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Classification

Physics Abstracts

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## Extended and localized states, polarons, excitons and solitons in irradiated N-methyl derivatives of pyridinium with TCNQ

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**Résumé.** — Les molécules dérivées du pyridinium par addition de groupements méthyl forment avec les molécules de TCNQ (tétracyanoquinodiméthane) des sels à transfert de charge de stoechiométrie 1 : 2. L'empilement des molécules de TCNQ en chaînes devrait conduire à la formation de bandes au quart pleines. Malgré cela, de tels systèmes sont des isolants avec un gap proche de 0,6 eV.

En désordonnant ces composés, l'irradiation ralentit les porteurs de charge et en modifie le nombre. Elle crée donc une large variété de situations nouvelles permettant de tester la nature des excitations magnétiques et de celles qui transportent du courant ou de l'énergie. Nous avons pour cela mesuré la conductivité électrique et le pouvoir thermoélectrique de 22 échantillons « purs » et irradiés de 3 différents dérivés de la pyridine (avec TCNQ). Nous présentons aussi une expérience préliminaire de résonance paramagnétique électronique et discutons l'ensemble de ces résultats à la lumière des modèles les plus courants.

Dans les échantillons nominale pur ainsi que ceux faiblement désordonnés, un modèle d'électrons indépendants occupant des états étendus (semi-conducteur de bande) rend compte de façon surprenante des traits essentiels du transport. Mais le succès de ces explications phénoménologiques n'est que superficiel et ne peut rendre compte de l'ensemble des propriétés même quand des états localisés sont introduits au bord des bandes pour mieux décrire les comportements électroniques dans les échantillons les plus désordonnés.

Les mobilités déduites d'un modèle à un électron sont faibles ( $\sim 1 \text{ cm}^2/\text{V}\cdot\text{s}$ ) même dans les échantillons dits purs. Elles suggèrent donc la présence très probable d'états polaroniques. La transition entre le comportement à faibles désordres et le comportement à forts désordres peut être considérée comme une transition entre grands et petits polarons.

De toutes les façons, l'introduction de l'interaction électron-phonon ne suffit pas à expliquer le caractère isolant de ces composés. Il faut encore introduire de fortes interactions électroniques qui font des dérivés de la pyridine associés à TCNQ soit des isolants de Mott, soit des isolants de Peierls formés à partir d'une bande à demi-pleine de fermions sans spin. Dans le premier cas, c'est l'exciton qui est l'excitation susceptible de créer des porteurs de charge alors que dans le second cas c'est la paire soliton-antisoliton. Toutes deux présentent la symétrie électron-trou que suggère l'expérience. Il est bien possible qu'il s'agisse ici d'une mise en évidence des solitons de charge  $\pm 1/2$  prédits par Hubbard et Rice.

**Abstract.** — N-methyl derivatives of pyridinium with TCNQ are 1 : 2 charge transfer salts of tetracyanoquinodimethane. Despite the fact that the TCNQ chains should be *a priori* quarter filled bands, these systems are insulators with a gap of approximately 0.6 eV.

Disordering these systems by irradiation slows down the charge carriers and changes their density. It creates a large variety of new experimental situations where the current carrying, heat carrying and magnetic excitations can be examined and compared. Conductivity and thermopower data concerning 22 nominally pure and irradiated samples of 3 different compounds are presented and discussed together with a preliminary electron spin resonance experiment, and compared to the most current models in the field.

In nominally pure samples and at low irradiation doses, a single-electron, extended state semiconducting picture explains surprisingly well the main features of the transport properties. But the success of this phenomenology is only superficial and cannot explain the whole set of results, even when localized states near the band edges are introduced for the purpose of describing the high-disorder limit.

The mobilities deduced from the above model are very low ( $\sim 1 \text{ cm}^2/\text{V}\cdot\text{s}$ ), even in the non-irradiated samples, and suggest the possible presence of polaronic states. The low disorder to high disorder crossover observed in the transport properties could be viewed as a large polaron to small polaron transition.

However, turning on the electron-phonon interaction is, by no means, enough for understanding the insulating character of these compounds. One also needs substantial electron-electron interactions. N-methyl derivatives of pyridinium with TCNQ are either Mott insulators, or spinless fermion half-filled band Peierls insulators. The main current carrying excitations are excitons in the former case and soliton-antisoliton pairs in the latter. Both excitations exhibit the electron-hole symmetry suggested by the experimental results. Possibly pure and irradiated N-methyl derivatives of pyridinium with TCNQ provide an experimental indication of the presence of solitons with charge  $\pm e/2$  predicted by Hubbard and Rice.

## 1. Introduction.

When considered from the point of view of their transport properties only, the N-methyl derivatives of pyridinium with TCNQ behave as organic semiconductors with a gap of the order of a few tenths of an eV. Recently Przybylski and Graja [1] have shown that in a relatively large homologous group of these organic TCNQ pyridinium derivatives, conductivity and thermopower data can be interpreted in a classical, partially compensated semiconductor scheme. The consequence of such a view is that most of the features of the electronic transport, especially at low temperatures, are related, even in the nominally pure compound, to donor and acceptor impurities introducing localized levels in the gap. One of the best ways for checking the relevance of this model is to increase the disorder in a controlled way and to follow the evolution of the transport properties, and through it the filling of the gap.

The mobilities of electrons and holes determined from the conductivity and thermopower data by Przybylski [2] were found to be of the order of  $1 \text{ cm}^2/\text{V}\cdot\text{s}$  in the nominally pure sample. Such a slow electron gas present in a rather low density is exposed to all kinds of localization dangers. In the present work, irradiation allows a further investigation of the transport properties in the localization range with respect to the defect concentration.

While the transport properties of N-methyl derivatives of pyridinium with TCNQ call for an extended state semiconductor picture, the magnetic properties of the same compounds require a completely different approach. The magnetic susceptibilities measured by Bulka, Graja and Flandrois [3] on three compounds of the series are typical of Heisenberg systems of localized spins interacting through exchange integrals of the order of 10 K. How is it possible to reconcile the extended single-electron picture of Przybylski with the correlated picture for magnetism? The introduction of disorder by irradiation creates a large variety of new experimental situations in which both pictures can be compared and discussed. This has been made possible by preliminary measurements of the magnetic properties of irradiated N-methyl derivatives of pyridinium with TCNQ presented in the present paper.

## 2. Experimental techniques and results.

The irradiations of single crystals of N-methyl derivatives of pyridinium with TCNQ were performed in the electron accelerator of Fontenay-aux-Roses. The samples were irradiated at 21 K, with 2 MeV or 2.5 MeV electrons at selected doses from 0 to  $100 \text{ mC}/\text{cm}^2$ . Three different compounds have been irradiated, the donor molecules of which are represented in figure 1, namely NMe 3,5 Me Py(TCNQ)<sub>2</sub>, NMe 4 Me Py (TCNQ)<sub>2</sub> and NMe 2,6 Me Py (TCNQ)<sub>2</sub>.

For each irradiation dose, a few crystals were available for D.C. conductivity and Seebeck coefficient measurements. The perfect homogeneity of the damage produced by irradiation is illustrated by figure 2, where the damage profile in a sample irradiated by fast electrons of different energies is reported. The curves have been calculated using a stopping power model derived from the Bethe formula with some additional sophistication [28]. The damage rate  $-(1/\rho)(dE/dx)$  by electrons of initial energy  $E = 2 \text{ MeV}$  is constant over a range  $x$  of about 8 cm of crystal ( $\rho$  is the density,  $\rho = 1.27 \text{ g}/\text{cm}^3$ ). An electron dose of  $1 \text{ mC}/\text{cm}^2$  corresponds to an absorbed energy in the sample of 180 megarads ( $1 \text{ rad} = 100 \text{ ergs}/\text{g}$ ). The concentration of defects is proportional to this absorbed energy as usual in irradiated organic conductors [4].

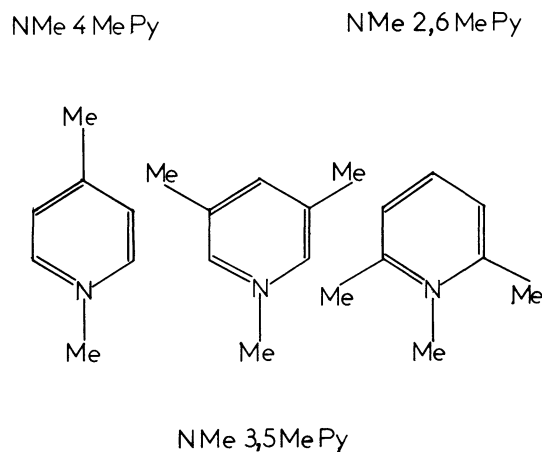


Fig. 1. — Donor molecules of the three charge transfer complexes studied in the present work.

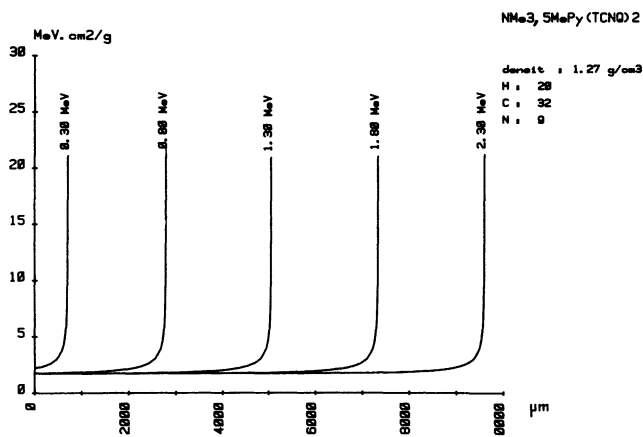


Fig. 2. — Energy deposition rate  $-(1/\rho)(dE/dx)$  by fast electrons of initial energies  $E$  from 0.3 to 2.3 MeV as a function of the distance  $x$  in a sample of NMe 3,5 Me Py (TCNQ)<sub>2</sub> submitted to irradiation ( $\rho$  is the density).

D.C. conductivity measurements on pure and irradiated samples along the needle axis of the crystal were carried out by the four-probe method. Thermoelectric power measurements were performed by the alternating temperature gradient technique proposed by Chaikin and Kwak [5, 2].

Figures 3 to 5 show the long axis conductivity of single crystals of each kind as a function of the irradiation dose expressed in mC/cm<sup>2</sup>. There is no important effect of the temperature, as seen on these curves, from 100 K to 300 K. At low doses the conductivity increases as a function of the dose to a value about ten times larger. Then, at a dose of about 20 mC/cm<sup>2</sup>, it saturates and reaches a maximum. In the discussion, this initial concentration range will be associated with a doping effect of the defects. After the dose of 20 mC/cm<sup>2</sup>, the conductivity starts decreasing. Related to some localization process, this decrease is much faster in NMe 3,5 Me Py (TCNQ)<sub>2</sub>, which is the most one-dimensional of our series, than in NMe 2,6 Me Py (TCNQ)<sub>2</sub>, which is more two-dimensional. The conductivity anisotropy is  $\sim 10$  in the 3,5 Me compound while it is 1 in the 2,6 Me system [2].

Figures 6 and 7 show the typical temperature behaviour of the conductivity in the doping range at radiation induced defect concentrations lower than those of the conductivity maximum of the previous figures. The nominally pure sample always present two distinct activation energies; the larger one, visible at high temperatures, will be associated to an «intrinsic regime», while the lower to an extrinsic regime. Irradiation pushes the intrinsic regime to higher temperatures, an inflection plateau appears in the 3 mC/cm<sup>2</sup> curve which is, in turn, pushed to higher temperatures leaving a rather single activated curve. The high concentration regime is illustrated by figures 8 and 9. After the dose of the

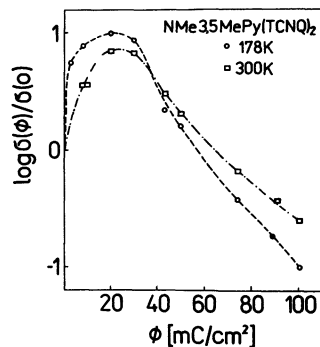


Fig. 3. — Logarithm of the normalized conductivity of NMe 3,5 Me Py (TCNQ)<sub>2</sub> plotted as a function of the irradiation dose at two different temperatures.

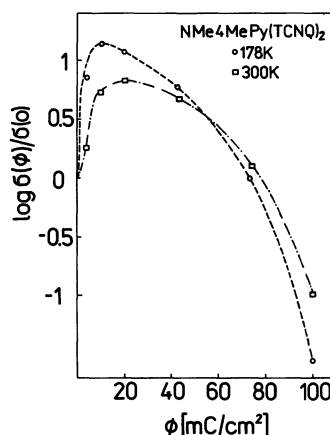


Fig. 4. — Logarithm of the normalized conductivity of NMe 4 Me Py (TCNQ)<sub>2</sub> plotted as a function of the irradiation dose at 2 different temperatures.

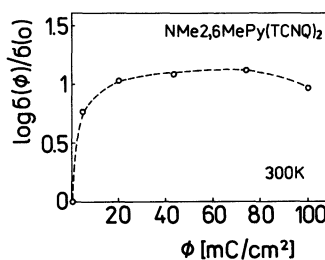


Fig. 5. — Logarithm of normalized conductivity of NMe 2,6 Me Py (TCNQ)<sub>2</sub> plotted as a function of the dose at room temperature.

maximum (20 mC/cm<sup>2</sup>), the conductivity is single activated over the entire temperature range. Then the activation energy increases monotonically with the irradiation doses.

The results of the Seebeck coefficient measurements are presented in figures 10, 11 and 12. For nominally pure samples of NMe 3,5 Me Py (TCNQ)<sub>2</sub> and NMe 4 Me Py (TCNQ)<sub>2</sub>, the thermoelectric power is large

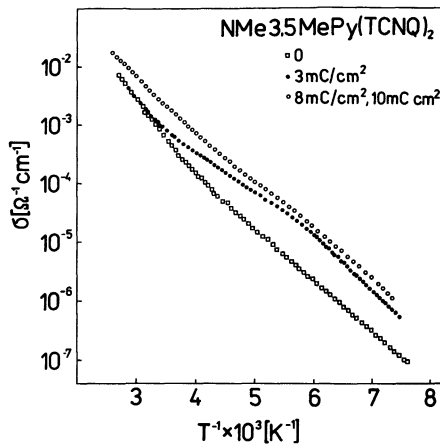


Fig. 6. — Temperature dependence of the conductivity of NMe 3,5 Me Py (TCNQ)<sub>2</sub> at low doses, in the doping range. Two activation energies are clearly visible in the nominally pure sample. At 3 mC/cm<sup>2</sup> an exhaustion plateau appears. It is pushed to higher temperatures by further irradiation.

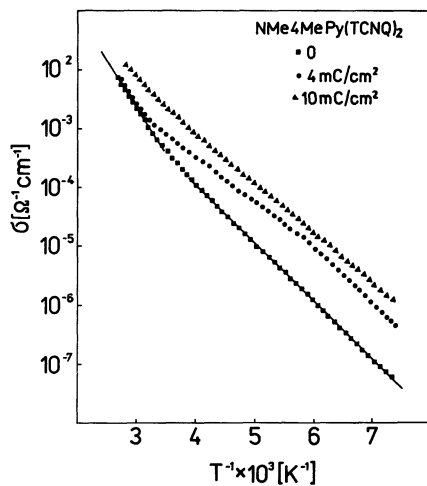


Fig. 7. — Temperature dependence of the conductivity of NMe 4 Me Py (TCNQ)<sub>2</sub> at low doses, in the doping range ; see figure 6.

and positive at low temperatures and becomes small and negative at temperatures above 300 K. In the case of NMe 2,6 Me Py (TCNQ)<sub>2</sub>, the Seebeck coefficient is negative on the whole temperature range but changes abruptly around room temperature from the large low temperature values to the small high temperature ones. It will be emphasized further on that, in all three cases, such behaviours were excellently fitted by the extrinsic-intrinsic semiconductor model [1, 2]. The thermoelectric powers of all three compounds are negative after electron irradiation regardless of the sign of the initial thermopower. Generally the values of *S* versus 1/*T* are aligned on a straight line, the slope of which is approximately the Peltier coefficient. The absolute values of the *S* versus 1/*T*

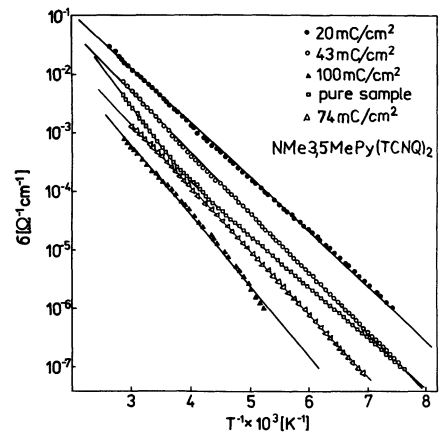


Fig. 8. — Temperature variation of the conductivity of NMe 3,5 Me Py (TCNQ)<sub>2</sub> above the conductivity maximum of figure 3, in the « localization » range. The conductivity is single activated with an activation energy increasing with the irradiation disorder.

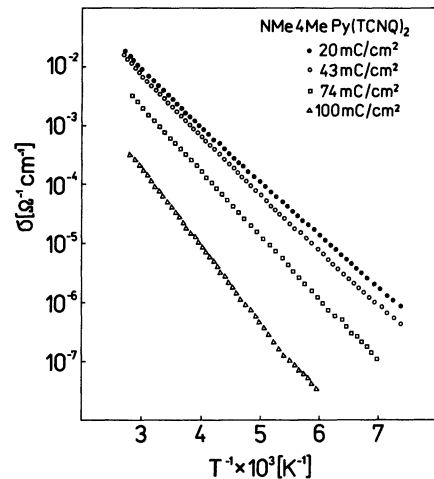


Fig. 9. — Temperature variation of the conductivity of NMe 4 Me Py (TCNQ) in the localization range ; see figure 8.

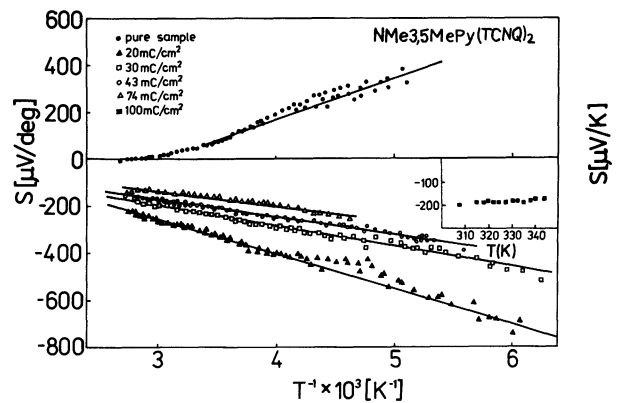


Fig. 10. — Temperature dependence of the Seebeck coefficient measured on nominally pure and irradiated crystals of NMe 3,5 Me Py (TCNQ)<sub>2</sub>.

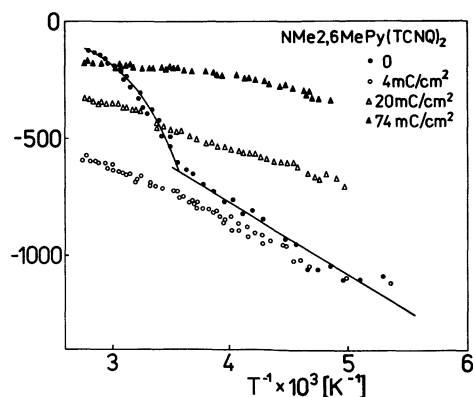


Fig. 11. — Temperature dependence of the Seebeck coefficient measured on nominally pure and irradiated crystals of NMe 2,6 Me Py (TCNQ)<sub>2</sub>. The full curve represents a fit to the extrinsic-intrinsic semiconductor model.

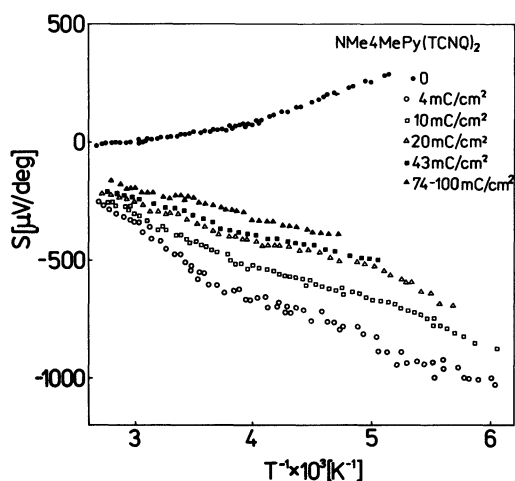


Fig. 12. — Temperature dependence of the Seebeck coefficient measured on pure and irradiated crystals of NMe 4 Me Py (TCNQ)<sub>2</sub>.

slope as well as the activation energies for the conductivity have been displayed in table I for the 21 nominally pure and irradiated samples of this work. It is very important to notice that, for the low doses (doping range), the activation energies for the conductivity in the extrinsic regime and the  $S$  versus  $1/T$  slope ( $\sim$  Peltier coefficient) agree within 0.01 eV. At higher doses (localization regime) the agreement becomes worse and worse due to the fact that the activation energy for the conductivity increases while the slope of  $S$  versus  $1/T$  decreases, even reaching values very close to zero (that is to say a temperature-independent Seebeck coefficient).

Some samples of nominally pure and irradiated NMe 4 Me Py (TCNQ)<sub>2</sub> were introduced in the Bruker electron-spin resonance spectrometer of Fontenay-aux-Roses in order to get an idea of the effect of the defects on the magnetic properties. A very

narrow single-electron line was recorded from 4 K to 300 K. The peak-to-peak linewidth of the absorption line was about 0.25 G at room temperature and 0.2 G at 100 K, regardless of the defect concentration, up to a dose of 50 mC/cm<sup>2</sup>. The  $g$ -factor, which was slightly crystal orientation dependent, was found to be very close to the free electron value. No singlet-triplet structure was visible in the ESR spectra, confirming the Heisenberg character of the system<sup>(1)</sup>. The spin susceptibility was found to reproduce approximately the curve measured previously and more accurately by Bulka, Graja and Flandrois [3], except for a low temperature Curie-like tail growing linearly with the irradiation dose. The numbers of localized spins in the Curie tails were deduced by direct comparison with a copper sulfate calibrated crystal. From 0 to 50 mC/cm<sup>2</sup>, irradiation was found to introduce  $6 \times 10^{+18}$  spins/cm<sup>3</sup> per mC/cm<sup>2</sup>, that is to say  $3.4 \times 10^{16}$  spins/cm<sup>3</sup>.Mrad. In table II most of the results of this preliminary ESR work are listed.

### 3. Discussion.

**3.1 INTRODUCTION.** — Hundreds of charge transfer complexes containing the acceptor molecule TCNQ (7, 7, 8, 8-tetracyano-p-quinodimethane) have been studied in the past twenty years. Only a few of them are room temperature organic metals [7]. It is well known that electron-electron or electron-phonon interactions are obstacles to the achievement of a metallic state. The former interaction can, in the end, lead to a Mott insulator state [8], while the latter can finally produce polaronic situations where electrons are bounded to a local lattice distortion that they induce [9]. Of course, other collective phenomena having the same causes like superconductivity, Peierls state, or spin density wave condensation can also be responsible of the instability of the metallic state, but part of these questions are not relevant for the interpretation of the present results. When some disorder is present in real crystals or induced artificially for an investigation purpose, the slowing down of electrons is a further reason for the enhancement of all localization effects. A disordered solid is more polaronic than a perfect one [9], and disorder and electron interactions can add their effects to transform a semimetal with positive temperature coefficient of resistivity (TCR) into a dirty, negative TCR solid [10-12].

The low-dimensional character of most of these solids, where the TCNQ molecules are organized in segregated stacks, has been recognized as a further menace preventing the establishment of a metallic state. Theoretically, in a strictly one-dimensional solid (in the absence of an electric field), all states are

<sup>(1)</sup> In most of its aspects this line is very similar to the ESR signal found in alkali TCNQ salts [6].

Table I. — Values of the activation energy deduced from the conductivity and the Seebeck coefficient measurements independently of the sign of the majority carriers.

Salt	Irradiation dose [mC/cm <sup>2</sup> ]	Activation energy from $\sigma$ vs. $1/T$ [eV]	Slope of $S$ vs. $1/T$ [eV]
NMe 3,5 Me Py (TCNQ) <sub>2</sub>	0	0.18 0.28 (*)	0.17
	3	0.17	0.16
	8	0.17	0.16
	10	0.18	0.16
	20	0.18	0.15
	30	0.19	0.10
	43	0.20	0.08
	74	0.22	0.05
	100	0.23	0.03
NMe 4 Me Py (TCNQ) <sub>2</sub>	0	0.19 0.32 (*)	0.18
	4	0.18 0.32 (*)	0.18
	10	0.17	0.17
	20	0.18	0.14
	43	0.20	0.14
	74	0.22	0.11
	100	0.26	0.11
NMe 2,6 Me Py (TCNQ) <sub>2</sub>	0	0.29 0.32 (*)	0.29
	4	0.21	0.21
	20	0.19	0.18
	43	0.18	0.11
	74	0.18	0.06
	100	0.19	0.06

(\*) Intrinsic activation energy.

localized by any infinitesimal random potential [13] and electronic conduction could only occur *via* phonon assisted hopping. Moreover, in principle, turning on the electron-phonon coupling on a strictly one-dimensional solid causes all the electronic states to become polaronic and the high temperature conductivity to become activated in the temperature range corresponding to the classical limit for the motion of polarons [14].

In spite of all these difficulties, TTF-TCNQ (tetrathiofulvalene-TCNQ) and related compounds are indeed high temperature metals, at least from the point of view of their transport properties. They exhibit in their metallic state a typical Drude behaviour which can be considered as being related to the transport properties of travelling waves, even if the electron mean free path is a few molecular distances only. But the magnetic properties of TTF-TCNQ are more obscure when considered within the frame of a single electron picture : the value of the magnetic susceptibility, far above the Pauli value, calls for an enhancement by Coulomb interactions. In the same way, the presence of a  $4k_F$  instability together with the  $2k_F$  Peierls distortion is hardly understandable without the help of Coulomb interactions.

The same kind of paradox can be raised in organic semiconductors too. On the one hand, N-methyl derivatives of pyridinium with TCNQ belong to a series of complexes where the role of electron interactions is very clear ; this is especially true for the magnetic properties and will be demonstrated further on in the last part of the discussion. On the other hand, N-methyl derivatives of pyridinium with TCNQ have been recognized to exhibit the transport properties of partially compensated semiconductors, where the mobilities of electrons and holes were found to be of the order of  $1 \text{ cm}^2/\text{V.s}$ . The introduction of irradiation disorder has created a large variety of new experimental situations in which the extended states semiconductor picture can be checked. In the first part of the present discussion the semiconductor scheme will be discussed in more depth with relation to the doping process in the low-disorder limit and the localization process in the high-disorder limit. But, of course, this kind of single-particle, extended state model can be considered only as a phenomenology for the purpose of describing the conductivity and thermopower data more quantitatively. Thus, a highly correlated electron picture will be developed to explain more accurately the role of defects in the transport and magnetic properties of the nominally pure as well as irradiated samples.

**3.2 THE SURPRISING SUCCESS OF THE SINGLE-PARTICLE SEMICONDUCTOR PHENOMENOLOGY AND THE DOPING EFFECT OF IRRADIATION DEFECTS.** — Przybylski [1, 2] has successfully fitted the conductivity and thermopower data of nominally pure N-methyl derivatives of pyridinium with a simple one-electron semiconductor model with deep lying localized impurity states

influencing conduction at low temperatures by their thermal ionization. It is not necessary to recall here the transport formulae for doped semiconductors in the intrinsic or the extrinsic regimes ; they can be found in textbooks [15] and their application to organic low-dimensional semiconductors has been carefully studied in references [1] and [2]. These formulae lead to a picture of the excitation gap illustrated in figure 13. The necessity to fit simultaneously conductivity and thermopower data in three different directions makes this simple analysis quite powerful. It is important to stress a few interesting results of these fits.

i) In all the compounds of this series analysed up to now the intrinsic activation energies are very close to each other.

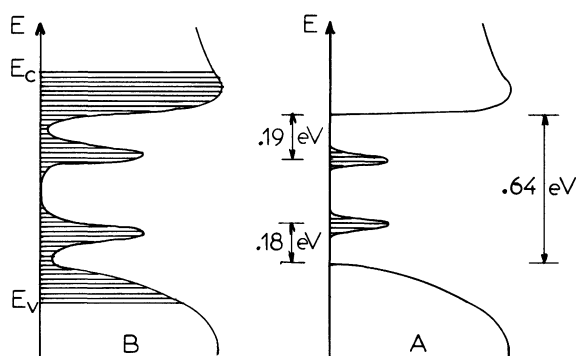


Fig 13. — Single particle excitation gap in nominally pure (A) and heavily irradiated (B) N-methyl derivatives of pyridinium. The numbers in part A of the figure refer to NMe 4 Me Py (TCNQ)<sub>2</sub> (see Table I). The localized states sitting between mobility edges  $E_v$  and  $E_c$  have been hatched. Notice the electron-hole symmetry of the system.

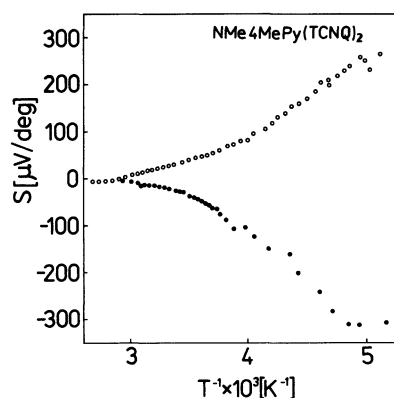


Fig 14. — The densities of donor and acceptor states in the gap of nominally pure NMe 4 Me Py TCNQ<sub>2</sub> are very close to each other. Only a difference less than 1 % is responsible for the p-type or n-type character of the material, and indeed the nominally pure crystals can be obtained of both types, depending on the batch, as shown by these two thermopower curves of two nominally pure crystals. Notice the symmetry of the two curves as a proof of the impurity levels symmetry with respect to the mid-gap.



ii) It is absolutely impossible to fit the transport data by assuming the existence of a single type of localized states in the gap. Both types, donors and acceptors, have to be present in a concentration of a few  $10^{15}/\text{cm}^3$  in the case of the nominally pure samples. Moreover, the compensation of impurities has to be high in order to fit the data, and donor and acceptor levels, with densities close to each other, are usually found symmetrical with respect to the midgap.

iii) Because of this strong compensation, the nominally pure samples of NMe 4 Me Py TCNQ<sub>2</sub> can be found to be equally likely of the n-type or of the p-type, depending on the batch as illustrated in figure 14. Because of the symmetry of the impurity levels with respect to the midgap, the excitation energies which determine the conductivity as well as the thermopower are independent of the sign of the majority carrier. For a given compensation (let us say  $|N_D - N_A/N_D| \sim 1\%$ ), and at a sufficiently low temperature, the Fermi level is either pinned by the acceptor or the donor level, and what is basically seen in the transport properties is either the excitation distance  $E_C - E_D$  between the conduction band edge and the donor level, or the distance  $E_A - E_V$  between the acceptor level and the valence band edge, depending on the sign of the majority carrier. In the present cases  $E_C - E_D = E_A - E_V \simeq 0.2$  eV has been reported in table I, independent of the sign of the majority carrier.

iv) The mobilities of the nominally pure samples are found to be very low, between 1 and  $4 \text{ cm}^2/\text{V} \cdot \text{s}$ .

Irradiations at doses lower than  $20 \text{ mC}/\text{cm}^2$  fully confirm the picture previously developed for nominally pure samples. The continuous increase of the number of impurity states pushes the intrinsic regime to higher temperatures and pins the Fermi level close to the impurity levels. As the dose increases, the two-slope conductivity curve is transformed by the occurrence of an exhaustion range plateau [15] and finally becomes single activated in the whole temperature range (Figs. 6 and 7). This is in perfect agreement with the single-electron, extended-state semiconducting picture. In this range of concentrations, irradiation defects mainly act as dopants. This is supported by the fact that the Peltier coefficient (absolute value of the slope of the Seebeck coefficient *versus*  $1/T$ ), is, within the experimental errors, always equal to the extrinsic activation energy for conductivity (see table I). The Peltier coefficient is well known to be the heat transported coherently per carrier, i.e. the total energy of the carrier relative to the chemical potential. The fact that it coincides with the activation energy for conductivity implies that the limiting process for the conduction is the excitation of localized carriers to extended states. Irradiation defects increase the conductivity by increasing the number of localized states which can be easily ionised.

The most surprising results of the fits in this range of concentrations ( $\phi < 20 \text{ mC}/\text{cm}^2$ ) is that the new levels introduced by irradiation in the 3 different com-

pounds are found to coincide, within the experimental accuracy, with the donor and acceptor levels present in the nominally pure sample. What is even more surprising is the fact that irradiation introduces donor and acceptor levels at the same time and that the electron-hole symmetry is conserved : there is only a small donor level excess of the order of 1 % of the total. These observations, which in the single-electron picture could be understood only in terms of accumulation of coincidences, will be one of the reasons for a further understanding of the transport processes in the series of charge transfer salts of interest.

**3.3 THE LOCALIZATION RANGE.** — After the dose of  $20 \text{ mC}/\text{cm}^2$  the conductivity starts decreasing and its activation energy, which has become unique in the whole temperature range, increases while the Peltier coefficient is decreasing (see Table I). The increase in the activation energy with irradiation corresponds to the appearance of an activated part in the mobility of the carriers. The increasing difference between the Peltier and the activation energy coefficients confirms that the system is indeed entering a localization range in which the conductivity is limited by some kind of incoherent jumping process. A proof of that has been given, for instance, by Overhof [16] : since in a hopping process near the Fermi level, jumps of positive and negative energies both contribute to the conductivity, the hopping carriers do not bring any coherent energy with them, their Peltier coefficient is essentially zero and only a small result due to the asymmetry of the density of states is expected [16].

Since we know that the system is entering a localization regime, it is important to decide whether the single-electron picture developed in the doping regime can be extended to the localization regime, provided that the classical ideas of Mott are introduced into the scheme [17]. The increase of localized states introduced by irradiation can lead at high doses to a localization of the electronic states in the band tails near the band gap. Following Mott and Davis [17], this produces the appearance of mobility edges in the conduction ( $E_c$ ) as well as the valence ( $E_v$ ) bands, separating the localized states below  $E_c$  and extended states above  $E_c$  (see Fig. 13B). Assuming that the Fermi level is pinned within the bandgap by the large number of impurity levels present there, the conduction could be due to three different processes acting in parallel :

- i) hopping through localized states at the Fermi level,
- ii) excitations above the mobility edge followed by a coherent motion within the extended states,
- iii) lower energy excitations to localized states near  $E_c$  within the band tail followed by a non-coherent motion between these localized states. Of these three processes, only the third can qualitatively explain a difference between the non zero Peltier coefficient and the activation energy, since the conductivity would be

$$\sigma = \sigma_0 \exp - (E/k_B T) \exp - (W/k_B T),$$

where  $E$  is the position of the excited empty states with respect to the Fermi level and  $W$  the diffusive short-range hopping term, while the thermopower would contain simply the excitation term

$$S = - (k_B/e) ((E/k_B T) + \text{const.}).$$

This model is known as the Mott C.F.O. model and is frequently used to interpret the transport properties of amorphous semiconductors. The principal objections to this model have been collected by Emin in a recent paper on this subject [18]. The main point is that, in the band tail where the transport occurs by hopping through localized states, there are very few available states corresponding to a given excitation energy and it is only under extraordinary conditions that the mobility due to such hopping can be sufficient to yield a significant contribution to the conductivity. This very serious objection regarding amorphous semiconductors is slightly less serious in our case because more states are available near a band edge in 1D or 2D than in 3 dimensions. Nevertheless, in the present case, the room temperature conductivity in the localized regime is of the same order as the conductivity in the nominally pure sample where the states were assumed to be extended (see Figs. 3 to 5). Following Emin, it is natural to try to develop a polaronic picture in order to propose an alternative explanation of the transport properties in the whole defect concentration range and to try to better understand the difference between the Peltier coefficient and the activation energy for the conductivity.

**3.4 THE POLARONIC PICTURE.** — In a recent paper [2], Przybylski has already noticed that the low mobility values that were resulting from the fits of the transport properties of the methyl derivatives of pyridine with TCNQ correspond to the limit of application of the one-electron, extended states picture. The high effective masses of the carriers that were found suggested a possible influence of polaronic states in the slowing down of carriers [2]. Indeed, turning on the electron-phonon interaction in a low mobility electronic system leads to the creation of polaronic states. In this situation, the charge carrier is viewed as being more or less severely localized in the vicinity of only a few atoms. In fact, under equilibrium conditions, the atoms surrounding the localized carrier are displaced substantially in response to its presence. These atomic displacements are such as to produce a potential well for the carrier which act to bind it to its location [18]. Transport properties due to polarons have been extensively studied in a famous paper by Holstein [19]. When the spatial extent of the self-trapped carrier is substantially larger than the atomic separation (large polarons), there is no dichotomy between polarons and quasi-free carriers. The classical, extended-state transport equations for semiconductors do apply to this case provided that the effective mass of the carriers is increased due to the binding to the lattice. To the

contrary, when the spatial extent of the polaron is of the order of the lattice separation (small polarons) the transport properties of self-trapped electrons become very different from those given by a model which does not include electron-phonon interactions properly. The most important feature of this motion is a crossover from a low temperature quantum behaviour to a high temperature classical incoherent motion (small polaron hopping). In the incoherent regime the conductivity is activated with an energy which differs from the Peltier coefficient by the small polaron hopping term.

The advantage of the small polaron hopping picture with respect to the Mott picture in explaining a difference between the conductivity activation energy lies in the fact that direct small polaron formation and hopping do not necessarily require the presence of disorder when in Mott's C.F.O. picture any incoherent motion is strongly related to disorder and can occur through a very limited number of localized states only. There are polaronic states bounded to defects, but free polaronic states are present too, even when triggered by disorder, and can greatly increase the number of low mobility states available for incoherent motion that are needed to explain the properties of the system. Two other recent theoretical results are in favour of a polaronic picture of the systems of interest in the present paper. First, anisotropy in conduction greatly favours polaronic situations [14]. Second, Cohen, Economou and Soukoulis have demonstrated that the extended eigenstates above the mobility edge collapse to localized polarons as the electron-phonon interaction is turned on [27]. This result was very recently obtained by combining the scaling theories of polarons and localization [14, 27].

Returning to irradiated N-methyl derivatives of pyridinium with TCNQ, the polaronic picture could be as follows. Turning on the electron-phonon interaction in a system with mobilities from 1 to 4 cm<sup>2</sup>/V.s makes all states polaronic, even in the nominally pure samples. But these initial polarons are large and the usual results of the one-electron band picture apply very well provided that the effective mass is increased due to some binding to the lattice. But when the irradiation damage becomes large enough to slow down the carrier motion sufficiently, the polarons become small. In this picture, some of the small polaronic states are bounded to defects but most of them are free, because increasing the time that a carrier resides at a site can trigger small polaron formation [18]. The presence of disorder provides sufficient slowing of intersite motion to drive a system over the threshold from its carriers being quasi-free or large polaronic to form small polarons.

Qualitatively, such a picture can very well explain the important discrepancy between the Peltier energy and the single activation energy for conductivity found in what we have called the localization range (doses larger than 20 mC/cm<sup>2</sup>). The dimensionality of the system plays an important role in this range as shown

by the results of figures 3, 4 and 5. NMe 3,5 Me Py (TCNQ)<sub>2</sub> is the most one-dimensional of the compounds studied in the present work : its lower conductivity anisotropy is about 10. This compound exhibits a rather fast exponential decrease in conductivity in the localization range. In contrast, NMe 2,6 Me Py (TCNQ)<sub>2</sub> is two-dimensional [2], its anisotropy in the conduction plane is only 1.1 and the localization effects induced by irradiation are much weaker than in the previous case, while the doping speeds are equivalent.

Even if the calling upon polarons helps a little in interpreting, at least qualitatively, the large variety of new situations created by the irradiation of the compounds of interest, it is still not sufficient to understand all the features of these electronic systems. The following section is an attempt to point those things which are not understandable in terms of a single-electron picture, even including electron-phonon interactions. Some of these features are related to the transport, most of them to the magnetism of N-methyl derivatives of pyridinium with TCNQ.

### 3.5 THE FAILURE OF THE SINGLE-ELECTRON MODELS. —

The present section deals with different properties of the pure and irradiated compounds : the thermopower in the transverse direction, the magnetic susceptibility of the nominally pure samples, the magnetic properties due to irradiation-induced defects, and the particular position of the defect levels in the gap.

In the nominally pure samples the thermopower has been measured in three different crystallographic directions [2]. In the least conducting of these directions the thermopower was found by Przybylski to be temperature independent. The usual interpretation of such a behaviour is as follows. Thermopower  $S$  can be viewed as a measure of the entropy per carrier. One generally expects a large thermopower for semiconductors (few carriers with many possible states per carriers) whereas in the metallic state the entropy of the degenerate electron gas is small. In the case where electrons are localized and their kinetic energy becomes so small that it can be neglected, the thermopower reflects the number of static configurations of electrons sitting at random on equivalent sites. Chaikin and Beni [20] have extensively analysed this regime. From figure 15 it is clear that, given a certain number of sites and a certain number of electrons sitting at random on these sites, the number of possible configurations depends very much on the size of the Coulomb correlation

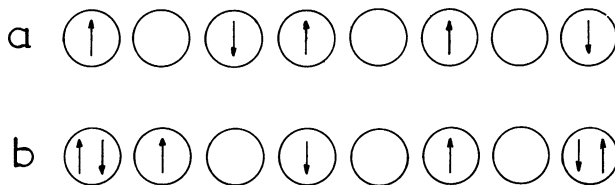


Fig. 15. — Possible site configurations for localized electrons : a) large on site repulsion, b) small electron interactions.

energy  $U$  between electrons with respect to  $k_B T$  (which determines the probability of singly- and doubly-occupied states). In the case of strong on-site Coulomb interaction ( $U \gg k_B T$ ) (Fig. 15a).

$$S_1 = - (k_B/e) \ln [2(1 - \rho)/\rho]$$

where  $\rho$  is the fraction of TCNQ molecules occupied by an electron, whereas in the case of weak Coulomb interaction (Fig. 15b) the thermopower can be written

$$S_2 = - (k_B/e) \ln [(2 - \rho)/\rho].$$

In N-methyl derivatives of pyridinium with TCNQ there are two acceptor molecules for one donor, thus it is generally thought that, in these systems,  $\rho = 1/2$ . In these conditions the highly correlated electrons model predicts a thermopower of  $-60 \mu\text{V/K}$  and the nearly-free model predicts  $-96 \mu\text{V/K}$ . Przybylski has already noticed that the value that he has measured cannot be explained without the help of Coulomb interactions [2] : indeed he has precisely found  $-60 \mu\text{V/K}$ . This means that the Coulomb interaction is sufficiently strong to correlate the electrons apart in the transverse direction so that they behave as free spins. How is it possible to assume that Coulomb interactions do not play a significant role in the longitudinal direction which was usually treated in a single-electron picture ?

Another important property which cannot be understood without the help of electron correlations is the magnetic susceptibility. It has nothing to do with the typical behaviour for band semiconductors and has been satisfactorily fitted [3] with a 2D-Heisenberg model with a small exchange integral of about 10 K.

The magnetism of the defects is also an important argument for the evidence of electronic correlations. The present study provides two independent estimates of the defect concentration induced by a given amount of energy absorbed by the sample from the incident radiation. From the Curie-like tail in the magnetic susceptibility, we have found in NMe 4 Me Py (TCNQ)<sub>2</sub> (see Sect. 2) a fraction of spins of  $1.6 \times 10^{-5}$  per TCNQ molecule and per megarad of absorbed energy. The fits of the conductivity and thermopower (see Sect. 3.1) allow a second determination of the number of doping centres introduced by irradiation. In NMe 4 Me Py (TCNQ)<sub>2</sub> this number is  $5 \times 10^{-7}$  per TCNQ molecule and per megarad. This means that each doping centre corresponds to approximately 30 new spins in the Curie-like tail. Thus, NMe 4 Me Py (TCNQ)<sub>2</sub> appears as a system where spin excitations are far easier than charge excitations, and this is typical behaviour for correlated electrons [21]. Indeed, the present studies of N-methyl derivatives of pyridinium with TCNQ revealed several properties of the defect levels which seem difficult to understand in terms of a single-electron picture :

i) the excitation gap is divided into three equal parts by the donor and acceptor levels (see Fig. 13) ;

ii) irradiation produces donor and acceptor levels at approximately equal rates;

iii) the impurity levels corresponding to irradiation defects sit precisely at the same place as the levels which pre-exist in nominally pure samples.

In order to connect all these results together it is important to answer the following question :

**3.6 WHY ARE N-METHYL DERIVATIVES OF PYRIDINIUM WITH TCNQ INSULATORS ?** — Most of the useful elements for understanding the properties of TCNQ salts with one donor molecule for two acceptors are contained in references [22] and [23] and references therein. The starting point for the solution of this problem is a quarter filled band TCNQ chain which is not *a priori* insulating ; but looking more carefully at the structure measured at room temperature and 175 K by Graja *et al.* [24] and partially reproduced in figure 16 reveals a strong dimerization of the TCNQ chain. The TCNQ diads embracing a donor molecule exhibit a ring-to-bond overlap typical of a good electron transfer  $t$ , while the other diads, which do not sit in front of a donor, correspond to a bad ring-to-ring transfer  $t' \ll t$ . Due to this dimerization, a large gap of amplitude  $\simeq 4 t$  opens at the middle of the band separating two narrow subbands of width  $\simeq 4 t'$ . According to the independent electron picture, this compound is still a metal (a half-filled band metal). In order to explain the insulating character with a gap  $\simeq 0.6$  eV, we need either a strong tetramerization or substantial Coulomb interactions to keep the electrons apart from each other. There are no signs on the structure of a 0.6 eV band tetramerization : of course the donor molecules are asymmetric and bring with them some

dipole moment (Fig. 1); of course the electrostatic donor-acceptor interaction could give rise to regular site energies of the acceptor chain [23], provided that the asymmetric donor molecules are ordered ; of course this could perhaps lead to some strong tetramerization as shown in figure 17, provided that the electrostatic donor acceptor-interaction would be of several tenths of an eV ; but it has been clearly demonstrated at 300 K as well as 178 K that there is no dipole ordering, each cation occupying one of the two centro symmetrically-related positions in a disordered manner [24]. Thus, there is no band tetramerization corresponding to a gap opening of 0.6 eV, and substantial Coulomb interactions are needed to explain the insulating character of N-methyl derivatives of pyridinium with TCNQ.

In the limit of very strong Coulomb interactions,  $U \gg 4 t \gg 4 t'$ , electrons behave as spinless fermions. The Fermi level, which was sitting at  $\pi/4 a$  in the uniform band picture, is pushed to  $\pi/2 a$ , each state being singly occupied [23]. The system is then a dimerized spinless fermion insulator, as viewed in figure 18B. In the approximation  $U = \infty$ , which completely neglects double occupancy, the spin and particle motions are completely decoupled. The electron spins behave like free spins giving a Curie law susceptibility and the particle motion can be described as that of a gas of spinless fermions. According to the theories of Hubbard [25] and Rice and Mele [26], the fundamental excitations of such a system are soliton-antisoliton pairs of respective fractional charge  $+ e/2$  and  $- e/2$ . The formation energy of such a pair is  $2 \Delta/\pi$ , where  $2 \Delta \simeq 4 t$  is the Peierls gap. Since  $2 \Delta/\pi$  is an energy less than  $2 \Delta$  required to promote a spinless fermion from the top of the filled valence gap to the bottom of the upper Peierls sub-band in absence of soliton distortion, it follows that the dominant low current carrying excitations of the chain will consist of thermally activated states of positively and negatively

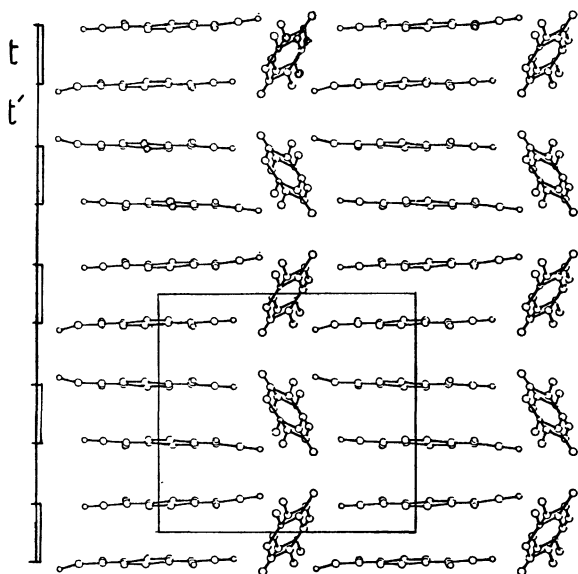


Fig. 16. — Typical structure of N-methyl derivatives of pyridinium with TCNQ projected along the lowest conductivity C-axis. Two different transfer integrals appear along the TCNQ chain :  $t$  corresponds to a ring-to-bond overlap,  $t' \ll t$  corresponds to a ring-to-ring overlap.

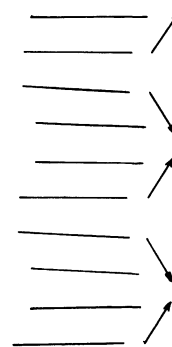


Fig. 17. — Schematic hypothetical structure of the TCNQ chains in the N-methyl derivatives of pyridinium salts. The donor molecules have dipole moments represented by arrows. Assuming that these dipole moments are ordered and that the electrostatic donor acceptor interaction is several tenths of an eV, these salts could be band insulators with tetramerized TCNQ chains ; but the recent structure determinations show that cations are not ordered.

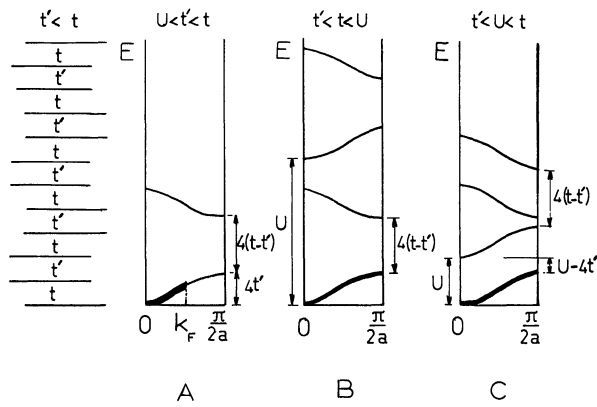


Fig. 18. — Excitations spectra of a charge transfer 1/2 dimerized chain of TCNQ with two transfer integrals  $t' < t$ . Picture A corresponds to the band case (independent electrons). In picture B, a large on-site Coulomb repulsion  $U$  has been introduced; the chain becomes a spinless fermion Peierls insulator with gap  $4(t - t')$ . In case C, the main interaction is  $t$ , but a substantial Coulomb interaction  $U$  is nonetheless present; the chain is then a Mott insulator with a Mott indirect gap  $U - 4t'$ .

charged soliton states. Indeed, the experimental excitation gap picture of figure 13A could represent such a situation, the 0.18 eV or 0.19 eV corresponding to the formation energy of the soliton-antisoliton pair. The properties of such fractional charge excitations will be described more accurately in the appendix.

A rather different and alternative situation can occur in the 2:1 TCNQ salts, in the case when  $4t' \ll U \ll 4t$ :  $U$  is moderate and the main interaction is the transfer within the diade. This picture implies that pairs of TCNQ molecules are so bonded that they behave as single molecular entities with respect to the propagation term  $t'$ . Then  $U$  is the on-site effective Coulomb interaction within the diade considered as a single site. The relation  $U \gg 4t'$  results in a Mott insulator of correlated electrons sitting on dimer pairs. The Cou-

lomb gap is  $U - 4t' \simeq U$  (Fig. 18). The magnetic properties are those of a Heisenberg chain with low exchange between sites. The main current carrying excitation of such a system is the electron-hole pair. It will be at an energy close to the electron-electron repulsion energy  $U$  and will contribute to the conductivity through both the electron excited and the hole left behind. The presence of a radiation induced defect could perhaps decrease the electron-electron repulsion  $U$  locally by favouring the electron-hole separation. Such a defect should be viewed as a screen between electrons and holes. Under such conditions, the energy necessary to create an unbound electron-hole pair could change from 0.6 eV in the bulk to 0.2 eV in the vicinity of a defect according to the symmetric level structure of figure 13.

#### 4. Conclusion : solitons or excitons ?

There is no way of explaining the insulating ground state of most of the 1:2 TCNQ charge transfer salts without including substantial Coulomb interactions. This fact was recognized years ago by several groups [21-23] and is fully confirmed by the present study. Is it possible to decide whether N-methyl derivatives of pyridinium with TCNQ are Mott insulators or spinless fermion Peierls insulators ? Experimentally, the magnetic properties are those of a Heisenberg system where spin excitations are far easier than current carrying excitations. These results seem to favour the Mott insulator picture of figure 18C because in the case of spinless fermions, spins and charges are completely decoupled and the magnetism should be Curie-like. It is clear that radiation induced defects decrease the energy to promote charge carriers. In the spinless fermion picture, defects have simply to change the charge transfer locally in order to create soliton-antisoliton pairs with a formation energy much lower than the gap (see appendix). In the Mott insulator picture, defects have to favour the electron hole separation;

Table II. — Characteristics of the ESR line of nominally pure and irradiated NMe 4 Me Py (TCNQ)<sub>2</sub>:  $\Delta H$  is the ESR linewidth measured at 300 K and 100 K.  $N_s$  is the number of spins in the Curie-like tail per cubic centimeter of crystal and  $C_s$  the molar concentration of spins in %;  $\phi$  is the dose in mC/cm<sup>2</sup> and  $R$  the absorbed energy in Mrads.

$\phi$ mC/cm <sup>2</sup>	$R$ Mrad	$\Delta H$ (300 K) G	$\Delta H$ (100 K) G	$N_s$ spins/cm <sup>3</sup>	$C_s$ spin/TCNQ molecule
0	0	0.31	0.2	$5.7 \times 10^{18}$	0.19 %
10	1 800	0.24	0.18	$8.3 \times 10^{19}$	2.8 %
43	7 700	0.25	0.2	$2.41 \times 10^{20}$	8 %
100	18 000	2.4	2.4	$2.3 \times 10^{20}$	8 %

they can be helped in this task by polaron formation stabilizing the carriers.

The present experimental state of the art is probably not sophisticated enough to decide between these two schemes, even if we are tempted to give some small advantage to the Mott insulator picture. The solution of the problem has probably to be found in further experiments in the fields of magnetism and optics [29].

It is worth mentioning that, in a very recent paper, Conwell expresses the idea that, due to the presence of interchain potentials, the main excitations in large  $U$  systems could be bipolarons with integer charge rather than solitons with half-integer charge [30].

**Appendix.**

**SOLITONS WITH CHARGE  $\pm e/2$  IN HIGHLY CORRELATED 1 : 2 SALTS OF TCNQ.** — The present appendix is an attempt to better understand the ground state and current carrying excitations of the spinless fermion Peierls insulator studied by Rice and Mele [26]. For this purpose, it is useful to say a few words about the Wigner lattice approach to this problem by Hubbard [25], because in his model the soliton excitations are easier to picture in the real space due to the complete localization of electrons and the classical (non quantum) character of the interaction model. More precisely, Hubbard studied a highly correlated chain in which the electronic coupling to the lattice is neglected but a nearest neighbour Coulomb repulsion  $V < U$  between electrons is included. The ground state of the quarter filled chain is a Wigner lattice in which every other site of the chain is occupied by an electron. There is a two-fold degeneracy of the ground state which is easily visible in figure 19A. Hubbard has treated the band propagation term as a perturbation of the electron interaction Hamiltonian ( $U \gg V \gg t$ ). He noticed the following properties of these chains.

- i) The electron (or hole) dimers as those shown on figure 19B can be viewed as domain boundaries separating the twofold degenerate configurations.
- ii) The dimers can propagate as a whole due to the perturbation  $t$  (Fig. 19B).
- iii) The energy cost of this soliton defect is only  $V \ll U$ .
- iv) This defect brings a charge  $\pm e/2$ . The demonstration of this last point is contained in figure 19C; the injection of a supplementary electron produces a

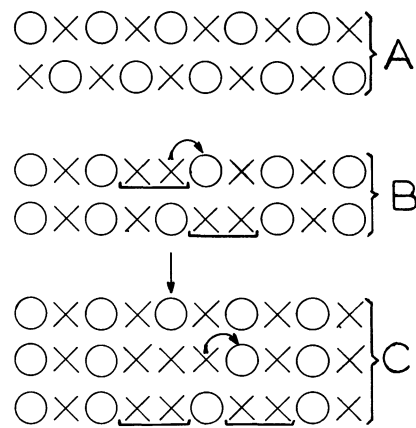


Fig. 19. — Wigner lattices in a quarter filled chain [25]. The two configurations of the degenerate ground state are shown in A. B represents a defect boundary between the two configurations (soliton) and its propagation. In C, a supplementary charge has been injected at the position of the arrow; its propagation reveals its equivalence to two previous defects.

trimer which can easily be separated into two dimers due to the propagation term  $t$ ; each of these dimers brings half of the initial charge.

- i) The addition of a single electron or hole to the chain leads to the formation of two spinless soliton states with charge  $q = e/2$  for the case of the electron and  $q = -e/2$  for the case of the hole.
- ii) In the limit of weak electron-lattice coupling, the energy of formation of a fractionally charged soliton is  $\Delta/\pi$ , where  $2 \Delta$  denotes the energy gap of the spinless Peierls system.
- iii) The dominant low temperature current carrying excitations of the chain will consist of thermally activated pairs of fractionally charged solitons of the form  $(e/2, -e/2)$ .

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