap, such as predicted by a 1-D Ginzburg-Landau theory, because we believe it is incompatible with the observed Peierls transition. The Parquet or Solymon renormalization group approaches seem much more suitable since they predict low temperature divergence in both SD and charge density (CD) responses, the former being dominant for repulsive intra-chain electron interactions. The maximum in the \( \text{Im} \chi(2k_F) \) constant volume curves cannot be explained by inter and intra-chain Coulomb forces only, within first order renormalization theory [7]. Second order renormalization can, however, predict such a maximum [8]. But it is our feeling that the ensuing constant volume temperature profile, whose maximum is governed by the weak backward-scattering inter-chain Coulomb interaction, is not so readily reconciled with figure 1 and especially the important room temperature effects. Moreover, the validity of second order renormalization theory is challenged by a number of people [23, 24]. The above considerations, plus the obvious involvement of phonons in the structural transition, lead us to focus on phonon mechanisms as a probable cause of the pseudo-gap. We thus adopted a strictly 1-D model Hamiltonian with both electron-electron repulsion and electron-phonon interaction.

Pseudo-gap effects have been studied in the absence of Coulomb interactions [25, 26, 27]. The effect of phonons in the presence of these interactions has been discussed by several people [6, 19, 21], but not in the context of pseudo-gaps. In the case of TTF-TCNQ, which has a Debye temperature \( \theta_D \approx 80 \text{ K} \), the static approximation [6, 27] can be used to great advantage for the temperature range of figure 1. The effect of the electrons on the phonons is reduced, in this limit, to the random phase approximation to the phonon propagator:

\[
D(k) = \frac{D_0}{1 - g^2 D_0 N(k)}
\]

where \( D_0 = \frac{2}{\theta_D} \) is the bare phonon propagator, \( g \) is the electron-phonon interaction, and \( N(k) \) is the CD response of the electron gas at wave number \( k \). The feed-back effect of the phonon on the electrons is not so simple. The correction to \( \chi(2k_F) \) and \( N(2k_F) \) to first order in \( g^2 \) is of the self-energy type. This suggests using the Migdal approximation to the self-energy [6, 27] of the electron propagator which, in the static approximation, is expressed as:

\[
\Sigma(p, i\omega_n) = -Tg^2 \int \frac{dk}{2\pi} D(k) G(p + k, i\omega_n),
\]

where \( T \) is the temperature, \( \omega_n \) is the Matsubara frequency, \( D(k) \) is the effective vertex-corrected phonon propagator to be defined shortly, \( G(p, i\omega_n) \) is the electron propagator

\[
G(k, i\omega_n) = [i\omega_n - r(k \cdot k_F)]^{-1}
\]

in which \( r \) is the Fermi velocity.

The important electron-phonon scattering in eq. (2), which is responsible for the pseudo-gap, occurs at \( k = 2k_F \). There are thus logarithmic screening effects which modify the electron-phonon vertex. Within the usual \( g \)-ology formalism, one can write the leading terms of the expansion of \( D \) in the bare coupling constants \( g_1 \) and \( g_2 \), those corresponding to the vertex-correction diagrams of figure 2a, as:

\[
\text{D}(2k_F + q) = \text{D}(2k_F + q) \times
\]

\[
\left[ 1 + \frac{1}{\pi v} (2g_1 - g_2) \ln v + \cdots \right],
\]

given the expansion for the phonon self-energy at \( 2k_F \):

\[
\Pi(2k_F) = \frac{g^2}{\pi v} \ln v \left[ 1 + \frac{1}{2\pi v} (2g_1 - g_2) \ln v + \cdots \right]
\]
where \( g_1 \) is the backward scattering constant, \( g_2 \) is the forward scattering constant, and 

\[
\nu = \max \left( \nu_{q}, \nu_{T} \right) / \nu_{F} ,
\]

\( \nu_{F} \) being a quantity of the order of the Fermi energy. Using the usual renormalization group rules [22], one obtains

\[
D(2k_F + q) = D(2k_F + q) \overline{N}(2k_F + q)
\]

(6)

where

\[
\overline{N}(2k_F + q) = \nu \frac{\partial \overline{N}(2k_F + q)}{\partial \ln \nu} = \frac{v^2}{1 - g_1/\nu^2} \nu^2
\]

(7)

and

\[
\alpha = \frac{g_1 - g_2}{2 \nu^2} .
\]

The self-energy, eq. (2), will yield a pseudo-gap whenever \(|D|\) in eq. (6) stands out well over the background at \( q = 0 \), that is for

\[
\overline{N}(2k_F)[1 - g^2 D_0 N(2k_F)] > 1 .
\]

The width of the peak is given by the renormalization group approach, eq. (5), as \( \Delta q \sim T/\nu = \xi^{-1} \), \( \xi \) being identified as the phonon coherence length. Under these conditions, and further neglecting all contributions foreign to the pseudo-gap, eq. (2) becomes [26, 27],

\[
\Sigma(p, i\omega_n) \approx \frac{\Delta^2}{i\omega_n + \tau(|p| - k_F) + iT} .
\]

(9)

where

\[
\Delta^2 = \lambda T^2 \left[ \frac{\overline{N}(2k_F)}{(1 - g^2 D_0 N(2k_F))} - 1 \right].
\]

(10)

and

\[
\lambda = \frac{-g^2 D_0}{\pi \nu} .
\]

(11)

In as much as \( \Delta > T \), the concept of a pseudo-gap is meaningful. Ideally, a consistent treatment would require replacement of all the bare electron propagators in the Parquet diagrams by the self-energy corrected one

\[
G(p, i\omega_n) = [G(p, i\omega_n)^{-1} - \Sigma(p, i\omega_n)]^{-1} .
\]

(12)

One can, however, estimate the impact of the pseudo-gap on the electronic responses,

\[
R(\omega, 2k_F + q, T) = R(\nu, \nu')
\]

where \( \nu' = \max (\omega_q, \nu_{q}, \nu_{T})/\nu_{F} \) by realizing that it will attenuate the logarithmic divergence at small \( \nu' \) and saturate it whenever \( \nu' \lesssim \Delta/\nu_{F} \). We then propose a fourth energy cut-off \( \Delta \) such that

\[
\nu' = \max (\omega, \nu_q, \nu_{T}) / \nu_{F} .
\]

(13)

Within this approximation scheme, the electronic responses \( N(2k_F) \) and \( \chi(2k_F) \) can be calculated self-consistently with eq. (10).

Our primary interest is with \( \text{Im} \chi(2k_F) \). This quantity can be calculated within the Solyom renormalization group approach by calculating the leading terms in the bare coupling expansion, those corresponding to the diagrams in figure 2b,

\[
\lim_{\nu' \rightarrow 0} \text{Im} \chi(2k_F + q, \omega) = \lim_{\nu' \rightarrow 0} \text{Im} \chi(2k_F + q, \omega) \times \nu' \left[ 1 - \frac{g_2}{\nu} \ln \nu' + \cdots \right],
\]

(14)

where \( \chi(2k_F + q, \omega) \) is the SD response of the non-interacting electron gas. The renormalization group rules then give us

\[
\lim_{\nu' \rightarrow 0} \chi(2k_F + q, \omega) = \lim_{\nu' \rightarrow 0} \chi(2k_F + q, \omega) \chi(2k_F + q, \omega)
\]

(15)

where

\[
\chi(2k_F + q, \omega) = 2 \nu' \frac{\partial \chi(2k_F + q, \omega)}{\partial \ln \nu'}
\]

(16)

\[
= \left( 1 - \frac{g_1}{\nu} \ln \nu' \right)^{1/2} (v')^{\alpha}.
\]

The effect of the pseudo-gap as proposed in eq. (13), although sufficient for the real part of the response
functions, is incomplete as far as the imaginary part is concerned. This latter quantity is quite sensitive to the electronic density of states $\Omega(0)$ within the pseudo-gap,

$$\lim_{\omega \to 0} \text{Im} \chi'(2 k_F + \omega) \propto \omega \Omega(0)^2.$$  \hspace{1cm} (17)

We then propose to replace $\Omega(0)^2$ in this last equation by $\Omega(0)^2$, the average being calculated by the substitution of $G$ for $\Omega$ in the definition of $\chi'$, which then becomes

$$\chi'(k, i \omega_n) = \int \frac{dp}{2\pi} \sum_{\alpha} G(p, i \omega_n) G(p + k, i \omega_n + i \omega_n).$$  \hspace{1cm} (18)

A second correction is needed, namely for the band edge effects of a more realistic tight binding band. This can be estimated by comparing

$$\chi'(2 k_F) = - \frac{\ln (E_F/T)}{2 \pi v},$$

for the non-interacting gas to the same tight binding quantity [6]

$$\chi'(2 k_F) = - \frac{\ln (4.56 T_F/T)}{2 \pi v},$$

where $T_F$ is the Fermi energy. We thus propose to replace $E_F$ by $4.56 T_F$.

In order to try out our model, we decided to characterize each type of chain, TTF and TCNQ, with six parameters: $v$, $\lambda$, $\gamma_1$ (300 K), $\gamma_2$ (300 K), $\gamma_1$ (60 K), $\gamma_2$ (60 K), which we could adjust to reproduce $\text{Im} \chi'(2 k_F)$ at the 60 K volume, for $T = 60$ K and 300 K, and at the 300 K volume, for $T = 300$ K, further adjusting the position of the maximum at this latter volume to its approximate position in figure 1. This left two independent parameters. In order to restrict the arbitrariness further, we chose to calculate the static magnetic susceptibility and adjust it to the experimental value at 300 K. We made use of the Landau Fermi liquid formula proposed by Lee et al. [7]

$$\chi(0) = \Omega^*(0) \left(1 + \frac{\gamma_1}{4} \left(\frac{\gamma_2}{\pi v \ln \nu'}\right)\right),$$  \hspace{1cm} (19)

where

$$\Omega^*(0) = \frac{2}{\pi v^*} = \frac{2}{\pi v} \left(1 - \frac{\gamma_1}{2 \pi v}\right).$$  \hspace{1cm} (20)

We further corrected for pseudo-gap effects by combining the effect of the renormalized Fermi velocity $v^*$ and the pseudo-gap $\Delta$ in an average $\Omega^*(0) = - 2 \text{Re} \chi'(0)$ calculated from eq. (18) but with $v^*$ substituted for $v$ in eqs. (3), (9) which enter eq. (12). This correction should be reasonable provided the pseudo-gap is not too large.

### Table 1

<table>
<thead>
<tr>
<th>Fitted values of the chain parameters</th>
</tr>
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<tbody>
<tr>
<td>$\chi_{\text{TTF}}(0)/\chi_{\text{TCNQ}}(0)$</td>
</tr>
<tr>
<td>--------------------------------------</td>
</tr>
<tr>
<td>3/2</td>
</tr>
<tr>
<td>7/3</td>
</tr>
<tr>
<td>TTF</td>
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<td>TTF</td>
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</tbody>
</table>

Typical values for these fits at 60 K and 300 K for both values of the ratio $\chi_{\text{TTF}}(0)/\chi_{\text{TCNQ}}(0) = 3/2, 7/3$ current in the literature, are shown in table I. In the calculations, we have allowed for thermal expansion effects on the bandwidths, i.e. on $v$ and $\lambda$, which change by 6% and 12%, respectively, and for changes in band occupancy [28]. The temperature profile for $\text{Im} \chi'(2 k_F)$ and $\chi'(0)$ which result from these fits, and the further assumption of an exponential dependence of the bare coupling constants on the intermolecular spacing $b$, are shown in...
FIG. 4. — Calculated temperature dependence of the total static susceptibility (— — —) compared with experiment (continuous line). The value of \( \chi(0) \) at room temperature is the only experimental point used in the fit.

\[
\chi(0) \text{ (10}^7 \text{emu/mole)}
\]

\( T \) (K)

\[
\begin{array}{|c|c|}
\hline
& 0 & 60 & 120 & 180 & 240 & 300 \\
\hline
X(0) & 0 & 5 & 10 & 15 & 20 & 25 \\
\hline
\end{array}
\]

\[ \frac{\partial \ln \chi(2 k_F)}{\partial \ln b} \] (dashed line) for TCNQ.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure5}
\caption{Initial pressure coefficient of the conductivity for TTF-TCNQ, versus temperature, for two samples. Calculation of \( \frac{\partial \ln \chi(2 k_F)}{\partial \ln b} \) (dashed line) for TCNQ.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure6}
\caption{Calculated profile of the transition temperature as a function of the relative change of the lattice constant \( b \), in a transverse mean-field approximation.}
\end{figure}

where \( g_1^2 \) is a transverse Coulomb coupling constant and \( \chi_{1-CDW}(2 k_F) \) is the total one-dimensional charge density response. We estimated that

\[
\chi_{1-CDW}(2 k_F) \approx N(2 k_F)(1 - g^2 D_0 N(2 k_F)).
\]

A representative pressure profile of \( T_c \) for the TTF and TCNQ stacks is shown in figure 6, assuming a constant inter-chain coupling. It is interesting to note that the value of \( g_1^2/2 \pi \xi \) required for an ambient pressure \( T_c \) of 60 K is of the order of 0.01, in quite good agreement with the estimate of Lee et al. [7].

We wish, at this point, to draw attention on the fact that the results shown in figures 3 to 6 are quite insensitive to the exact ratio \( \chi_{TF}(0)/\chi_{TCNQ}(0) \) used in the fits.

4. Discussion. — There are a number of points we now wish to discuss with regard to the applicability of the previous theory to TTF-TCNQ electronic properties.

Let us first examine the values of the fitted parameters in table I. The values for \( g_1^2/2 \pi \xi \) and \( g_2^2/2 \pi \xi \) indicate that the intra-chain Coulomb interaction is long-range in contrast with the more usual Hubbard delta type interaction. These parameters are also seen to vary considerably with inter-molecular spacing. This indicates highly important non-logarithmic screening effects which increase with pressure and tend to equalize \( g_1 \) and \( g_2 \). The values of the band and electron-phonon coupling parameters are also seen to be in good agreement with the theoretical estimates based on molecular orbital calculation [30]. The bandwidths are also compatible with the thermopower measurements in TTF-TCNQ [15]. It should be
mentioned at this point that, even though there is some leeway in the value of the parameters of table I, the quality of the fits does not allow for much more than 10\% uncertainty in all parameters. As to the value of $\lambda$, an upper limit can be derived from the behaviour of the resistivity. Rather crudely forgetting about the existence of chains of different nature, the observed resistivity of TTF-TCNQ can be written $\rho(T) = \rho_0 + \rho_{ph}(T) + \rho_i(T)$ where $\rho_0$ and $\rho_{ph}(T)$ are the residual (temperature independent) and the phonon temperature dependent terms respectively. Actually, these last two contributions cannot explain the very large initial pressure coefficient of the conductivity observed around ambient temperature. Near 300 K, we can expect $\rho_{ph} > \rho_0$ and

$$\frac{\partial \ln \rho_{ph}}{\partial \ln b} \sim -2 \gamma_b = -7$$

where $\gamma_b$ is the axial Gruneisen constant equal to $\frac{\partial \ln \rho_0}{\partial \ln b}$ and obtained from the compressibility experiments [3].

This value of $\frac{\partial \ln \rho_{ph}}{\partial \ln b}$ is almost one order of magnitude smaller than the observed initial pressure coefficient $\frac{\partial \ln \rho}{\partial \ln b} \sim -50-60$ [10]. One is led to conclude that, at least in the low pressure domain, the resistivity of TTF-TCNQ is governed by the contribution $\rho_i$, $\rho_i \gg \rho_{ph} > \rho_0$, which must be strongly pressure dependent. The high pressure situation, however, is presumably different since $\frac{\partial \ln \sigma}{\partial \ln b}$ becomes quite significantly smaller under pressure [32]

$$\left|\frac{\partial \ln \sigma}{\partial \ln b}\right|_{P=30 \text{ kbar}} \leq 15.$$  

We thus believe that, under these high pressure conditions, the phonon contribution to the resistivity might be as important as the resistivity of unknown origin $\rho_i$, the temperature dependence of the constant-pressure resistivity approaching the linear power law. An upper limit to the electron-phonon coupling constant can thus be derived from the high pressure resistivity since [33]

$$\omega_p \frac{\partial \rho}{\partial T} = 2 \frac{\pi k_B}{h} \lambda,$$  

all factors being taken at 30 kbar. With the use of $\frac{\partial \rho}{\partial T} = 10^{-6} \Omega \text{ cm.K}^{-1}$ [32] and $\omega_p = 1.4$ eV [28] at 30 kbar, eq. (22) leads to $\lambda_{30 \text{kbar}} = 0.35$. In the tight binding band picture $\lambda \sim t_\|$, and therefore with $\Delta t_\|/t_\| \mid_{0 \rightarrow 30 \text{ kbar}} \approx 36 \%$, we can expect $\lambda_0 \approx 0.26$.

This upper limit for $\lambda$ is in good agreement with the value derived from the fit in table I.

The measurement of the initial pressure coefficient of the resistivity in TTF-TCNQ has been extended towards higher temperatures $\sim 360$ K. The experiments have been conducted with a helium gas pressure equipment between 0 and 2 kbar. The temperature, measured inside the pressure cell with a copper-constantan thermocouple, was kept constant within $\pm 0.1$ K as the pressure was slowly varied. In order to derive the value of $\frac{\partial \ln \rho}{\partial \ln b}$, we have used a longitudinal compressibility of 0.47 $\%$ kbar$^{-1}$ at ambient temperature [31]. The relative temperature dependence of the compressibility has been derived from the LA phonon branch determined by inelastic neutron diffraction [34]. The results are displayed on figure 5 for the two samples studied. The agreement with previous measurements of $\frac{\partial \ln \rho}{\partial \ln b}$ between 60 K and 300 K is satisfactory. The new feature is the existence of a maximum in $\frac{\partial \ln \rho}{\partial \ln b}$ around 300 K. The calculated values of $\frac{\partial \ln \rho}{\partial \ln b}$, which are also plotted in the same figure, show the same magnitude although the maximum is shifted roughly by 100 K towards the lower temperature. The position of the maximum, here as in the constant volume curves of figure 2, does not seem too reliable and should not be taken too literally. Figure 5 nevertheless tends to support the proportionality relation between $\ln \rho(2 k_F)$ and $\rho/T$ already mentioned in the introduction.

It now seems proper to discuss the limit of validity of our theoretical model. Towards the low temperature side, the static approximation used for the phonons might be expected to break down whenever $T \lesssim \theta_0$ [6,27], whereas interchain tunnelling effects, leading to a three dimensional band picture, come into consideration when $h/T \tau_\tau = t_\perp$ [1, 11]. This latter condition is fulfilled in TTF-TCNQ around 60 K at ambient pressure. Towards the high temperature side, one can question an expansion in $\ln (E_F/T)$, as in the Parquet or renormalization group approaches, whenever $\chi(2 k_F) \sim \chi(0)$. This occurs for

$$\ln (4.56 T_F/T) \sim 2,$$

that is near ambient temperature in TTF-TCNQ using the band parameters of table I. Moreover, the Landau-Fermi liquid formula, eq. (19), used for the static magnetic susceptibility, is itself of limited temperature range. This formula predicts a continuous increase of $\chi(0)$ with temperature. This is obviously incorrect. For instance, the Shiba-Pincus [35] computer simulation for a half-filled tight-binding band clearly exhibits a maximum in $\chi(0)$ at the pseudo-magnetic ordering temperature $T \sim t_{\|}/g_1$. This maximum is expected to occur near ambient temperatures for
TTF-TCNQ again using the values in table I [36] in contrast, for instance, with the case of TSeF-TCNQ which shows no maximum in \( \chi(0) \) up to 375 K [37] but which is also expected to have much smaller values of \( g_1/2 \pi v \). There is finally one last limiting criterion for applicability of our model to TTF-TCNQ. The chains are expected to lose their coherent 1-D character and become diffusive whenever the electron mean free path becomes of the order of the intermolecular spacing. This again occurs at ambient temperature [11].

We shall finally comment on the pressure dependence of the transition temperature calculated from the extrapolated lattice spacing dependence of \( g_1 \) and \( g_2 \) between 60 K and 300 K, corresponding to \( \Delta h/h \sim 2.3\% \). Figure 6 shows the predicted pressure dependence of \( T_c \) as calculated by a transverse mean-field theory, up to \( \Delta h/h \sim -8\% \) corresponding to \( \approx 30 \) kbar in TTF-TCNQ. The main feature is the possibility of a minimum in \( T_c \), depending on the values of the parameters. This minimum is associated to a change of regime between a Parquet-type situation dominated by the Coulomb intra-chain interaction and a mean-field type situation (the \( V > |U| \) limit of reference [6]). As to comparison with the actual experimental phase diagram of TTF-TCNQ [38], a minimum has actually been observed at 30 K and 5 kbar in what is believed to be the transition of the TTF stack. However, the transition of the TCNQ stack is found to increase slightly under pressure, going through a sluggish maximum till a pressure of 15 kbar where both transitions merge into a single one. These experimental facts can still perhaps be reconciled with figure 6 in the following way. It is evident that the Parquet is incomplete in the sense that it does not include, for instance, the effect of the higher order terms in the Solyom renormalization group approach [22]. With the \( g_1/2 \pi v \) and \( g_2/2 \pi v \) parameters in table I, the second order contribution is about half of the first order one at 60 K while it is nearly the same size at 300 K. It is then obvious that already at 60 K the Parquet stands to be corrected while it is definitely insufficient at 300 K, in the line with the discussion of the previous paragraph. It is not even certain that the renormalization group to any finite order can even be used at 300 K. A totally different approach, perhaps like the one proposed by Hubbard [40], is possibly needed. It is our feeling that any attempt to further correlate the electrons beyond the Parquet, which is after all only an improved mean-field like approximation [6], would increase the spin fluctuations at the expense of the CD ones and increase the fitted value for \( 2 \pi v/|g_{311v}| \). This should put TTF-TCNQ closer to the change in regime described above.

As a consequence, the curve of figure 6 labelled for TCNQ might conceivably correspond to the TTF stack, while the real TCNQ behaviour at ambient pressure would correspond to the one near minimum, that is \( T_c \) increasing slightly with pressure as predicted by a more conventional mean-field picture. The slight decrease of the TCNQ transition noticed between 10 and 15 kbar, could be explained by the depressive effect of either or both of the tunnelling [39] or the forward scattering between TCNQ chains [7]. In the region of the phase diagram above 15 kbar, the pressure increase of the single phase transition, aside from longitudinal lock-in considerations, can possibly be explained by an enhancing effect of the forward-scattering interaction between stacks of different nature [7]. In this respect, it is our belief that TSeF-TCNQ, from the pressure dependence of its single phase transition, may be located around 15 kbar in the more general phase diagram of TTF-TCNQ [32, 41].

Finally we wish to comment again about the large volume dependence derived for the intra-chain repulsions \( g_1 \) and \( g_2 \) in this work. The surprising result being actually the contrast between the moderate volume dependence of the bandwidth (explainable by a tight binding model) and the large volume dependence of \( g_1 \) and \( g_2 \). We already said above that part of this volume dependence may be attributed to important non-logarithmic intra-chain screening effects not taken into account in our Parquet approximation. But a comparison between the properties of TTF-TCNQ and HMTSF-TCNQ suggests also other possibilities. These two compounds do not have significantly different bandwidths. This feature is indicated either by a tight binding band structure estimate

\[
(4 t_\parallel \sim 0.45-0.55 \text{ eV}),
\]

or by the measurement of very similar plasma frequencies for both systems.

However, susceptibility and \( T_1 \) conductivity are quite different in these two compounds [2, 42]; HMTSF-TCNQ behaving as a weakly magnetic compound compared to TTF-TCNQ.

The only significant difference in the structures is the existence of much stronger interchain couplings (presumably through the nitrogen-chalcogen bonds) in HMTSF-TCNQ than in TTF-TCNQ.

Therefore, as another possibility for the large screening effects of \( g_1 \) and \( g_2 \) we would like to suggest the interchain coupling. This is supported by the HMTSF-TCNQ, TTF-TCNQ comparison and the large volume dependences. This would mean that the volume dependence of \( g_1 \) and \( g_2 \) in table I, is mainly due to changes in the \( a \) and \( c \) directions. We notice that such a suggestion is also strongly supported by the finding of large piezo-resistivity for the longitudinal resistivity connected with the transverse strains [43]. The volume dependence and the screening of \( g_1 \) and \( g_2 \) will be discussed in a forthcoming publication [44].

5. Conclusion. — Even though the bare \( 4k_F \) response function has been estimated by Lee et al. [7],
the exact nature of the non-logarithmic screening at this wave number eludes the Parquet approach and prevents any numerical estimates being made.

In conclusion, the proposed approach which combines summation of Parquet diagrams and phonon pseudo-gap effects does reconcile several crucial aspects of the physics of TTF-TCNQ:

i) large enhancement of magnetic response,
ii) strong volume dependence,
iii) existence of an intrinsic maximum in the constant volume temperature dependence of \( \text{Im} \chi(2 k_F) \), even though the phase transition occurring at low temperatures are of the CDW-PLD type,
iv) a decrease of \( \chi(0) \) by a factor of 2 from 300 K to 60 K.

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References