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Toshihiro Takahashi, Denis Jérôme, Francis Masin, Jean-Marc Fabre, Louis Giral. ^{13}C NMR studies of TTF (^{13}C)-TCNQ. *Journal of Physics C: Solid State Physics*, 1984, 17 (21), pp.3777-3792. <10.1088/0022-3719/17/21/011>. <hal-04944369>

HAL Id: hal-04944369

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Submitted on 4 Mar 2025

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^{13}C NMR studies of TTF(^{13}C)-TCNQ

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Received 11 November 1983, in final form 6 February 1984

Abstract. The ^{13}C NMR relaxation time T_1 and Knight shift K have been measured in the organic conductor TTF-TCNQ with ^{13}C -enriched TTF molecules. A clear anomaly in T_1 and K shows that the gap in the conducting band of the TTF stack opens only below 38 K. No T_1 or K anomalies have been observed either at 54 or at 49 K. We propose a new decomposition of the total spin susceptibility into contributions coming from individual TTF and TCNQ bands, which is based on ^{13}C NMR Knight shift data. The salient new information provided by this work is that the ratio χ_0/χ_F is larger than unity above 60 K. The present results have been used to reanalyse the ^1H NMR data in the literature. We have reached the conclusion that the TTF band is broader (~ 0.65 eV) than the TCNQ band (~ 0.40 eV). The observed large enhancement of the Korringa relation suggests that the Coulomb correlation energy U is of the order of the band width for both stacks.

1. Introduction

The organic salt tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) has been the most extensively investigated compound among the quasi-one-dimensional organic conductors. Since the first observation of its strong temperature-dependent conductivity (Coleman *et al* 1973, Ferraris *et al* 1973), an enormous number of investigations on TTF-TCNQ and many other isostructural compounds have been performed in order to clarify the complex properties of this system (Jérôme and Schulz 1982). However, to date, the full understanding of all observed physical properties has not been achieved. The main reason for the complexity of the TTF-TCNQ family is that these 'partially' charge-transferred salts have two kinds of conductive stacks: the donor (TTF) and the acceptor (TCNQ) stacks. Both of these contribute to the observed properties in different ways because of their different electronic characteristics.

TTF-TCNQ undergoes a transition at 54 K, from a metallic phase at higher temperatures to a semiconducting phase at lower temperatures. This transition accompanied by a lattice distortion with a wavevector $2k_F$ (k_F is the Fermi wavevector) along the conductive b axis is associated with the Peierls instability of the 1D metallic system (Denoyer *et al* 1975). Below this transition, two other transitions were found at 38 K

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(Jérôme *et al* 1974) and 48 K (Comès *et al* 1975) which are characterised by changes in the modulation period of the superlattice along the a axis. The sequence of phase transitions has been fairly well explained by considering the Peierls ordering at different temperatures on both kinds of stacks. This is one among several features showing that it is important to distinguish the different roles of the TTF and TCNQ stacks for observable quantities, in order to understand this system. However, it is not easy to separate individual contributions coming from the two stacks. The almost only exception is for magnetic properties, where magnetic resonance techniques have been used as powerful probes (Rybczewski *et al* 1975, 1976, Soda *et al* 1977, Tomkiewicz *et al* 1977).

The first attempt to determine the contribution of separate stacks to the spin susceptibility has been performed by the measurement of ^1H NMR spin-lattice relaxation in a sample where either TTF or TCNQ molecules were selectively deuterated (Rybczewski *et al* 1975). Assuming the Korringa relation, the quantity $(T_1 T)^{-1/2}/a_{\text{H}}$ was considered as a measure of the 'local susceptibility' of each stack, where a_{H} , T_1 and T are the hyperfine coupling constant of ^1H nuclei on each molecule, the measured spin-lattice relaxation time and the temperature, respectively. However, the Korringa relation in this material was found to be drastically modified owing to one-dimensional diffusive spin correlation and Coulomb enhancement of the spin susceptibility (Soda *et al* 1976, 1977).

A more reliable temperature dependence of the spin susceptibility of the TCNQ stack was derived from that of the Knight shift of ^{13}C nuclei on TTF-TCNQ (^{13}C), assuming a temperature-independent hyperfine field (Rybczewski *et al* 1976). The value of the ratio $\chi_{\text{O}}/\chi_{\text{F}}$ determined by the ^1H relaxation rate at 300 K was used as a normalisation factor to separate the total spin susceptibility χ_{T} into χ_{O} and χ_{F} throughout the whole temperature range (χ_{O} and χ_{F} are the spin susceptibilities of the TCNQ and TTF stacks, respectively).

The decomposition of χ_{T} into χ_{O} and χ_{F} has been obtained by a precise analysis of the temperature dependence of the EPR g -value (Tomkiewicz *et al* 1977). The g -value of the observed single lorentzian EPR absorption line is expected to be an average of g -values of separate stacks weighted by the respective spin susceptibility when the difference between the Larmor frequencies of the donor and acceptor stacks is small in comparison with the spin hopping rate between them. Hence the observed g -value is:

$$g = (g_{\text{O}}\chi_{\text{O}} + g_{\text{F}}\chi_{\text{F}})/\chi_{\text{T}} \quad \chi_{\text{T}} = \chi_{\text{O}} + \chi_{\text{F}}.$$

Thus, if the individual g -values $g_{\text{O,F}}$ for both stacks are known, the measured g -value enables us to determine the ratio $\chi_{\text{O}}/\chi_{\text{F}}$ at each temperature.

These methods have led to the almost consistent results that χ_{O} and χ_{F} in the metallic region have nearly the same temperature dependences and that the 54 K transition is driven only by the TCNQ stack. However, the relative magnitude of χ_{O} and χ_{F} depends largely on the process used to derive it: $\chi_{\text{O}}/\chi_{\text{F}} \approx \frac{3}{2}$ by the ^{13}C NMR method and about $\frac{2}{3}$ by the EPR method (Tomkiewicz *et al* 1974). Furthermore, different conclusions have been drawn regarding the transition temperature at which a large anomaly in the spin susceptibility of the TTF stacks (opening a gap) takes place. These methods are more or less indirect, especially for the properties of the TTF stack. The first purpose of the present work on TTF(^{13}C)-TCNQ is to obtain direct and complementary information on the TTF stack in order to contribute to the understanding of the spin susceptibility decomposition.

The electron spin susceptibility by itself is an important physical quantity which has raised many questions about the nature of the electron system of this material. First, attention was paid to the peculiar temperature dependence of χ ; it is not constant in

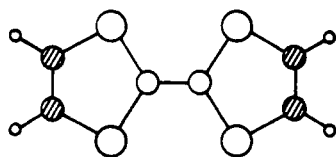
temperature as expected for the Pauli susceptibility of weakly interacting conduction electrons but decreases roughly linearly with decreasing temperature even in the metallic conduction region (Scott *et al* 1974). Secondly, Torrance *et al* (1977) have pointed out that the absolute value of χ_{spin} at high temperature is very much enhanced above the value expected for free electrons with an independently determined band width. They argued that the enhancement is due to the Coulomb correlations of the order of $U/4t_{\parallel} \sim 1$ ($4t_{\parallel}$ is the longitudinal band width). This picture claimed that the model with negligible Coulomb correlations should be drastically improved. However, the calculation based on the Hubbard model of the Coulomb correlation (Torrance *et al* 1977) failed to reproduce the observed temperature dependence of χ_{spin} .

In this paper, we propose a new decomposition of χ_{spin} into the contributions of TTF and TCNQ stacks, based on NMR Knight shift data. We use this result to determine experimentally some important parameters which characterise the electronic properties and to reanalyse the NMR information obtained so far, especially the ^1H relaxation data of Soda *et al* (1977). It is shown that the TTF and TCNQ stacks exhibit quite different electronic properties.

In the next section, we describe the experimental procedure utilised to perform ^{13}C NMR measurements on the TTF(^{13}C)-TCNQ sample. Section 3 is devoted to the analysis of the results. In § 4, we discuss the electronic properties on both stacks following the formalism of Soda *et al* (1977).

2. Experimental

The ^{13}C NMR measurements were performed on a powdered sample in which 95% of the carbon atoms on the 4, 4', 5 and 5' positions of the TTF molecules, had been selectively replaced by the ^{13}C isotope (Fabre *et al* 1981). Figure 1 shows the positions of the enriched carbon atoms of the TTF molecule.



TTF

Figure 1. The TTF molecule (the ^{13}C -enriched sites are the shaded circles in the 4, 4'-5, 5' positions).

Accurate Knight shift measurements were carried out at Bruxelles by means of a pulsed-NMR spectrometer at 42 MHz. The external magnetic field was generated by a superconducting magnet and controlled within an accuracy of ± 3 ppm during the time of the measurement. The free induction signal after the $\pi/2$ pulse is detected by a pulsed-NMR spectrometer, Brüker SXP 4-60. The signal-to-noise ratio is improved by numerical integration in a two-channel digital integrator and analysed by a microcomputer. At a given temperature the free induction decay (integrated 512 times) was observed at different frequencies in a range ± 5 kHz around the expected resonance

frequency (in the vicinity of 42 MHz). The initial frequency increment of 1 kHz was progressively reduced to steps of 100 Hz after successive approximations.

The resonance frequency was determined at each temperature by the minimisation of the 'orthogonal' signal. We found the present method fairly well adapted to the accurate determination of the NMR resonance frequency of solid state NMR lines. The Knight shift K , at a given temperature is calculated by the relative difference between the resonance frequency and the value at 4.2 K. The overall temperature dependence of the ^{13}C shift is given in figure 2.

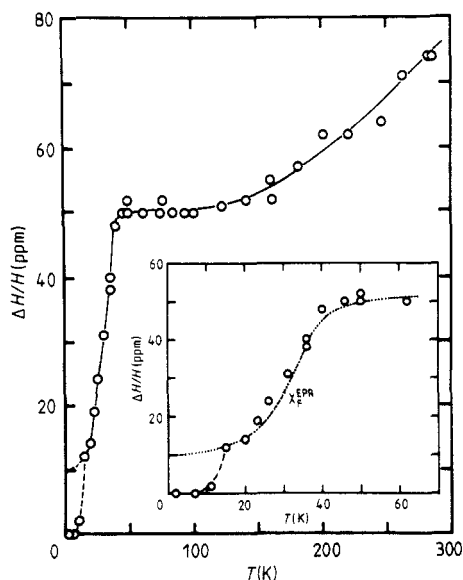


Figure 2. The temperature dependence of the resonance frequency shift of ^{13}C on TTF molecules. The inset shows the details at low temperatures. The broken line indicates the local susceptibility of the TTF stack derived by the g -value analysis of EPR absorption (Tomkiewicz 1980). The full curve is a guide to the eye.

The absorption signal obtained by a Fourier transform of the free induction is a doublet with a splitting of about 23 G, due to the dipolar interaction between near-neighbour carbon nuclei. This structure limits the accuracy of the Knight shift determination, especially at high temperature.

The nuclear spin-lattice relaxation rate was measured (at Orsay) on the same sample with a pulsed-NMR technique using sequences of saturating comb pulses. A home-made pulsed spectrometer with a single-coil probe was operated at 45 MHz. The recovery of the free induction signal after a $\pi/2$ pulse following the comb pulse was used to determine the relaxation time T_1 .

The time recovery is exponential over more than one decade in time above the transition temperature (≈ 38 K, see below). At lower temperatures, the relaxation is given by a form more complicated than a single exponential. We have neglected the initial rapid decay of the relaxation curve and have taken the longest component, to which more than 70% of the total intensity contributes. The data of the ^{13}C relaxation rate T_1^{-1} in the temperature region between 4.2 and 70 K are shown in figure 3.

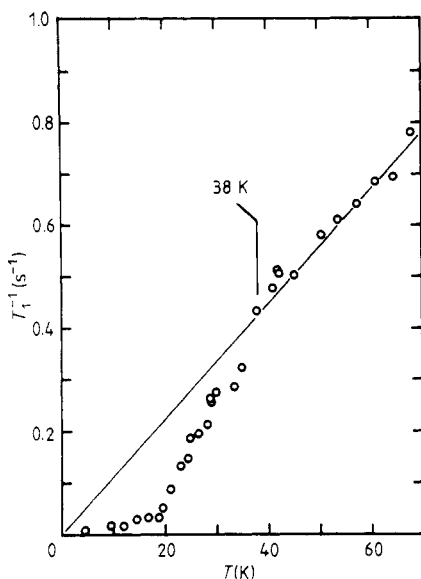


Figure 3. The ^{13}C spin-lattice relaxation rate plotted against temperature (^{13}C in TTF*-TCNQ). The straight line shows the Korringa-type relation; $T_1T = 90$ s K.

3. Results and analysis

The ^{13}C resonance on TTF stacks was found to have a rather small *positive* relative Knight shift: the resonance frequency at a constant field increases at decreasing temperatures. The total frequency shift from 2 K up to room temperature is +77 ppm. This is in striking contrast with the case of ^{13}C on CN groups of TCNQ stacks, where a negative frequency shift of -396 ppm was observed (Rybczewski *et al* 1976).

If the conduction electron (hole) band is of pure p character, a negative hyperfine field H_{hf} due to the polarisation of inner s orbitals should be generally expected. The observed positive shift on TTF stacks suggests some admixture of s character in the electron orbital on the ^{13}C sites of TTF molecules, which may partially cancel the negative H_{hf} of the p component thus leading to a relatively small value of $|H_{\text{hf}}|$. For comparison the strong negative frequency shift of the resonance of ^{13}C atoms in CN groups of TCNQ reflects the p character of the electron wavefunction.

At high temperatures ($T > 40$ K), the temperature dependence of the ^{13}C shift is rather small; the shift between 50 and 300 K is only about one third of the total temperature dependence, with nearly no temperature dependence between 50 and 120 K.

Below 40 K, the ^{13}C shift starts to decrease rapidly as the temperature decreases and reaches its constant low-temperature value at about 10 K. This anomaly corresponds to a lower phase transition temperature of TTF-TCNQ of about 38 K. No anomaly is observed either at 54 or at 49 K.

The spin-lattice relaxation rate T_1^{-1} of ^{13}C on TTF stacks follows a behaviour which is consistent with the Knight shift data in the measured temperature region. Above 38 K, $(T_1T)^{-1}$ is almost constant in temperature (figure 4). There is no anomaly either at 54 or at 49 K. Below 38 K, $(T_1T)^{-1}$ begins to decrease rapidly, corresponding to the rapid drop of the Knight shift (spin susceptibility).

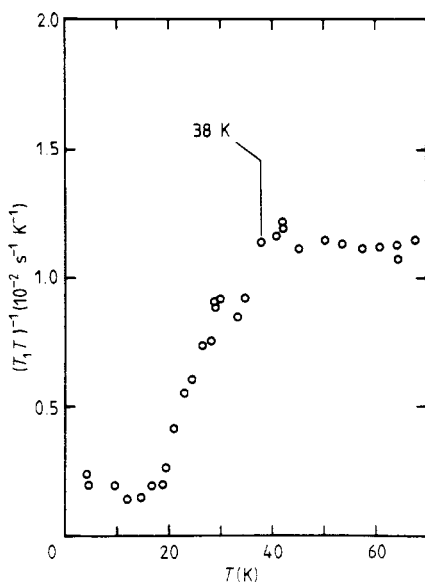


Figure 4. The temperature dependence of $(T_1 T)^{-1}$. The data are the same as in figure 3.

These features provide direct evidence that the 38 K transition is related to the TTF stacks and that a real gap opens on the TTF stacks at this temperature. This agrees well with the conclusion of the g -value analysis performed by Tomkiewicz *et al* (1977).

Below the transition temperature of 38 K, the spin susceptibility χ_s and the relaxation rate T_1^{-1} are expected to be activated as

$$T_1^{-1} \propto \exp(-\Delta/T) \quad \chi \propto (C/T) \exp(-\Delta/T)$$

where the 'magnetic' gap $E_g = 2\Delta$. In figure 5, normalised T_1^{-1} (●) and $(\Delta H/H)T$ (○) are plotted on a logarithmic scale against reciprocal temperature. The slope below 38 K gives $\Delta \approx 80$ K, which is slightly smaller than the value derived by EPR data ($\Delta \sim 125$ – 100 K ($T < 30$ K)) (Tomkiewicz *et al* 1977).

EPR and static susceptibility measurements always reveal some amount of Curie component at low temperatures (Scott *et al* 1974, Hermann *et al* 1976). The authors usually subtract this component, considering it as an impurity contribution. This may lead to some ambiguity in the determination of the low-temperature value of the spin susceptibility. In principle, the Knight shift measurement does not meet this kind of problem because paramagnetic impurities may give an excess broadening of the NMR signal but not a shift of the resonance. The spin–lattice relaxation rate T_1^{-1} is, on the other hand, affected by the impurities, which usually produce a temperature-independent contribution to the relaxation rate. In fact, the discrepancy below 15 K from the exponential dependence is removed by subtracting a constant value of $T_1^{-1} \sim 1.0 \times 10^{-2} \text{ s}^{-1}$. A concentration of paramagnetic impurities less than 10 ppm is enough to explain this contribution. This amount of impurities is reasonable in the powdered sample of the present work.

Furthermore, we noticed a small anomaly in the Knight shift data below 15 K. A 10 ppm difference occurs therefore between the extrapolated value from the high-temperature side and the low-temperature value. In this temperature region, Tomkiew-

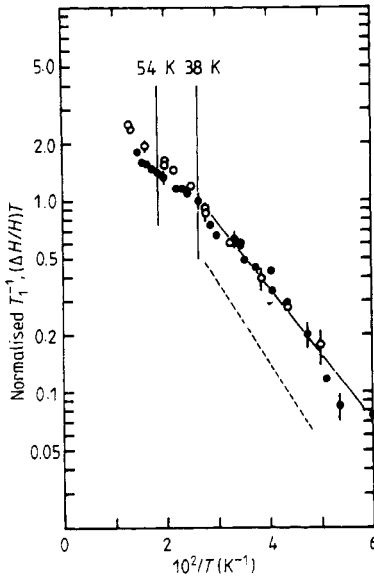


Figure 5. Semi-logarithmic plot of normalised T_1^{-1} (●) and $(\Delta H/H)T$ (○) plotted against the inverse of temperature. The straight lines show activation-type temperature dependences: full curve, $\exp(-80 \text{ K}/T)$; broken curve, $\exp(-100 \text{ K}/T)$.

icz *et al* (1977) have reported that the EPR signal reveals two other components which may come from the individual ion radicals TTF^+ and $TCNQ^-$. They discussed the possibility that conduction electrons (holes) are trapped by defects or that their motion is restricted to short strands in individual stacks. We suggest that the magnetic character of the electronic system of TTF-TCNQ may change below about 15 K. The paramagnetic component observed by susceptibility and relaxation measurements may originate from this unknown mechanism. In the analysis of figure 5 we assume that the zero-shift position is 10 ppm higher than the value of 2 K. This modification of the Knight shift data leads to a better agreement with the results of static spin susceptibility measurements throughout the entire temperature range below about 38 K.

Considering these kinds of ambiguity in the static susceptibility, Knight shift and relaxation rate, we confirm that the magnetic activation energy $\Delta \sim 100 \text{ K}$ can consistently explain the magnetic properties of TTF stacks in the temperature region between 38 and 15 K.

Now we turn to the metallic region above 38 K, where the susceptibility (Knight shift) is almost constant in temperature and the relaxation rate is proportional to the temperature. This suggests that a Korringa relation in a metallic system can be applied:

$$(T_1 T) \left(\frac{\Delta H}{H} \right)^2 \langle k \rangle = \left(\frac{\hbar}{4\pi k_B} \right) \left(\frac{g\pi_B}{\gamma_N \hbar} \right)^2 \quad (1)$$

Here $\Delta H/H$, \hbar and k_B are the Knight shift, the Planck constant and the Boltzmann constant, respectively. $g\mu_B/\hbar = \gamma_e$ and γ_N are the gyromagnetic ratios of the electron and nucleus. We have also introduced an effective enhancement factor $\langle k \rangle$. In 1D conductors T_1^{-1} is essentially determined by the value of the component of the electron susceptibility $\chi(q)$ at $q \approx 2k_F$. Hence $(T_1 T)^{-1}$ is usually enhanced more than the Knight shift which derives from the uniform susceptibility $\chi(q = 0)$, (see § 4 of the present article). Using

the values of $T_1 T \sim 90$ s K and $|\Delta H/H| \sim 40$ ppm (after the correction discussed above) we obtain $\langle k \rangle \sim 29$. The large enhancement of the Korringa relation (1) is consistent with the ^1H relaxation measurements of Soda *et al* (1977). This is direct evidence that the Coulomb correlation energy U is comparable with the band width of the conduction electrons in this system, as we will discuss in the last section.

The NMR Knight shift is proportional to the local susceptibility of individual stacks: $(\Delta H/H) = H_{\text{nt}}\chi_s$. The Knight shift of ^{13}C on TCNQ stacks has already been measured by Rybaczewski *et al* (1976), so that now we can try to decompose the total susceptibility χ_T into χ_F and χ_Q (the local susceptibilities), by using only the ^{13}C NMR shift. We use the relation for the normalised values as

$$\chi_T(T)/\chi_T(300\text{ K}) = (1 - x)\chi_Q(T)/\chi_Q(300\text{ K}) + x\chi_F(T)/\chi_F(300\text{ K}) \quad (2)$$

with a fitting parameter x . The best decomposition was obtained for $x = 0.35$, as shown in figure 6. The total susceptibility derived (x in the figure) agrees fairly well with the measured static susceptibility (broken curve) within experimental errors.

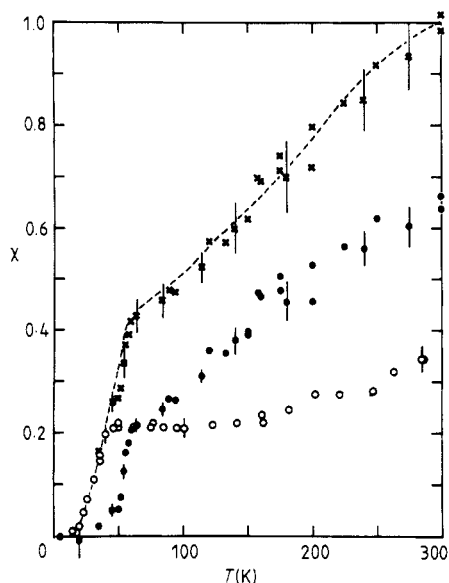


Figure 6. Decomposition of the total spin susceptibility (the broken line) into the local susceptibility on TTF (○) and TCNQ (●) stacks. The closed circles were taken from Rybaczewski *et al* (1976) and the open circles are the present results. The crosses are the sum of both contributions.

The temperature dependence of the local susceptibility of TTF and TCNQ stacks is quite different from each other. The temperature dependence of χ_T between 50 and 150 K must be attributed to the TCNQ stacks since χ_F is nearly temperature independent in this temperature domain. At 300 K, χ_Q is nearly a factor two larger than χ_F . These features are in striking contrast with the data of previously determined local susceptibility by other indirect methods (Rybaczewski *et al* 1976).

Using the values of $\chi_T \sim 5.9 \times 10^{-4}$ emu mol $^{-1}$ (Scott *et al* 1974) at 300 K and the

total shift of the ^{13}C resonance for separate stacks, the hyperfine fields are calculated to be

$$H_{\text{hf}}^{(\text{Q})} \sim -5.8 \text{ kOe} \quad H_{\text{hf}}^{(\text{F})} \sim +1.8 \text{ kOe.} \quad (3)$$

Thus the ^{13}C hyperfine coupling constants $a = 2H_{\text{hf}}(\gamma^{13\text{C}}/\gamma_e)$ are

$$a_{\text{Q}} \sim -4.1 \text{ Oe} \quad a_{\text{F}} \sim 1.3 \text{ Oe.} \quad (4)$$

4. Discussion

The new decomposition of the total spin susceptibility into local susceptibilities of separate stacks is quite different from that previously obtained by EPR and NMR (Rybczewski *et al* 1976) measurements, as pointed out above (Tomkiewicz 1980). We must consider the reason for this difference.

The ^{13}C NMR analysis of Rybczewski *et al* (1976) was based on the same principle as the present one; namely, the local susceptibility should be proportional to the NMR Knight shift, provided the hyperfine coupling constant is temperature independent. They, however, used only the data available for TCNQ stacks. They derived $\chi_{\text{Q}}/\chi_{\text{T}}$ from the ratio of the ^1H relaxation rates of both stacks at 300 K, assuming equal Coulomb enhancement factors.

Furthermore, subsequent frequency dependence data for the ^1H relaxation rate obtained by Soda *et al* (1977) have revealed a strong frequency dependence which is particular to the spin-spin correlation function in 1D conductors. Therefore, the relation between the relaxation rate and susceptibility used by Rybczewski *et al* (1976) is probably inappropriate. The EPR g -decomposition technique of Tomkiewicz *et al* (1977) was based on a different principle. They assumed temperature-independent values of the intrinsic g -values, g_{Q} and g_{F} , and determined the ratio $\chi_{\text{Q}}/\chi_{\text{F}}$ at each temperature from the relation:

$$g_{\text{obs}}(T) = g_{\text{Q}}\chi_{\text{Q}}/\chi_{\text{T}} + g_{\text{F}}\chi_{\text{F}}/\chi_{\text{T}.} \quad (5)$$

If we use the relation (5) our results for the local susceptibility, together with the g -values of the separate stacks of Tomkiewicz (1980), fail to reproduce the observed temperature dependence of the g -value. Therefore we are forced to conclude that hyperfine fields and/or g -values of separate stacks cannot be temperature independent between 4.2 and 300 K.

Generally speaking, both the EPR \mathbf{g} -tensor and the NMR hyperfine field are related to the nature of the atomic orbitals which are partially occupied by the electrons, so that their temperature dependences are expected to be very small. Thermal variations of these quantities should be attributed to the modification of the atomic orbital with interband mixing caused by a structural distortion (modification of crystal field due to thermal expansion) molecular reorientation or superlattice formation. As to the g -shift from the free-electron value, the modification of the atomic level scheme may directly affect the contribution of the spin-orbit interaction, since the g -shift for the unperturbed (pure) atomic orbital is zero (quenching of angular momentum). On the contrary, the expectation value of the hyperfine field for the unperturbed orbital generally has a large value, so that the admixture with other orbitals is expected to lead to only a relatively small correction. Thus we expect that a possible thermal effect on the atomic orbitals is more important for the g -shift than for the hyperfine coupling. In fact, the assumption

of a thermal variation of the g -shift for separate stacks by 2×10^{-3} would be sufficient to explain the observed temperature dependence of the g -value according to the present analysis. On the other hand, assuming the g -value decomposition (with constant g) to be valid, one would have to assume a thermal variation of the hyperfine field by 50%. There is no experimental justification for this picture and no available theoretical calculation for TTF-TCNQ. A precise determination of the atomic orbital spectrum and a knowledge of the thermal variation of the structure should help to solve the problem. Consequently, we believe that a temperature dependence of the g -factors for the separate stacks is the most likely assumption. Hereafter, we discuss how the present data for the decomposition of the spin susceptibility may modify the model of the electronic bands of TTF-TCNQ.

4.1. Enhancement factor $\langle \kappa \rangle$ of the Korringa relation

The enhancement factor $\langle \kappa \rangle$ introduced earlier is an important parameter in the discussion of the dynamical properties of the electron system. Soda *et al* (1977) presented an analysis of ^1H NMR relaxation in TTF-TCNQ in the metallic region ($T > 100$ K), according to the quasi-1D picture of conduction electrons and the RPA theory of the electron Coulomb correlation. We will briefly review their analysis in order to compare with the value of $\langle \kappa \rangle$ derived above.

The NMR spin-lattice relaxation produced by the contact hyperfine interaction is written in terms of the (imaginary part of) the dynamic electron susceptibility in the form:

$$T_1^{-1} = \frac{2k_B T}{\hbar^2} \sum_{\mathbf{q}} |a_{\mathbf{q}}|^2 \frac{\chi_{\perp}(\mathbf{q}, \omega_N)}{\omega_N} \quad (6)$$

where $a_{\mathbf{q}}$ is the hyperfine coupling constant and $\omega_N = \gamma_N H_0$. In the case of a quasi-1D conductor, it is enough to take only the $|\mathbf{q}| \approx 0$ and $|\mathbf{q}| \approx 2k_F$ components in the summation over \mathbf{q} . The dynamic susceptibility is related to the spin correlation function by the general fluctuation-dissipation theorem. For $|\mathbf{q}| \approx 0$ components the 1D diffusive nature of the electron motion along the conductive axis gives the so-called 'long-time tail' of the spin autocorrelation function which leads to a large enhancement of the relaxation. This component has a remarkable field dependence which is expressed as $(T_1 T)^{-1} \propto H_0^{-1/2}$. If there is an interchain hopping motion characterised by a time τ_{\perp} , one can observe a crossover from the 1D $H_0^{-1/2}$ dependence valid at high fields to a 3D field-independent value of $(T_1 T)^{-1}$ at lower fields when $\omega_e \tau_{\perp} \sim 1$ is satisfied ($\omega_e = \gamma_e H_0$; electron Zeeman frequency). For $|\mathbf{q}| \sim 2k_F$ components, where the effect of the 1D diffusion may not be important, the enhancement due to the electron Coulomb correlation is much larger than for $|\mathbf{q}| \sim 0$ components, because of the $2k_F$ anomaly in the SDW response function. The final expression of the field-dependent relaxation rate is expressed in terms of the experimental parameters C_1 and C_2 as follows:

$$(T_1 T)^{-1} = C_1 g(\omega_e) + C_2 \quad (7)$$

where

$$\begin{aligned} C_1 &= (2S)^{-1} \chi_S^2 a_{\text{H}}^2 (\tau_{\perp} / \tau_v)^{1/2} \kappa_0(\alpha) \\ C_2 &= (2S)^{-1} \chi_S^2 a_{\text{H}}^2 \kappa_{2k_F}(\alpha) \\ g(\omega_e) &= \left(\frac{1 + (1 + \omega_e^2 \tau_{\perp}^2)^{1/2}}{2(1 + \omega_e^2 \tau_{\perp}^2)} \right)^{1/2} \quad S = \frac{(g\mu_B)^2 \hbar}{4\pi k_B}. \end{aligned} \quad (8)$$

$\chi_s = \chi_Q$ or χ_F and τ_v is the electron scattering lifetime related to the spin diffusion constant D by $D = v_F^2 \tau_v (1 - \alpha)$ within the random-phase approximation. The enhancement factors introduced above are given within the RPA as

$$\begin{aligned} \kappa_0(\alpha) &\approx (1 - \alpha)^{1/2} \\ \kappa_{2k_F}(\alpha) &\approx (1 - \alpha)^2 / \langle (1 - \alpha F(q)^2) \rangle_{q \sim 2k_F} \end{aligned} \quad (9a)$$

using $\alpha = U\chi'_0(0, 0) / \frac{1}{2}N_0 (g\mu_B)^2$ and the Lindhard function $F(q) = \chi'_0(q, 0) / \chi'_0(0, 0)$. $\chi'_0(q, \omega)$ is the real part of the non-interacting particle susceptibility and N_0 is the Avogadro number.

Soda *et al* (1977) have measured the field dependence of ¹H NMR relaxation in selectively deuterated TTF-TCNQ samples, and have determined the temperature dependence of the three empirical parameters in equation (8). Furthermore, they have discussed the dynamics of the electrons and the effect of Coulomb correlation using the above formula and the local susceptibility data. Thus, their analysis should be dependent on the determination of the ratio of local susceptibilities.

Using the relation $\Delta H/H = (a/\gamma_N \hbar)\chi_s$, the effective enhancement factor of the Korringa relation introduced above can be expressed as

$$\langle \kappa \rangle = \frac{1}{2} [(\tau_{\perp} / \tau_v)^{1/2} g(\omega_e) \kappa_0(\alpha) + \kappa_{2k_F}(\alpha)] \quad (9b)$$

or

$$\langle \kappa \rangle = (S/\chi_s^2 a_H^2) (C_1 g(\omega_e) + C_2) \quad (9c)$$

in terms of the notation given above. The expression (9) depends on the model chosen to describe the electron system, but contains only electronic parameters and the external field. Thus, we can compare the results of ¹H NMR with the present ¹³C-NMR data. Extrapolating the temperature dependence of C_1 , C_2 and τ_{\perp}^{-1} for TTF stacks below 100 K, we obtain approximately:

$$C_1 \sim 0.1 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1} \quad C_2 \sim 0.9 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1} \quad \tau_{\perp} \sim 2.4 \times 10^{-11} \text{ s}.$$

For the external field of 42.0 kOe of our experiment and $\chi_F \sim 1.27 \times 10^{-4} \text{ emu mol}^{-1}$ (the present decomposition), we obtain the following results between 100 and 40 K

$$\frac{1}{2}(\tau_{\perp} / \tau_v)^{1/2} \kappa_0(\alpha) \sim 3.0 \quad \frac{1}{2} \kappa_{2k_F}(\alpha) \sim 27 \quad g(\omega_e) \sim 0.45$$

and thus $\langle \kappa \rangle \sim 28$. This agrees fairly well with the value of $\langle \kappa \rangle \sim 29$ derived in the previous section for the TTF stack. As for the TCNQ stack Rybaczewski *et al* (1976) obtained $K^2 T_1 T = (7 \pm 1) \times 10^{-7} \text{ s K}$ at 300 K. This value corresponds to $\langle \kappa \rangle = 6.0 \pm 0.9$. ¹H relaxation data for the TCNQ stack at 300 K are $C_1 \sim 1.10 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1}$, $C_2 \sim 1.32 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1}$ and $\tau_{\perp}^{-1} \sim 1.28 \times 10^{11} \text{ s}^{-1}$. Using the value of $g(\omega_e) \sim 0.70$ at 10 MHz (the frequency used in the measurements of Rybaczewski *et al* (1976)) and $\chi_Q \sim 3.8 \times 10^{-4} \text{ emu mol}^{-1} \sim 0.65 \chi_T$ (300 K)) we obtain $\langle \kappa \rangle \sim 4.9$, which is consistent with ¹³C NMR results. Thus, the enhancement factor $\langle \kappa \rangle$ determined by the ¹H NMR and ¹³C NMR (for TTF and TCNQ stacks) measurements agree well with each other. We think this is an indirect support for the present derivation of the local susceptibility.

4.2. Band width $4t_{\parallel}$ and the Coulomb enhancement parameter

We can estimate the parameters $4t_{\parallel}$ and α by reanalysing the ¹H relaxation data of Soda *et al* (1977) if we apply the random-phase approximation to the Hubbard model of Coulomb correlations and the tight-binding band model.

At 300 K, the values of $\chi_F \sim 2.1 \times 10^{-4} \text{ emu mol}^{-1}$, $\chi_Q \sim 3.8 \times 10^{-4} \text{ emu mol}^{-1}$ and the parameter $C_2 \sim 1.67 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1}$ (for TTF) and $1.32 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1}$ (for TCNQ) enable us to calculate $\kappa_{2k_F}(\alpha) \sim 38$ and ~ 6.1 for TTF and TCNQ stacks respectively. Using equation (9), together with the definition of the uniform spin susceptibility $\chi_s = \chi_F/(1 - \alpha)$ and the Lindhard function $F(2k_F, T) = \frac{1}{2} \ln 4.56T_F/T$ we can solve these equations for $4t_{\parallel}$ and α self-consistently as:

$$\begin{aligned} 4t_{\parallel}^F &\sim 0.65 \text{ eV} & 4t_{\parallel}^Q &\sim 0.40 \text{ eV} \\ \alpha^{(F)} &\sim 0.60 & \alpha^{(Q)} &\sim 0.66. \end{aligned} \quad (10)$$

Here we have used a tight-binding relation for the non-interacting Pauli susceptibility

$$\chi_P = \frac{N_0 \mu_B^2}{\pi t_{\parallel} \sin(\pi\rho/2)} \sim \frac{0.511 \times 10^{-4}}{4t_{\parallel} \text{ (eV)}} \text{ emu mol}^{-1} \quad (11)$$

and the Fermi energy $\varepsilon_F = k_B T_F \sim 2t_{\parallel} [1 - \cos(\pi\rho/2)] \sim 0.2 \times 4t_{\parallel}$ for both stacks ($\rho \sim 0.59$). We have neglected the small temperature dependence of the tight-binding susceptibility.

A striking feature of these results is that the band width of the TTF stacks is *larger* than that of the TCNQ stacks. This seems to contradict the previously accepted pictures: the TTF band is probably twice as broad as the TCNQ band.

The 'narrower' TTF band was suggested by the band calculation of the extended Hückel model by Berlinsky *et al* (1974) and was accepted because of the observation in transport properties that the dominant carriers are electrons located on TCNQ stacks (Jérôme and Schulz 1982). However, the band calculation depends on a basic assumption: the same authors have also obtained $|t_{\parallel}^Q| \sim 0.11 \text{ eV}$ and $|t_{\parallel}^F| \sim 0.18 \text{ eV}$ including 3d atomic orbitals for TTF stacks. These results agree well with those of the present analysis.

The enhancement parameter $\alpha = UD(\varepsilon_F)/N_0$ for a tight-binding model is written as

$$\alpha = \frac{U}{2\pi t_{\parallel} \sin(\pi\rho/2)} \sim 0.80 U/4t_{\parallel} \quad \rho = 0.59.$$

We obtain $U/4t_{\parallel} \sim 0.75$ and 0.81 for TTF and TCNQ stacks respectively. Care must be taken that our formulae are only valid in the limit of small correlations ($U/4t_{\parallel} < 1$). Therefore, the value of $U/4t_{\parallel}$ must be considered at best as a qualitative estimate. However, interpolating between large- U and small- U calculations, as performed by Torrance *et al* (1977), it is found that the results are not seriously modified. We claim here that $U/4t_{\parallel}$ is of the order of unity on both stacks, as in the original work by Soda *et al* (1977).

In figure 7(a), we have plotted the temperature dependences of the parameters α , U and the normalised density of states, derived from the C_2 data of Soda *et al* (1977) and the definition:

$$\bar{D}(\varepsilon_F) = D(\varepsilon_F)/(0.80/4t_{\parallel}). \quad (12)$$

Here we assumed that the band widths $4t_{\parallel}^F \sim 0.65 \text{ eV}$ ($T_F^{(F)} \sim 1500 \text{ K}$) and $4t_{\parallel}^Q \sim 0.40 \text{ eV}$ ($T_F^{(Q)} \sim 900 \text{ K}$) are constant in temperature. The results are strongly dependent on the model and we must take care of their condition of validity, as already pointed out. It is, however, interesting to point out that the temperature dependence of the spin susceptibility and of the α parameter can be attributed mainly to that of the band structure density of states, $D(\varepsilon_F)$. In the broad temperature region, the on-site Coulomb energy U is found to be nearly constant. The density of states of TCNQ stacks starts to decrease appreciably below about 150 K.

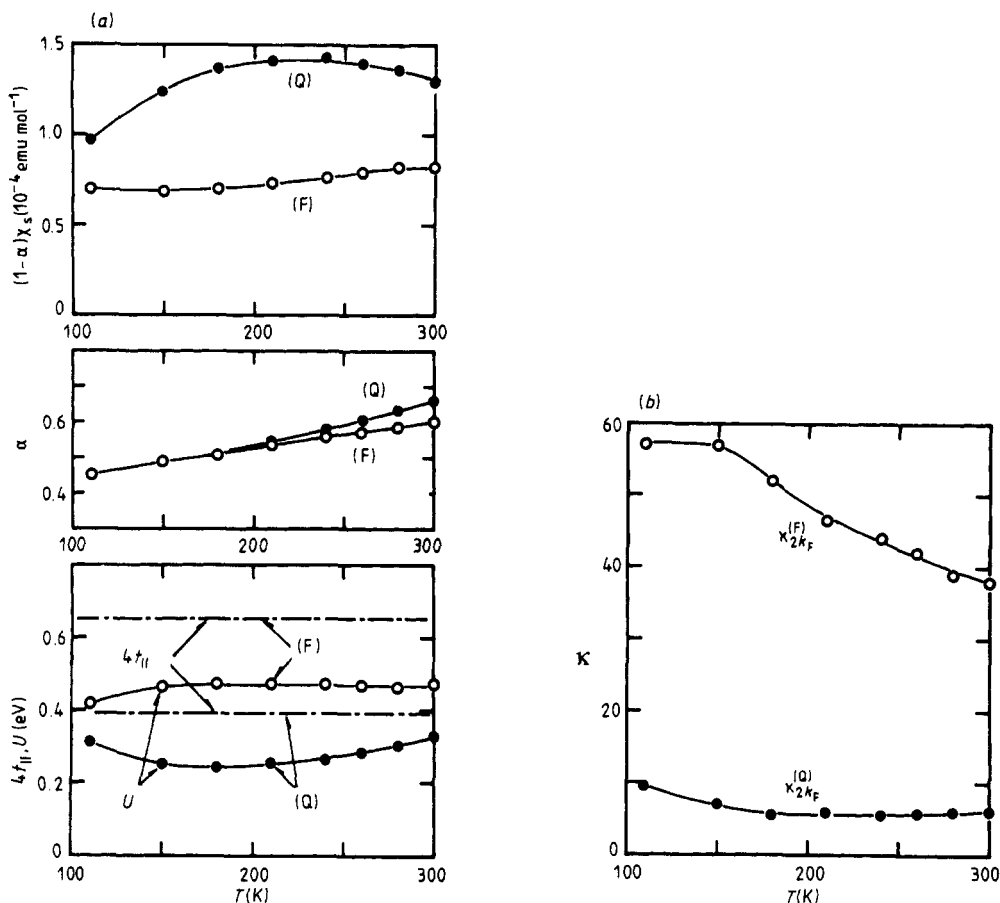


Figure 7. Temperature dependence of the parameters (a) α , $U\chi_p \propto D(\epsilon_F)$, and (b) κ_{2k_F} , for the TTF and TCNQ bands, by reanalysing the ¹H relaxation data (Soda *et al* 1977) using the present decomposition of spin susceptibility.

4.3. Spin diffusion constant

The coefficient C_1 derived from the ¹H relaxation measurement enables us to evaluate the spin diffusion constant D . We rewrite C_1 in terms of D as:

$$C_1 \sim (k_B/\hbar^2) |a_H|^2 \chi_s (b^2 \tau_{\perp}/D)^{1/2}$$

and we obtain

$$D \sim [(k_B b/\hbar^2) |a_H|^2 \chi_s / C_1]^2 \tau_{\perp} \tag{13}$$

where b is the lattice constant along the highly conducting axis ($b \sim 3.819 \text{ \AA}$). The ratio $D^{(F)}/D^{(Q)}$ for TTF and TCNQ is

$$\begin{aligned} D^{(F)}/D^{(Q)} &\sim |a_H^{(F)}/a_H^{(Q)}|^4 (\tau_{\perp}^{(F)}/\tau_{\perp}^{(Q)}) (C^{(8Q)}/C^{(F)})^2 (\chi_F/\chi_Q)^2 \\ &\sim 0.018 (\chi_F/\chi_Q)^2 \quad T \sim 300 \text{ K} \end{aligned}$$

since $a_H^{(F)}/a_H^{(Q)} \sim 1.26/1.5$, $\tau_{\perp}^{(F)}/\tau_{\perp}^{(Q)} \sim 1$, $C_1^{(F)} \sim 5.8 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1}$ and $C_1^{(Q)} \sim 1.1 \times 10^{-2} \text{ s}^{-1} \text{ K}^{-1}$ at 300 K. Using the present result $\chi_F/\chi_Q \sim 0.35/0.65$ (at 300 K), this ratio leads to

$D^{(F)}/D^{(Q)} \sim 5 \times 10^{-3}$; that is, the spin diffusion constant in the TTF stack is much smaller than in the TCNQ stack.

In the *nearly-free-electron* model, D is related to the electron scattering time τ_v as $D \sim v_F^2 \tau_v$ (v_F is the Fermi velocity), so that $D^{(F)}/D^{(Q)}$ can be considered as a measure of the ratio of τ_v between TTF and TCNQ. Thus, this result means that the scattering time in the TTF stack is much shorter than in TCNQ. The thermopower (Chaikin *et al* 1973) and the Hall effect measurements (Cooper *et al* 1977) have suggested that for the transport properties in TTF–TCNQ the dominant contribution at atmospheric pressure comes from the electrons on the TCNQ stacks. This picture has also been supported by the fact that the metal–insulator transition takes place at 54 K, the temperature where a large gap opens in TCNQ stacks.

The absolute values at 300 K are calculated from equation (12) as $D^{(Q)} \sim 3.3 \text{ cm}^2 \text{ s}^{-1}$ and $D^{(F)} \sim 1.5 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$. The value of $D^{(Q)}$ appears to be somewhat larger in comparison with the simple evaluation of $D^{(Q)} \sim v_F^2 \tau_v (1 - \alpha) \approx 0.5 \text{ cm}^2 \text{ s}^{-1}$ using $\tau_v \sim 3 \times 10^{-15} \text{ s}$ (at 300 K) derived from the conductivity data, the tight-binding Fermi velocity ($1.8 \times 10^7 \text{ cm s}^{-1}$) and $\alpha = 0.6$. However, the derivation of the spin diffusion constant depends strongly on the model used to describe the electronic system, and a simple proportionality relation between the spin diffusion time and the electron scattering time may not hold in a more elaborate treatment.

5. Conclusions

In conclusion the present direct determination of local susceptibilities in TTF–TCNQ is in fairly good agreement with the determination based on the g -factor decomposition technique in the temperature domain where dominant spin excitations reside on the TTF chains (i.e. $T < 40 \text{ K}$). However, the g -factor decomposition technique has been discussed critically by Conwell (1980). The main difficulty encountered with this method of separating the spin susceptibility into two components relies on the implicit assumption made in equation (5) that the g -factors of the individual stacks maintain their molecular values independent of temperature. The decomposition of the susceptibility proposed in the present work suggests that the g -factor decomposition technique is not reliable when magnetic excitations become equally important on both chains, namely at $T > 50 \text{ K}$. The main results are:

(i) The TCNQ susceptibility is larger than the TTF susceptibility above 60 K. The ratio χ_Q/χ_F is temperature dependent and amounts to 1.85 at 300 K.

(ii) The electron band of the TTF chain in the conducting region, in comparison with that of the TCNQ stack, may be characterised by (a) a broader band width $4\epsilon_F^F = 0.65 \text{ eV}$ compared with $4\epsilon_F^Q = 0.40 \text{ eV}$, (b) a smaller temperature dependence of the spin susceptibility, especially between 50 and 150 K, (c) a larger and strongly temperature-dependent enhancement of the Korringa relation and (d) a shorter electron scattering time. The data at low temperature show conclusively that the density of states at the Fermi level on the TTF chain is not affected, within the accuracy of the T_1 measurements, by the existence of the transverse phase-sliding domain between 49 and 38 K (Comès *et al* 1976). The gap on the TTF stack occurs only at 38 K when the transverse periodicity of the charge density wave becomes $4a$.

The new analysis of the previous ^1H NMR data obtained by Soda *et al* (1977) using local susceptibilities derived from the present work has led to several important conclusions,

(i) The uniform susceptibility of the TCNQ stack (after removal of the enhancement factor due to Coulomb correlations) clearly displays a drop below 200 K, whereas the susceptibility of the TTF stack remains practically constant between 300 and 100 K. The drop of the TCNQ susceptibility is probably related to the occurrence of 1D precursor effects of the onset of the Peierls superlattice on the TCNQ stack. In fact, the longitudinal coherence length of the $2k_{\text{F}}$ 1D lattice distortion develops precisely in the temperature domain 200–150 K (Khanna *et al* 1976, Kagoshima *et al* 1976).

(ii) The small decrease at low temperature of the factor $\alpha = UD(E_{\text{F}})/N_0$ in the enhancement of the uniform spin susceptibility can be related to the effect of the thermal contraction on the band structure density of states $D(E_{\text{F}})$. Therefore, thermal contraction is responsible for a large fraction of the temperature dependence of the spin susceptibility χ_{s} between 300 and 100 K. The acceleration of the temperature dependence of $\chi_{\text{s}}^{(0)}$ clearly observed below about 160 K in figure 7(a) is very probably related to the opening of the fluctuating Fröhlich pseudo-gap at the Fermi level as mentioned above (Andrieux *et al* 1979). Furthermore, the temperature dependence of the susceptibility under constant pressure agrees fairly well with the pressure dependence at constant temperature determined from low-field ESR under pressure (Berthier *et al* 1976). As far as the b -axis contraction is concerned, cooling down to 100 K is equivalent to a hydrostatic pressure of about 5 kbar at room temperature.

(iii) The estimate of the intramolecular Coulomb repulsion from NMR data leads to $U/4t_{\parallel} \approx 0.75\text{--}0.80$ for both chains. Such a derivation of $U/4t_{\parallel}$ is based on the Hubbard model and therefore not too much quantitative significance must be attributed to the previous values. However, we are able to confirm that Coulomb interactions play a major role in TTF-TCNQ. The $2k_{\text{F}}$ response of the spin density wave excitations is much stronger on the TTF chain as compared with the TCNQ chain. This is a direct consequence of the Lindhard function $F(q, T)$ of a 1D band, as $F(2k_{\text{F}}, T)$ at a given temperature is more divergent for the TTF band than for the TCNQ one. Hence the renormalisation of the electron backward scattering by Coulomb correlations is likely to be larger for the TTF stack. It can be inferred from a comparison between the data of TTF in figure 7(b) and the temperature dependence of the 1D $4k_{\text{F}}$ diffuse x-ray scattering (Khanna *et al* 1976) that the TTF chain is predominantly responsible for the scattering at wavevector $4k_{\text{F}}$.

Admittedly the most surprising message provided by the reinvestigation of the magnetic properties of TTF-TCNQ is the discovery of a narrow TCNQ band with $4t_{\parallel}^{\text{Q}} = 0.40$ eV and a broader TTF band with $4t_{\parallel}^{\text{F}} = 0.65$ eV. We are aware that the small- U formalism that we have used for the derivation of $4t_{\parallel}$ may lead to an inaccurate determination of some of the band parameters since this is the intermediate- U situation that seems to prevail in TTF-TCNQ. A TTF band width of 0.65 eV represents very probably an upper-value estimate since according to plasma edge data any band width in TTF-TCNQ cannot be significantly larger than 0.5 eV. Finally, calculation of band widths using various molecular-orbital approaches give values in the range 0.5 to 1 eV (Ladik *et al* 1975, Karpfen *et al* 1975, Salahub *et al* 1976) and the extended Hückel method used by Berlinsky *et al* (1974) to calculate the molecular orbitals leads to a tight-binding band width of 0.72 eV for TTF including the 3d sulphur orbitals.

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