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The effects of a low temperature irradiation on TTF-TCNQ and related compounds

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Résumé. — Nous présentons des mesures de résistance électrique de TTF-TCNQ, TSF-TCNQ et HMTSF-TCNQ irradiés à 21 K par des neutrons rapides. A cette température une dose de $4{,}3 \times 10^{15}$ neutrons rapides/cm^2 multiplie la résistivité longitudinale de HMTSF-TCNQ par 5 alors qu'elle divise celle de TTF- par 5 et de TSF-TCNQ par 10.
La forme des courbes représentant l'évolution de la résistivité en fonction de la dose a pu être expliquée quantitativement en s'appuyant sur le modèle phénoménologique suivant : sous irradiation, les sels de TCNQ sont considérés comme des matériaux inhomogènes composés de petits volumes transformés par l'irradiation, plus (ou moins) conducteurs que le *matériau pur*, inclus au hasard dans une matrice de matériau non encore endommagé. On sait traiter ces systèmes inhomogènes en appliquant un modèle dit du *milieu effectif*. On peut estimer, grâce à cette théorie, le nombre n d'atomes contenus en moyenne dans le volume transformé autour de chaque défaut d'irradiation. On trouve :

$$n(\text{TTF-TCNQ}) \sim 29\,000\,, \qquad n(\text{TSF-TCNQ}) \sim 83\,000\,, \qquad n(\text{HMTSF-TCNQ}) \sim 53\,000\,.$$

L'agitation thermique restaure partiellement les effets d'une irradiation à basse température. On observe un pic de recuit centré autour de 140 K dans TTF-TCNQ et de 85 K dans TSF-TCNQ.

Abstract. — Measurements of the electrical conductivity of TTF-TCNQ, TSF-TCNQ and HMTSF-TCNQ samples which have been irradiated at 21 K with fast neutrons (1 MeV) are presented. At this temperature a fast neutron dose of 4.3×10^{15} neutrons/cm^2 increases the longitudinal resistivity of HMTSF-TCNQ by a factor of 5, decreases the longitudinal resistivity of TTF-TCNQ by a factor of 5 and decreases its transverse resistivity by an order of magnitude, and decreases the longitudinal resistivity of TSF-TCNQ by an order of magnitude.
A phenomenological quantitative analysis of the resistivity *versus* dose curves has been made. In this analysis the irradiated TCNQ salts are considered to be inhomogeneous materials composed of small damaged volumes more (or less) conducting than the pure material. These damaged volumes are included at random in a matrix of undamaged crystal. With this effective medium model, one can estimate the number of atoms n included in the transformed volume around a radiation induced point defect. For the materials above we found the following values :

$$n(\text{TTF-TCNQ}) \sim 29\,000\,, \qquad n(\text{TSF-TCNQ}) \sim 83\,000\,, \qquad n(\text{HMTSF-TCNQ}) \sim 53\,000$$

(absolute values of n are known within a factor 4 or 5).
The annealing effects on the low temperature radiation induced defects have been examined and an annealing peak is observed about 140 K in TTF-TCNQ and 85 K in TSF-TCNQ.
These results suggest that, at low temperature, irradiated crystals of TCNQ salts as well as so called *pure* crystals contain macroscopic inhomogeneities due to defects. All the materials are probably mixtures of more or less distorded volumes.

Introduction. — Organic conductors of the TTF-TCNQ family have always been thought to be extremely sensitive to structural defects. A few years ago, when the electronic properties of these crystals began to be the subject of much interest, structural defects or impurities were generally called upon when no perfect crystal explanation of the observed properties worked well or when one had simply to justify the scatter in one's experimental results. More recently, attempts have been made to introduce

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structural disorder in a controlled way in order to understand quantitatively the role played by the structural defects on the physical properties of organic conductors. Transport properties of alloys such as $(TTF)_x$-$(TSF)_{1-x}$-TCNQ [1] or $(HMTTF)_x$-$(HMTSF)_{1-x}$-TCNQ [2] have been examined and the results of three irradiation experiments (on TTF-TCNQ [3], HMTSF-TCNQ [4] and quinolinium-TCNQ [24]) have been published.

In a quasi-one-dimensional conductor, one of the principal effects of point defects, especially if they are charged, is to decrease the longitudinal scattering time $\tau_{\parallel}$ defined by the usual relation $\sigma_{\parallel} = ne^2 \tau_{\parallel}/m^*$. This time varies with the kind of defects, their concentration, and also with changes in temperature, pressure or stress. It is not surprising, therefore, to find that the principal TCNQ high conducting salts have been already classified from the point of view of their *cleanliness* [5], according to temperature, pressure [6] or elastoresistivity [7] measurements.

In the present paper, we report the effects of radiation damage on the d.c.-electrical conductivity of single crystals of TTF-TCNQ, TSF-TCNQ and HMTSF-TCNQ at low temperatures (below phase transitions).

1. **Experimental.** — The samples used in this study are described in table I.

Table I. — *Number, resistivity ratios and origin of the samples used in the present work.*

TCNQ salt	Number of irradiated crystals	$\sigma_{max}/\sigma_{300}$	Prepared by
—	—	—	—
TTF-	6	$\simeq 7$	Fabre and Giral
TSF-	1	$\simeq 11$	Engler
HMTSF-	2	$\simeq 3$	Bechgaard

Irradiation was performed using the Triton Nuclear Reactor at Fontenay-aux-Roses, and was carried out at liquid hydrogen temperature (21 K) using the VINKA device described by Conte and Dural [8]. The neutron flux at the sample was

$$3.9 \times 10^{11} \text{ neutrons/cm}^2.\text{s}$$

of which 6.5×10^{10} have an energy greater than 1 MeV.

During irradiation, the temperature was stable enough ($\Delta T \simeq 0.01$ K) to follow the resistance *versus* dose curves of the 9 samples.

For this purpose, a 48 channel, low noise, d.c. data acquisition system was used. Assembled in our laboratory, this system is composed of two Keythley 174, a low noise Nanomat scanner (noise < 50 nV), three Keythley d.c. current sources, an H.P. 9815 computing controller and three SEFRAM plotters.

2. **Irradiation effects : evaluation of the fraction of displaced atoms.** — A part of the energy given by a fast neutron to a crystal is in the form of atomic collisions. A fast neutron ($\simeq$ 1 MeV) will collide with a nucleus of an atom, giving that nucleus an energy of the order of 100 keV for a carbon or a nitrogen atom and several 10^4 eV for a sulphur or a selenide atom ; this interaction will in turn set off a cascade of atomic displacement each requiring about 5 or 10 eV. In this way each neutron that produces a primary ion will create several thousand defects in the lattice in the form of vacancy — interstitial Frenkel pairs.

The other part of the energy loss of the primary ions is in form of electronic excitation. In an insulating polymer or an insulating molecular crystal this electronic component is efficient in producing permanent chemical damage such as broken bonds or free radicals. It is well known that charged particles, X and Γ rays can be used to cross-link insulating polymers. The situation is radically different in conducting or semi conducting materials, even when the number of free carriers is low ($\sim 10^{18}$ carriers/cm^3). In a semi metal such as bismuth [21], in several simple or binary semi conductors, in semi conducting sulfides such as TaS_2 [23], and in several oxides such as UO_2, there is no evidence of permanent damage due to low energy ionization or electronic excitation. One of the authors of the present work recently investigated this point in the case of the polymer $(SN)_X$ [22] and the charge transfer salt HMTSF-TCNQ [4]. We think that in these conducting materials there are always carriers enough to avoid any permanent damage due to low energy ionization or electronic excitations.

The number of atomic displacements produced within a displacement cascade has been recently calculated by D. Lesueur [9] in the case of a crystal containing several kinds of atom. In the present paper, we use these results to estimate the fraction of atomic displacements after a given neutron dose. The basis of this calculation is given in the appendix below, and the results are the following :

— in TTF-TCNQ and TSF-TCNQ, 4.3×10^{15} fast neutrons/cm^2 (the maximum dose) correspond to a displaced atoms concentration of 2.2×10^{-5} at. fraction (within a factor of 3 or 4) ;

— in HMTSF-TCNQ, the same neutron dose corresponds to a slightly smaller number of defects : 1.7×10^{-5}.

As usual, the effects of the Γ rays and of the electrons produced by high energy ionizations are neglected in this rough calculation.

3. **Experimental results.** — Figure 1 shows the electrical conductivity of TSF-TCNQ before and after irradiation, in the temperature range 20-40 K. The single phase transition in *pure* TSF-TCNQ is revealed by an inflexion point in the log σ *versus* T

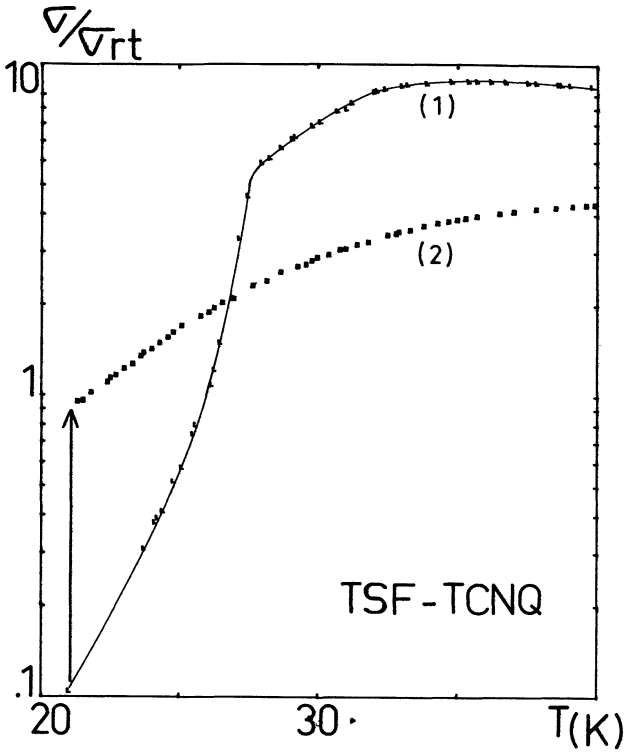

Fig. 1. — Conductivity *versus* temperature in TSF-TCNQ before (1) and after (2) an irradiation with 4.3×10^{15} fast neutrons/cm^2 corresponding approximately to a fraction of 2×10^{-5} displaced atoms.

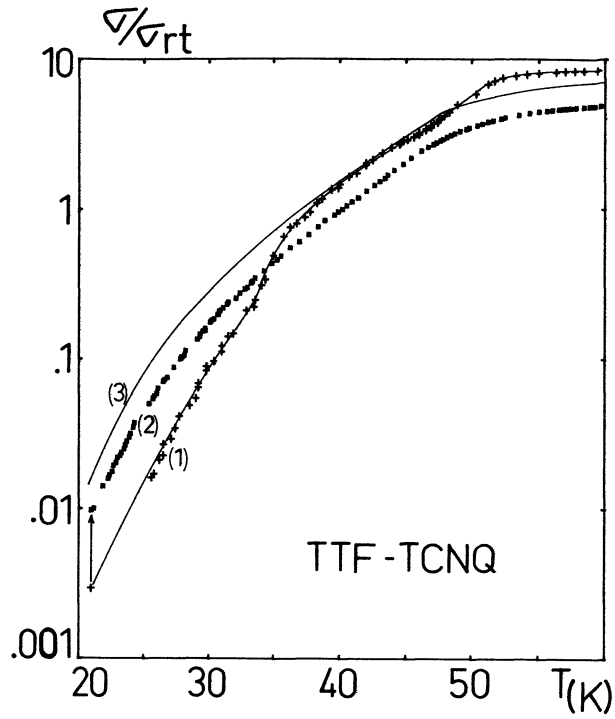

Fig. 2. — Conductivity *versus* temperature in TTF-TCNQ before (1) and after (2) an irradiation with 4.3×10^{15} fast neutrons/cm^2 corresponding to a fraction of displaced atoms of about 2×10^{-5} (dpa). Curve (3) has been recorded after an annealing at 300 K.

curve. A 6×10^{15} fast neutrons/cm^2 irradiation at 21 K increases the low temperature conductivity by an order of magnitude. The changes in curvature in the log σ *versus* T curve have completely disappeared. This result implies that concentration of defects of about 10^{-4} at. fraction smears the phase transition out of the conductivity curves.

Figure 2 shows the electrical conductivity of TTF-TCNQ before (1) and after (2) irradiations at 21 K, and after an annealing for 1 hour at 300 K (3). Curves (1) and (2) (before and after irradiation) exhibit qualitatively (but not quantitatively) the same features as those measured by Chiang, Cohen, Newman and Heeger before and after a room temperature irradiation of TTF-TCNQ [3]. After the low temperature irradiation with 4.3×10^{15} fast neutrons/cm^2 ($\sim 2.2 \times 10^{-5}$ at. fraction) the conductivity at 21 K increased by about a factor 4 and the phase transitions became quite unobservable on the resistance curves. In addition the conductivity maximum decreases by a factor of 2. Annealing for 1 hour at 300 K causes the maximum to recover near to its value before irradiation. On the contrary the annealing at 300 K has increased the effects of irradiation (curve 3), below the 38 K transition associated with the final locking of the charge density waves on the two chains.

Figure 3 shows the 21 K conductivity of the three TCNQ high conducting salts (HMTSF-, TTF-, TSF-)

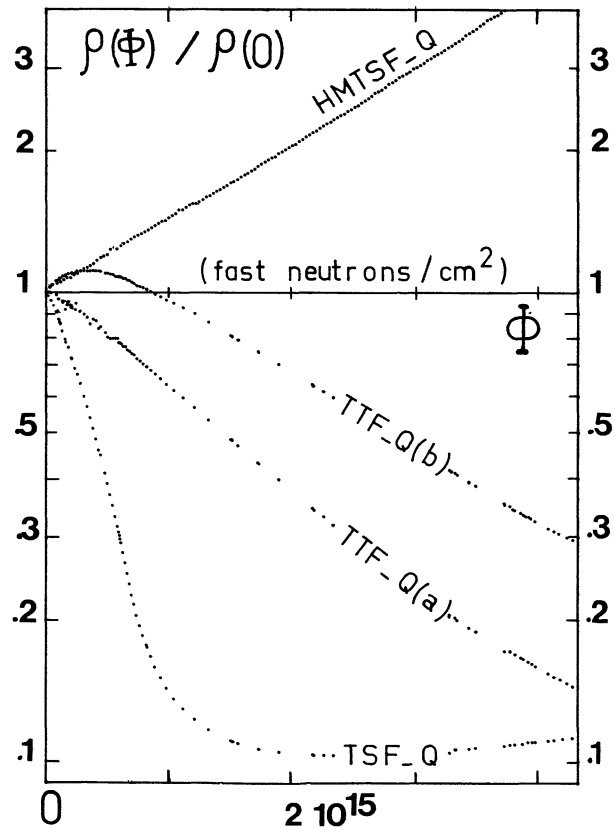

Fig. 3. — Resistivity *versus* dose curves for three high conducting TCNQ- salts irradiated with neutrons. In the case of TTF-TCNQ, (*b*) indicates the longitudinal resistivity and (*a*) the transverse one.

as a function of the particle dose. The increase in resistivity of HMTSF-TCNQ has already been reported in a previous paper [4]. After a small initial increase, the TTF-TCNQ longitudinal resistivity at 21 K decreases nearly exponentially with dose. Transverse resistivity of TTF-TCNQ essentially decreases with dose at the same rate, but no low dose increase is observed. These observations have been reproduced within 10 % with longitudinal measurements (b) on three other samples of the same batch and transverse measurements on one other sample. One can also see in figure 3 that irradiation is more efficient in damaging the TSF-TCNQ samples than the TTF-TCNQ ones. After a dose of 2.2×10^{15} fast neutrons/cm^2, in the case of TSF-, one can observe a saturation of the resistivity decrease.

4. **Analysis of the experimental results.** — In the following, we have attempted to analyse the resistivity *versus* dose curves of figure 3.

It would be very interesting to have an idea of the radiation induced defects configurations. As we have explained in § 2, a fast irradiation particle only sees individual atoms and displaces them from their normal positions to unusual ones. So, covalent bonds are broken, free radicals, more or less screened by the free carriers, are created and new chemical reactions can locally take place.

There are probably a lot of different possible defects configurations and one cannot speak about a precise Frenkel-pair such as in a metal or a ionic crystal, but about an average *point* defect with an average potential and an average range (or localization length).

In the following attempt to analyse the resistivity *versus* dose curves, we shall deal with this average point defect and try to measure its local efficiency in destroying the Peierls transitions effects at low temperature.

At low temperatures, TTF- and TSF-TCNQ are small gap semiconductors [14] HMTSF-TCNQ is more probably a low temperature anisotropic semimetal [16, 17]. The effects of radiation induced defects on the transport properties of several semiconductors [20] and a few semi metals [21] have been carefully investigated during the past few years. In both cases one generally applies a rigid band model where a radiation induced point defect affects the conductivity in two ways : first, it changes the mobility of the carriers and second, it is efficient in increasing or decreasing the number of carriers. One of the authors of the present paper recently tried to apply such an homogeneous rigid band model to the anisotropic semi metals polysulfur nitride $(SN)_X$ [22] and HMTSF-TCNQ [4].

Actually, in quasi-one-dimensional conductors such as TCNQ salts, the low temperature semiconducting or semimetallic state are reached through a Peierls transition which modifies the band structure of the compound. Figures 1 and 2 clearly demonstrate that point defects, even in low concentration, strongly affect the phase transitions of TTF- and TSF-TCNQ. So, the principal low temperature effects of these defects cannot be taken in account by a classical rigid band model but have to be related to large local changes in the band structure.

A classical phenomenological method to explain irradiation experiments is to suppose that each displacement cascade produced by an incident neutron transforms, on average, a given volume of the crystal. The physical reasons for those transformations will be examined in more details in the discussion below (§ 5).

Let us suppose that, at low temperatures, the irradiated TCNQ salts may be considered like inhomogeneous materials. In this hypothesis, the fraction of the crystal damaged by the displacement cascades should be composed of small volumes more (TSF- and TTF-) or less (HMTSF-) conducting than the *pure material* and that these volumes are included at random in a matrix of undamaged crystal.

The electrical resistances of binary mixtures have been the subject of extensive studies. One of the most successful methods of treating the transport properties of randomly inhomogeneous materials has been a self-consistent or effective medium approach studied by Landauer [10] and generalized by Cohen, Jortner [11] and Stroud [12]. Pan, Stroud and Tanner [13] applied that theory to TTF-TCNQ near the 38 K transition. In that temperature region, TTF-TCNQ was assumed to consist of small regions which are semiconducting and others which are conducting.

According to the effective medium theory, the conductivity σ of a material in which a fraction f_i has been transformed by irradiation and has the conductivity σ_i and the remainder $f_0 = 1 - f_i$ a conductivity σ_0 can be expressed as the solution of the equation :

$$f_i \frac{\sigma - \sigma_i}{g\sigma_i + (1 - g)\,\sigma} + f_0 \frac{\sigma - \sigma_0}{g\sigma_0 + (1 - g)\,\sigma} = 0 \,. \quad (1)$$

The quantity g denotes a depolarization factor describing the shapes of the homogeneities ($g = 0$ for needles parallel to the applied field, $g = 1$ for disks perpendicular to the applied field, and $g = 1/3$ for spheres).

This equation can be applied to explain the conductivity behaviour of irradiated samples. Let γ be the fraction of displaced atoms expressed in d.p.a. (displacement per atom), and n be the number of atoms which are included in the transformed volume around each charged point defect. If we neglect correlation between point defects in a displacement cascade (reasonable hypothesis in a material containing only light nuclei), the fraction f_0 of undamaged material after a dose γ may be written $f_0 = \exp(-\,n\gamma)$.

The solution of equation (1) is :

$$\frac{\rho(\gamma)}{\rho(0)} = \frac{\sigma_0}{\sigma} = \frac{2(1-g)}{[a^2 + 4\,g(1-g)\,k]^{1/2} - a}$$
$$a = (g - f_0) + (g - f_i)\,k \qquad (2)$$
$$k = \sigma_i/\sigma_0\,, \quad f_0 = e^{-n\gamma}\,, \quad f_i = 1 - f_0\,.$$

The shape of the inhomogeneities produced by irradiation is related to the shape of the displacement cascades which are essentially spherical. So, it is a good approximation to take $g \sim 1/3$ (spherical inclusions). Figure 4 shows theoretical curves using equation (2). Comparison from this curve with figure 3 clearly shows that the simple effective medium model agrees well with the main features of the low temperature irradiation curves.

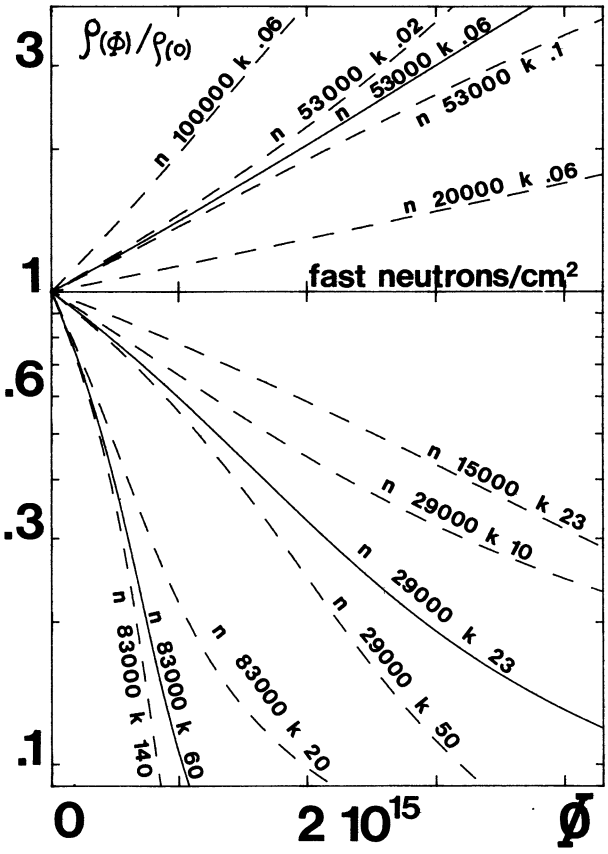

Fig. 4. — Set of resistivity *versus* dose curves calculated with the simple effective medium model. Full line curves correspond to the best fits of experimental curves of figure 3.

Nevertheless, this model is not able to explain the low dose increase in longitudinal resistivity for TTF-TCNQ, obviously a transitory one-dimensional effect. Also it cannot take into account the *high dose* saturation behaviour for TSF-TCNQ. Estimations for n (number of atoms included in the transformed volume around a radiation induced defect) and for $k = \sigma_i/\sigma_0$ can be deduced from this model (see Table II).

Table II. — *n is the number of atoms included in the transformed volume around a radiation induced defect. $k = \sigma_i/\sigma_0$ the ratio between the resistivities of transformed and « pure » phases.*

TCNQ salt	n	k
TTF-	~ 29 000	23
TSF-	~ 83 000	60
HMTSF-	~ 53 000	0.06

Obviously, the inhomogeneous model that has been presented here, works only at low temperatures (below the phase transitions). In the metallic state, radiation induced defects have very different effects on the transport properties [4, 24] : at 300 K conductivity always decreases under irradiation. The Pennsylvania group has given a very different and interesting interpretation of high temperature irradiation effects in TTF-TCNQ [4] which has been confirmed by recent experiments in our group [25]. This interpretation is not at all in contradiction with the present analysis.

5. **Discussion.** — TTF-TCNQ and TSF-TCNQ physical properties are dominated, at low temperature, by the occurrence of charge density waves associated with the Peierls instability [14]. The giant Kohn anomaly and divergent response functions are closely related to the quasi-one-dimensional character of those materials, i.e. there is no coherent transfer of the wave function between chains and transverse conductivity is diffusive. Nevertheless, the low temperature metal to semiconductor transition absolutely requires some tridimensional coupling, i.e. some transversal coherence between the charge density waves [15]. Irradiation induced defects locally destroy this Coulomb coherence. Within a given volume around each individual point defect, the complete achievement of Peierls transition is impossible. Irradiation produces volumes more conducting than the distorted matrix. The average number n of atoms affected by that transformation per point defect is 29 000 for TTF-TCNQ and 83 000 for TSF-TCNQ. This corresponds to a few tens of Angströms around each individual defect.

The case of HMTSF-TCNQ is different. Magnetorestance [16] and Hall effect [17] measurements have demonstrated that this compound behaves, at low temperatures, as an anisotropic, yet three-dimensional semimetal. In a *clean* specimen of HMTSF-TCNQ, the coherent transfer of the wave function between chains makes the electronic band structure three-dimensional and consequently suppresses the Peierls transition [18]. In a *dirty* system containing point defects, the coherent transfer of the wave function between chains is suppressed, thus the system is more one-dimensional, a kind of Peierls transition takes place locally (at about 20 K), and the resistivity

increases... A more precise analysis of the HMTSF-TCNQ case has been given in ref. [4]. There, the value of n is theoretically estimated with a simple order of magnitude calculation.

Curve 3 of figure 2 shows the effect, on a TTF-TCNQ sample, of annealing at 300 K following an irradiation with a dose of 4.3×10^{15} fast neutrons/cm^2. It is interesting to look a little more to the temperature behaviour of irradiation induced defects. Figure 5 shows the 0-300 K conductivity temperature curve of a sample of TSF-TCNQ. Curve 2 is the conductivity of the sample after the 21 K irradiation. The second peak, on this curve, near 80 K is related to a thermal rearrangement of the low temperature defects. It produces an unusual increase in conductivity at about the Debye temperature. This is the reason why curve 3 exhibits a conductivity maximum higher than curve 2 after an annealing at 300 K. On TTF-TCNQ, the annealing effects are qualitatively the same but the annealing temperature is 140 K.

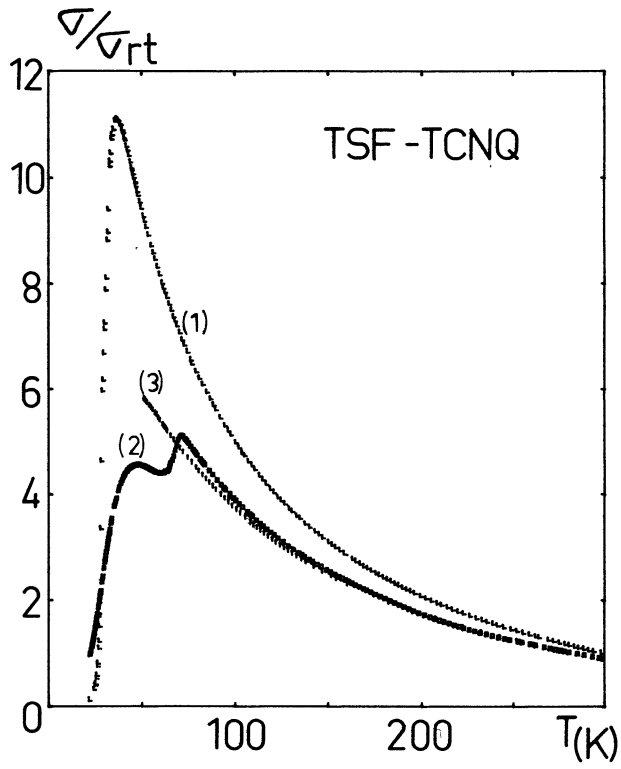

Fig. 5. — Irradiation of TSF-TCNQ followed by an annealing : (1) — before irradiation (2) — after irradiation, (3) — after irradiation and annealing. The second peak at ~ 80 K on curve 2 corresponds to a thermal rearrangement of the low temperature defects.

It is clear that the defects, which are directly radiation induced at 21 K, are different from the *relaxed ones* created by an irradiation at room temperature. It is not surprising the effects on TTF-TCNQ irradiated by Chiang *et al.* at room temperature are not the same as those seen in the low temperature irradiations in the present work. The low temperature defects are much more effective in decreasing the conductivity maximum and in displacing the temperature transitions.

6. **Conclusions.** — A low temperature radiation produced defect transforms a region a few tens of Angströms around it. It locally inhibits the usual phase transitions for the *pure* material by destroying the transverse coherence they need.

The scatter in the experimental transport data for the same transfer salt samples issuing from different batches suggests that structural disorder plays an important role even in the *pure* crystal. The irradiation results suggest that, at low temperatures, irradiated samples as well as so called *pure* samples contain macroscopic inhomogeneities due to defects. At low temperature, TCNQ salts are probably binary mixtures of more or less distorted volumes [13].

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APPENDIX

Calculation of the fraction of displaced atoms in a neutron irradiated TCNQ-salt

The average fast neutron of Triton Nuclear reactor has an energy E of about 1 MeV. It can collide with one of the atoms of the crystal (called primary atom) with a total cross section of about 10^{-24} cm^2. In a hard sphere elastic collision it can transfere to the primary atom a maximum energy

$$T = \gamma E = 4\, ME(1 + M)^{-2}$$

where M is the atomic mass of the displaced atom.

In TTF-TCNQ :

$$\gamma_H = 1 \quad \gamma_C = 0.284 \quad \gamma_N = 0.249 \quad \gamma_S = 0.118\,.$$

A 1 MeV neutron which has undergone a collision produces on average :

— 0.235 proton with 500 keV average energy,
— 0.530 carbon with 142 keV average energy,
— 0.117 nitrogen with 124 keV average energy,
— 0.117 sulphur with 59 keV average energy.

It is well known [19, 26] that a fast charged particle such as a 500 keV proton loses at least 99 % of its

energy by electronic excitation which does not produce any displacements. So we may neglect the displacements produced by the proton primaries. The energy available for atomic displacements is only 97 keV per incident 1 MeV fast neutron. In a recent calculation, D. Lesueur [9] estimated the number of displaced atoms in a displacement cascade when the energy given to the lattice for atomic displacements is T. The application of this calculation to TTF-TCNQ gives the following results : the average number of displacement per incident 1 MeV neutron having undergone a collision is, in the H lattice

$$N_H = 28\,000/2\,E_H$$

where E_H is the threshold energy for a stable displacement in this sublattice. For the other sublattices the results are

$$N_C = 99\,000/2\,E_C \quad N_N = 21\,000/2\,E_N\,,$$

and

$$N_S = 10\,000/2\,E_S\,.$$

In open structures such as those of the organic conductors, a reasonable value for these threshold energies is 5-10 eV.

So, within a factor of 3 or 4, the total atomic fraction of point defects for the maximum dose of 4.3×10^{15} f.n/cm^2 is $\sim 2.2 \times 10^{-5}$.

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