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Irradiation effects in quasi-one-dimensional organic conductors: The evidence of a transverse fixed-range phonon-assisted hopping

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Several highly conducting organic quasi-one-dimensional compounds such as tetrathiafulvalene-tetracyanoquinodimethane, tetramethyltetraselenafulvalene-dimethyltetracyanoquinodimethane, hexamethylenetetraselenafulvalene-tetracyanoquinodimethane, tetraselenatetracen-iodine, and nonstoichiometric tetrathiatetracene-iodine have been irradiated at low temperature with neutrons and at room temperature with x rays. After an irradiation dose corresponding to one broken molecule in a few hundreds the resistivity-versus-dose curves become exponential over a several orders-of-magnitude increase in resistance (up to six), and the conductivity-versus-temperature curves become single-activated over a large temperature range. A model is presented which is able to explain these features qualitatively and quantitatively. Irradiation defects are considered to divide the conducting chains into segments. The transverse motion of the electrons which was originally diffusive becomes a phonon-assisted hopping from segment to segment. Previous experimental results from the Pennsylvania and the Budapest groups are considered from the point of view of this new model.

I. INTRODUCTION

During the last ten years a large part of the interest devoted to quasi-one-dimensional organic conductors has been related to their transport properties in the metallic state above the phase transitions. In principle, in a one-dimensional system an infinitesimal random potential creates a localized state. All electronic eigenstates would therefore be localized, and dc electronic conduction could only occur via phonon-assisted hopping.[1,2] In practice, a large class of highly conducting tetracyanoquinodimethane (TCNQ) salts exhibit in their metallic state a typical Drude behavior characteristic of the transport properties of traveling waves.[3,4] Thus it is convenient to consider the longitudinal wave vector $k_{\parallel}$ as a good quantum number with an average lifetime $\tau_{\parallel}$ due to classical[5] or less classical[6] scattering by all the possible dynamic and static defects including the structural ones. Nevertheless, even the "best" highly conducting crystals such as tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) or tetrathiatetracene-iodine (TTT_2I_3), or the more up-to-date tetramethyltetraselenafulvalene-dimethyltetracyanoquinodimethane (TMTSF-DMTCNQ) (Ref. 7), ditetramethyltetraselenafulvalene-hexafluorophosphate ($TMTSF_2$-PF_6) (Ref. 8), or tetraselenatetracen-iodine [$(TST)_2I$] (Ref. 9) are poor metals at room temperature. Their longitudinal conductivities are coherent, but the electronic mean free paths along the chains are only a few molecular distances at room temperature. The recent experimental evidence[10,11] of a fluctuating Fröhlich component of the conductivity related to the sliding of the uncommensurable charge-density waves along the chains added a collective term to the low-coherence single-electron conductivity. Its coherence length is several tens of molecular distances and its intensity, which is maximum at the conductivity maximum, decreases with increasing temperature and vanishes at room temperature.[10]

The interest in the field of quasi-one-dimensional conductors was not only devoted to the best conductors among them. Quinolinium, phenazinium, acridinium, *N*-methylphenazinium (NMP), and TCNQ complexes were often considered as weakly disordered one-dimensional conductors. They have been the subject of recent[12-14] and less recent[15-17] works. At room temperature their longitudinal conductivity is known to be diffusive.[12,13,17] At low temperature, the shapes of the conductivity versus temperature curves have usually been attributed to quasi-one- or quasi-two-dimensional hopping.[13,15-17]

In both types of conductors that we have considered, the transverse conductivity is diffusive[18,19] in the metallic temperature range. Soda, Jerome, and Weger[19] have demonstrated that when the longitudinal component of the conductivity is coherent, the transverse conductivity, which, as usual for diffusive motion, is proportional to the interchain jumping frequency $\tau_\perp^{-1}$, and is proportional to the longitudinal collision time $\tau_\parallel$ because of the "one-dimensional golden rule."[10]

This very brief review of a few important concepts in the field of quasi-one-dimensional–conductor transport properties shows clearly that disorder is a subject which cannot be avoided. It determines $\tau_\parallel$, $\tau_\perp$, the coherence lengths of the charge-density waves, and the hopping processes at low temperatures. Thus it is not surprising that transport properties of irradiated samples have been the subject of recent extensive studies.

The first work was done by the Pennsylvania group, who published a high-temperature irradiation experiment on TTF-TCNQ.[20] They carefully analyzed the resistance versus temperature curve in the metallic temperature range and deduced a large and unusual deviation to Matthiessen's rule. This behavior, confirmed by more recent experiments on HMTSF-TCNQ and TTF-TCNQ in our group,[21] was one of the central points in the recent controversy about resistivity in organic metals.[22]

Until now, the Fontenay-aux-Roses group has been interested in the low-temperature effects of the radiation-induced defects. They have been found to destroy the transverse coherence between Peierls distortions on neighboring chains. Thus they inhibit the phase transitions related to the three-dimensional ordering of the charge-density waves. The low-temperature irradiations were performed on HMTSF-TCNQ,[23] TSF-TCNQ, and TTF-TCNQ (Ref. 24); an effective medium model has been applied to explain the shapes of the resistivity versus irradiation dose curves.[24] In collaboration with the Budapest group, we also irradiated nonstoichiometric TTT_2I_3 and compared the radiation-induced defects with chemical impurities.[25]

The Budapest group has also irradiated TTF-TCNQ, quinolinium $(TCNQ)_2$ and *N*-propylquinolinium $(TCNQ)_2$ at room temperature.[26,27] Their dielectric permeability measurements suggest that the irradiated material consists of segments decoupled from each other by the defects.

In the present paper, we present the results of new irradiation experiments on five different highly conducting complexes: The well-known two-chain systems TTF-TCNQ, HMTSF-TCNQ, and TMTSF-DMTCNQ, the single-chain radical-ion salt $(TST)_2I$, and the nonstoichiometric $TTT_2(I_3)_{1.04}$. The behavior of all these different organic conductors becomes very similar when they are irradiated. After a low damage dose corresponding to one broken molecule in a hundred or a thousand, all the resistivity versus temperature curves recorded after irradiation are essentially single-activated with activation energies of about several hundred Kelvin. These large similarities between systems that are so different suggest a very simple and general explanation related to the low dimensionality of these organic metals or semiconductors.

In the first part of this paper, we try to understand what an irradiation-induced defect is in a molecular conducting crystal. The experimental results are shown in the second part, and the third part attempts to explain them using a simple transverse hopping model. In the last part we show that this idea is of general applicability. The principal results of the Pennsylvania and the Budapest groups are discussed using this new approach.

II. IRRADIATION EFFECTS IN CONDUCTING MOLECULAR CRYSTALS

An 8-keV Cuα photon is able to produce (7–8)-keV photoelectrons.[28] These electrons will, in turn, lose their energy in the form of electronic excitations or ionizations.[29] 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 and x and Γ rays can be used to cross-link insulating polymers. The situation is radically different in conducting or semiconducting materials, even when the number of free carriers is low (~ 10^{18} carriers/cm^3). In a semimetal such as bismuth,[30] in several simple or binary semiconductors, in conducting sulfides such as TaS_2 (Ref. 31), 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 $(SN)_x$.[32] In a quite recent irradiation study,[33] the mechanisms of the defect production in conducting molecular crystals have been shown to be similar to those in usual molecular solids.[34-36] The defect-production rates have been demonstrated to be proportional to the total energy absorbed by the crystal. In the case of TMTSF-DMTCNQ, for instance, the production of defects in a concentration of 1 defect/molecule needs an absorbed energy of a 7.1 ± 1 keV/TMTSF-DMTCNQ unit.

A part of the energy given by a fast neutron to a crystal is in the form of atomic collisions. A fast neutron (~ 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 sulfur or a selenium atom; this interaction will in turn set off a cascade of atomic displacements, each requiring an energy of about 5 or 10 eV. In this way each neutron that produces a primary knock-on ion creates several thousand defects in the lattice.

Except for the displacement threshold energies, all the parameters determining the number of collisions and displacements in each sublattice are insensitive to the crystal structure and to the solid-state properties of the solid. One can roughly say that a fast particle only "sees" individual atoms and, if it is fast enough, just individual nuclei. If the mass and the atomic number of each component of the target are known and also the proportion in which they are present, the order of magnitude of the number of displacements produced by a given fast particle can be calculated. This can be done for neutrons using the theories of Lindhard[37,38] and the recent calculations of Lesueur.[39] The application of these calculations to TTF-TCNQ gives the following results[24]: The average number of displacements produced per incident 1-MeV neutron having undergone a collision is, in the hydrogen sublattice, $N_H = 28000/2E_H$, where E_H is the average threshold energy (in electron volts) for a stable displacement in the H sublattice. For the other sublattices the results are $N_C = 99000/2E_C$, $N_N = 21000/2E_N$, $N_S = 10000/2E_S$. In TTT_2I_3 the corresponding results are $N_H = 19000/2E_H$, $N_C = 90000/2E_C$, $N_S = 17000/2E_S$, and $N_I = 1500/2E_I$.

However, the primary knock-on ions responsible for the displacements lose only part of their energy in atomic collisions, this fraction depending essentially on their energy.[37] The other part of the energy loss of the primary ions or electrons is in the form of electronic excitation. In our case the total amounts of energy lost by electronic excitations and atomic collisions are nearly equivalent. Thus atomic collisions strongly dominate the total damage produced by the incident neutrons because one needs a few keV to produce a defect by the ionization channel and only a few eV to produce a similar defect by atomic collisions.

We are quite sure that irradiation displaces atoms from their usual positions but it is difficult to imagine how the crystal reorganizes itself around the defect centers and how these defects relax to stable configurations. The displacement of an atom breaks covalent bonds, locally produces free radicals which are more or less screened by the free carriers, and allows new chemical reactions to take place locally. There are probably many different possible configurations, and thus one cannot speak about a precise Frenkel pair structure but can speak more about an average configuration with an average potential around it. All the recent experiments show this potential to be high compared with the bandwidth. In TTT_2I_3 irradiation-induced defects have been shown to be much more effective in changing the transport properties than impurities in the iodine chains.[25] In the main highly conducting TCNQ salts, an irradiation-induced defect creates a much stronger perturbation than a replacement of a sulfur by a selenium atom.[40]

Thus it is quite natural to consider irradiation defects as strong barriers and the irradiated material to consist of segments decoupled from each other by the defects. The experiments discussed in the following sections give further information on this point.

III. EXPERIMENTAL RESULTS

The neutron irradiations were carried out at liquid-hydrogen temperature (21 K) in the Triton nuclear reactor at Fontenay-aux-Roses using the VINKA apparatus described by Conte and Dural.[41] The fast-neutrons (f.n.) ($E > 1$ MeV) flux at the sample was 2.5×10^{12} f.n./cm^{2}s. Following Refs. 24 and 39, this flux corresponds to a displacement rate in TTF-TCNQ of about 1.5×10^{-8} displacements per atom per second (d.p.a./s). The Γ-ray flux at the sample was 100 mW/s (measured by absorption in graphite). The displacement rate due to Γ rays was estimated to be only about 5×10^{-10} d.p.a./s. Each organic conductor was represented by four different samples. The results that we present here were perfectly reproducible from sample to sample.

The x-ray irradiations were carried out at room temperature with a usual x-ray generator with a copper tube. The flux at the samples was 41 kiloröntgen/min or ~ 4×10^{11} photons/cm^2 s.

Figure 1 shows the 21-K conductivity of TTF-TCNQ, $TTT_2(I_3)_{1.04}$, $(TST)_2I$, and TMTSF-DMTCNQ as a function of the irradiation dose. The low-temperature, low-dose increase in conductivity has already been reported and analyzed.[24] This initial increase is related to the Peierls transition. It is completely absent in the case of $(TST)_2I$ because there is no evidence of a Peierls transition down to 20 K and the irradiation occurs in the "metallic" state. After the initial increase the conductivity decreases exponentially over 3 orders of magnitude in the case of TTF, over 5 orders of magnitude in the cases of TTT_2I_3 and $(TST)_2I$, and over 6 orders of magnitude in the case of TMTSF-DMTCNQ.

Figure 2 shows the room-temperature conductivity of HMTSF-TCNQ and TMTSF-DMTCNQ as a function of the x-ray irradiation dose. In the

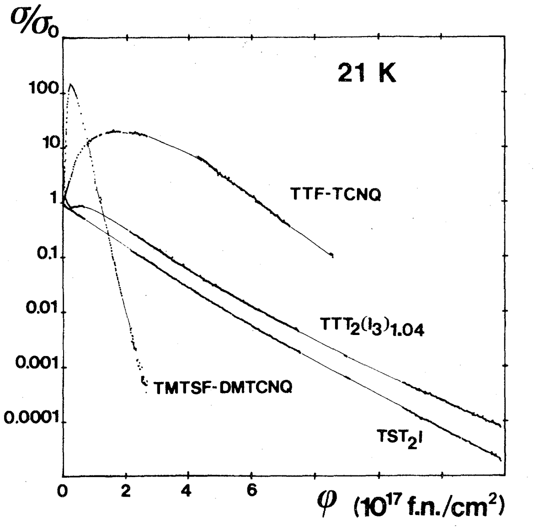

FIG. 1. Neutron irradiations of four quasi-one-dimensional organic conductors at 21 K. Their conductivity is plotted versus the neutron dose. After an initial increase related to the disappearing of the Peierls transition, the conductivities decrease exponentially over 3 to 6 orders of magnitude.

metallic state there is no initial increase in conductivity and the decrease is also exponential on a large dose range.

Figure 3 shows the resistivity versus temperature curves of TTF-TCNQ and TMTSF-DMTCNQ before and after an irradiation dose of 8.7×10^{17} f.n./cm^2. This corresponds to an atomic fraction of displaced atoms of $c=6\times10^{-3}$ or a molecular fraction of damaged molecules $1-\exp(-cn)\simeq0.1$, where n is the number of atoms per molecule. After the irradiation, the curves are single-activated with activation energies of 14 meV for TTF-TCNQ and 74 meV for TMTSF-DMTCNQ corresponding to 160 and 89 K, respectively.

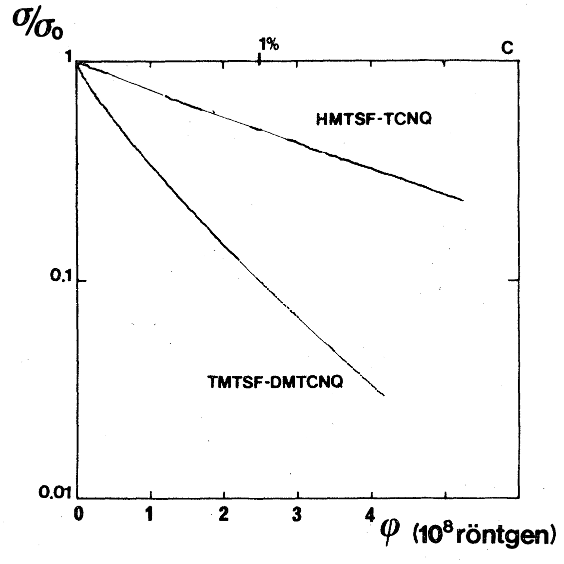

FIG. 2. X-ray irradiation of TMTSF-DMTCNQ and HMTSF-TCNQ at room temperature. Conductivity decreases exponentially with dose. The upper scale gives the percentage of damaged molecules in TMTSF-DMTCNQ.

Figure 4 shows the resistivity versus temperature curves of $(TST)_2I$ and $TTT_2(I_3)_{1.04}$ before and after an irradiation dose of 1.4×10^{18} f.n./cm^2. This corresponds to an atomic fraction of displaced atoms of about 8×10^{-3} or a molecular fraction of damaged molecules of 0.3. After this heavy

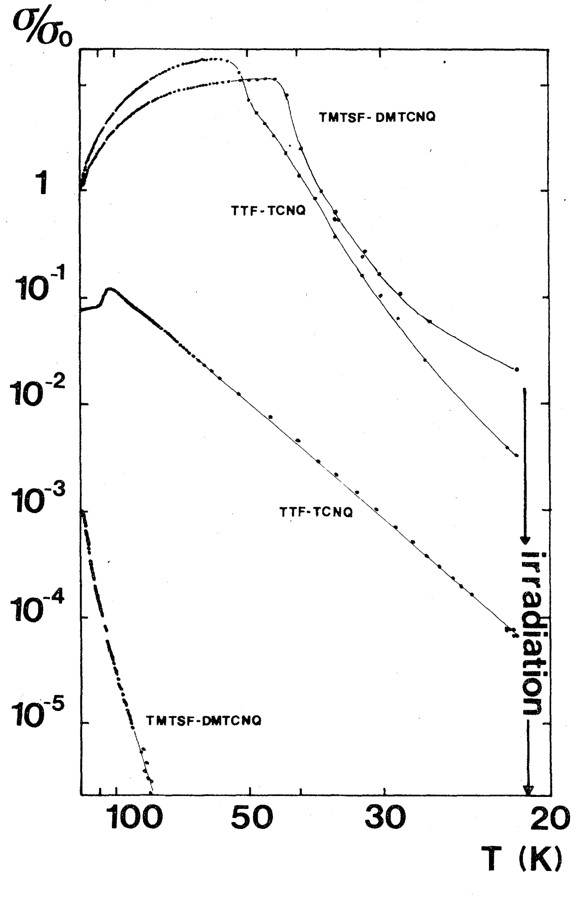

FIG. 3. Arrhenius plots of the conductivities versus (reciprocal) temperature of TMTSF-DMTCNQ and TTF-TCNQ, before and after an irradiation by 8.7 $\times10^{17}$ fast neutrons/cm^2. This neutron dose corresponds to a fraction of displaced atoms of about 6×10^{-3} displacement per atom (d.p.a.) or a fraction of damaged molecules of about 0.1 displacement per molecule (d.p.m.).

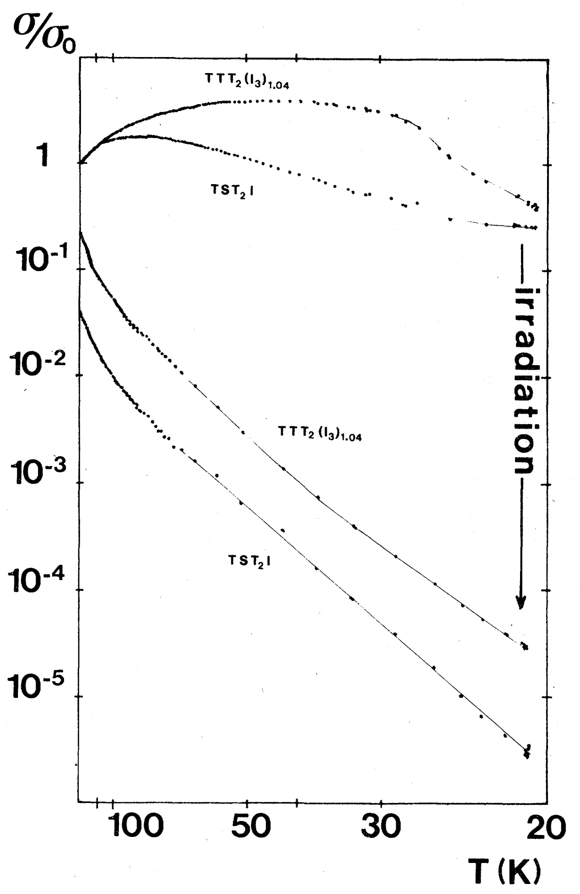

FIG. 4. Arrhenius plots of the conductivities versus (reciprocal) temperature of $(TST)_2I$ and $TTT_2(I_3)_{1.04}$, before and after an irradiation by 1.4×10^{18} fast neutrons/cm^2. This neutron dose corresponds to a fraction of displaced atoms of about 8×10^{-3} (d.p.a.) or a fraction of damaged molecules of about 0.3 (d.p.m.).

dose, the resistance versus temperature curves of the two radical-ion salts are activated with the same activation energy of 14 meV corresponding to 160 K.

At the end of this experimental section, we have to discuss briefly some effects which could have introduced a few uncertainties in our results. In assuming that the number of defects is given by the total number of displacements, one neglects all possible recombinations during irradiation and all annealing effects during the temperature changes. In two recent papers[21,24] annealing effects have been discussed in the cases of HMTSF-TCNQ, TTF-TCNQ, and TSF-TCNQ and shown to be small with respect to the irradiation effects. In the present low-temperature neutron experiments, the dose curves have been recorded directly at 21 K. Furthermore, the samples were warmed slowly to room temperature and the resistivity versus temperature curves recorded. Finally, they were cooled again and a second set of temperature curves were shown to be very similar to the previous one.

IV. INTERPRETATION OF PRESENT RESULTS

At the beginning of the low-temperature irradiation, conductivity increases with dose in all the samples which have been driven to a semiconducting state by Peierls transitions. At the irradiation doses corresponding to the conductivity maximum (Fig. 1), the phase transitions have been completely smeared out of the conductivity versus temperature curves. The density waves are still present but they cannot reach the transverse coherence that they need to achieve the phase transitions. In one of the TMTSF-DMTCNQ samples, for instance, the room-temperature longitudinal conductivity before irradiation was $\sigma_b(T=300, c=0)=300\ (\Omega\,\mathrm{cm})^{-1}$, and the anisotropy[42] was $k(T=300, c=0)=\sigma_b/\sigma_a=160$. At 21 K before irradiation these transport properties were $\sigma_b(21,0)=5\ (\Omega\,\mathrm{cm})^{-1}$ and $k(21,0)=90$. At 21 K after a 2×10^{16} fast-neutron dose corresponding to two broken molecules over 1000, the TMTSF-DMTCNQ had reached the conductivity maximum of Fig. 1 with the following values, similar to those recorded at room temperature in the metallic phase[42]:

$$\sigma_b(T=21\ \mathrm{K}, c=2\times 10^{-3})=200\,(\Omega\,\mathrm{cm})^{-1}$$

and

$$k(21,\ 2\times 10^{-3})=130\,.$$

This initial, low-temperature behavior of the irradiated samples has been carefully analyzed in Ref. 24, and an accurate study of the anisotropies of TMTSF-DMTCNQ under irradiation is being carried out.[42]

Let us concentrate here on the exponential conductivity decreases that can be observed in all the irradiated samples of Figs. 1 and 2. There is a great temptation to apply a very simple one-dimensional model to all the irradiated crystals. Let us suppose that an irradiation-induced defect is able to cut a chain and to prevent it from carrying any current. The conductivity is proportional to the number of unbroken fibers and will consequently decrease exponentially with dose. This model has been applied successfully by Zuppiroli and Friend[32] to explain the change in conductivity in polysulfur nitride irradiated with heavy ions. The fibrous character of $(SN)_x$ allows it to be considered as a bundle of conducting fibers insulated from one another.

There are, actually, many objections to the application of such a simple idea to conducting molecular crystals. The principal one is that the anisotropy of such crystals is only of the order of 100. Consequently, the chains are not at all independent from one another and it is impossible to explain how irradiation can increase the resistivity along the conducting axis by between 3 and 6 orders of magnitude without causing a similar increase in the transverse resistivity.

Let us concentrate now on this transverse resistivity which, as mentioned in the Introduction, is diffusive. It is related to the diffusion coefficient $D_\perp$ by the Einstein equation applied to a degenerate Fermi gas:

$$\sigma_\perp = [n(\epsilon_F)k_BT]e\mu_\perp\,, \quad \mu_\perp = eD_\perp/k_BT\,.$$

The coefficient $D_\perp$ is, in turn, determined by the interchain jumping rate $\tau_\perp^{-1}$ through the relation $D_\perp = l^2\tau_\perp^{-1}$, where l is the jumping distance.

In a pure crystal with infinite chains, Soda, Weger, and Jerome[19] have determined $\tau_\perp^{-1}$ for the case where the single-electron longitudinal conductivity is coherent with an average scattering time $\tau_\parallel$. They found that $\tau_\perp^{-1}$ is given by the one-dimensional golden rule.

$$\tau_\perp^{-1} = (2/\hbar)\,|t_\perp|^2\tau_\parallel/h\,, \tag{1}$$

where $t_\perp$ is the transverse transfer integral.

This model applies only if the electronic states coupled by $t_\perp$ have the same energy before and after the jump. When strong random potentials are created by irradiation, the chains are made of segments of variable lengths. The energies of electrons in each one-dimensional box bounded by the defects are slightly different from box to box: The kinetic energies of the electrons are different because of changes in the quantization of their levels and their potential energies are altered by the tails of the strong random potentials. One can say that the fields created by the defects modulate the transverse energy levels. Consequently, the diffusive transverse jumping becomes a phonon-assisted hopping: Each hop from one segment to an adjacent one needs the creation or the absorption of a phonon to provide the energy difference. In the usual way,[43,44,16] the hopping rate $\tau_\perp^{-1}$ is now modified and contains an activation factor which is multiplied with the spatial tunneling factor $(\tau_\perp^{-1})_0$:

$$\tau_\perp^{-1} = (\tau_\perp^{-1})_0 \exp(-\Delta E/k_BT)\,. \tag{2}$$

The exponential term gives the probability of a phonon to be created with the necessary energy.

The macroscopic transverse conductivity is determined by the percolation of electrons through this particular network, that is to say, by the critical paths which cross all the samples and which carry most of the current. These critical paths do not change with temperature, as only hops to nearest-neighboring boxes can occur. This situation is very similar to the fixed-range hopping in compensated p-type germanium.[43,45] This semiconductor was doped with donors and compensated with deep acceptors. All the deep levels were far from the Fermi level and were completely filled. Thus they could not contribute to any type of conduction. However, because of the random fields that they created in the sample, they modulated the donor levels and locally created small energy differences ΔE from site to site. Over a large range of temperatures and concentrations only hops between neighboring sites occurred and the critical paths did not change with temperature. In this case, the conductivity versus temperature curves are activated[43] with a low activation energy which is a complex average of the values of ΔE

In the case of the one-dimensional conductors, the higher the irradiation dose, the shorter are the segments and the higher is the modulation of the transverse energy levels. Thus the values of ΔE increase. In the evaluation of the average value $\langle\Delta E\rangle$ as a function of the molecular defect concentration c, it is convenient to consider only the first-order term and to write $\langle\Delta E\rangle = \epsilon c$. In this case, the transverse conductivity can be written as

$$\sigma_\perp(c,T) = (\sigma_\perp)_0 \exp(-\epsilon c/k_BT)\,. \tag{3}$$

The term $(\sigma_\perp)_0$ which accounts for the tunneling between chains in the presence of defects also depends on the temperature and the defect concentration. However, as discussed later, this conductivity term is dominated by the exponential factor over a large range of concentrations.

The longitudinal conductivity $[\sigma_\parallel(c,T)]$ can easily be deduced from the transverse conductivity using an interrupted strand model. Let us call $(\sigma_\parallel)_0$ the conductivity within a chain and let us suppose that each escape from a defects-bounded segment needs a transverse hop. This gives

$$\frac{1}{\sigma_\parallel(c,T)} = \frac{1}{(\sigma_\parallel)_0} + c\frac{l}{b}\frac{1}{\sigma_\perp(c,T)}\,.$$

One finally obtains

$$\sigma_\parallel(c,T) = \frac{(\sigma_\parallel)_0}{1 + k_0(l/b)c\exp(\epsilon c/k_BT)}\,, \tag{4}$$

$$k(c,T) = \frac{k_0}{k_0(l/b)c + \exp(-\epsilon c/k_BT)}\,, \tag{5}$$

where $k(c,T)$ is the anisotropy, l is the transverse hopping distance, and b is the usual longitudinal lattice parameter. $(\sigma_\parallel)_0$ and k_0, which are the parameters in the absence of hopping, are temperature and concentration dependent. However, the curves presented in Sec. III and in Refs. 20 and 24 show clearly that, over a large temperature range and especially after a short irradiation which destroys the effects of the Peierls transitions, the resistance versus dose curves are very flat compared to the increase in resistance observed here. The initial increase in conductivity shown by Fig. 1 is accounted for by $(\sigma_{\parallel})_0$, but the exponential decrease with defect concentration and with reciprocal temperature is essentially due to the exponential term

$$\sigma_{\parallel}(c,T) \sim \frac{(\sigma_{\parallel})_0}{k_0} \frac{b}{lc} \exp\left(-\frac{\epsilon c}{k_B T}\right).$$

If this very simple model is true, the values of ϵ deduced from the conductivity versus temperature curves or from the conductivity versus dose curves should have the same values. Table I shows the values deduced from these two curves.

In Fig. 5 the irradiation and temperature conductivity curves have been plotted versus $\varphi/k_B T$ where φ is the neutron dose. It is clear that for each irradiated organic conductor these two curves are the same over a large range of temperatures and concentrations when plotted versus $\varphi/k_B T$.

The good agreement obtained in the four different cases shows clearly that this very simple but general model can explain the high-dose behavior of these irradiated quasi-one-dimensional conductors. By high dose we mean a molecular concentration c of defects of the order or greater than $(k_0)^{-1}$ where the anisotropy k_0 is usually of the order of 100.

Such a model could also work in the case of the crystals of Fig. 2 irradiated at room temperature. These curves are also exponential-like. A study of the anisotropy of TMTSF-DMTCNQ under room-temperature irradiation is being carried out in our group to determine if this shape is really related to the segmentation of the chains.

TABLE I. Values of the parameter ϵ deduced from two different experiments (meV/molecular fraction).

ϵ (meV)	TTT_2I_3	TST_2I	TMTSF-DMTCNQ	TTF-TCNQ
From dose curves	45	46	750	110
From temperature curves	47	47	740	140

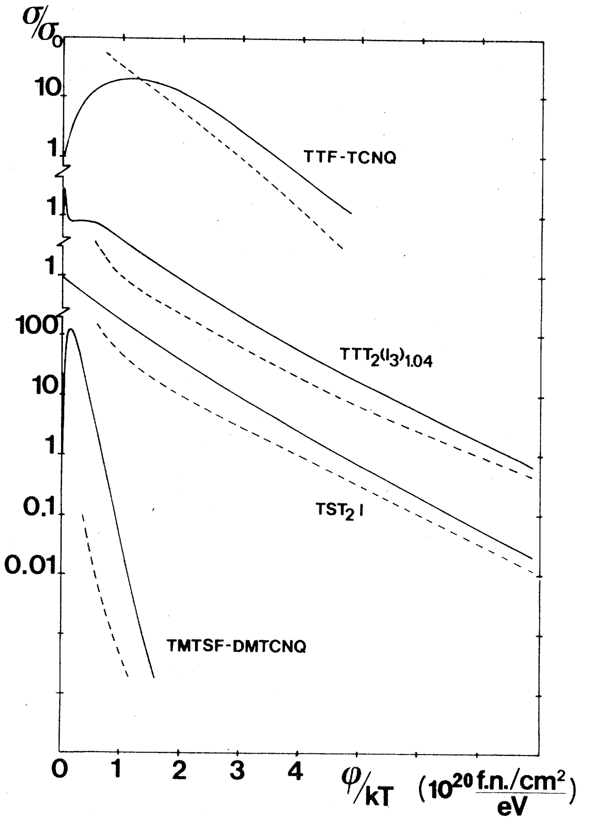

FIG. 5. Continuous lines are the conductivity versus dose curves of Fig. 1, the dotted ones are the conductivity versus temperature curves (after irradiation) of Figs. 3 and 4. Both types are plotted in a $\log_{10}$ scale versus $\varphi/k_B T$ where φ is the neutron dose and T the temperature. In this reduced scale, these two types of curves are very similar in large dose and temperature ranges.

V. DISCUSSION OF SEVERAL PREVIOUS RESULTS

As stressed in the interpretation of Sec. IV, the origin of the behavior observed and described here is to be found in the nature of the transverse conductivity. Originally diffusive before irradiation, it becomes a short-range phonon-assisted hopping when the chains are divided into segments by the irradiation-induced defects.

It is therefore not surprising to find a similar mechanism working in $Qn(TCNQ)_2$ even though the longitudinal conductivity is also diffusive. The Budapest group has proposed that this material, when irradiated, consists of segments decoupled from each other by defects.[26] More recently, Devreux, Nechtschein, and Grüner have directly determined the diffusion constant D using the spin-lattice relaxation time T_1.[46] They found that the diffusion constant and the conductivity both have the same behavior and vary exponentially with irradiation dose. We do not find this behavior surprising and consider that it can probably be explained by our hopping model.

In a now classical paper in the field of one-dimensional conductors, Chiang, Cohen, Newman, and Heeger[20] reported an unusual breakdown of Matthiessen's rule in irradiated TTF-TCNQ; the contribution of the irradiation-induced defects to the resistivity is greater at room temperature than near the resistivity minimum. They suggested that this result cannot be explained by single-particle conduction but can probably be understood in terms of a collective Fröhlich mode. Kaveh *et al.* tried to understand this unusual deviation in terms of phonon and libron drags.[22] However, one has to wonder if this change in the curvature of the resistance versus temperature curves is not simply due to the "blocking effect of the defects causing interchain series resistances to play an important role" (as mentioned elsewhere in Ref. 20).

Equation (4) in Sec. IV is equivalent to

$$\rho_{\parallel}(c,T)=[\rho_{\parallel}(c,T)]_0+c(l/b)\rho_{\perp}(c,T)\,. \tag{6}$$

The term with subscript 0 is the resistivity when one does not take into account the second term due to the segmentation of the chains by the defects. This introduces a transverse component into the longitudinal resistivity. The Pennsylvania group estimated their maximum defect concentration to be of the order of 1000 at. ppm. This gives a molecular concentration of $c \sim 10^{-2}$. Taking into consideration that the anisotropy is about 100, the second term in Eq. (6) cannot be considered as negligible compared with the first. This leads to a very simple explanation of the breakdown of Matthiessen's rule: The coefficient of c in Eq. (6) is not temperature independent such as in a metal but, as observed, increases with temperature. A similar analysis of this breakdown in terms of the blocking effect of defects has been recently given by Seiden and Bloch.[47]

VI. CONCLUSION

Four of the "best" quasi-one-dimensional organic conductors have been found to be "equal" with respect to the effects of irradiation when molecular-defects concentrations are greater than 10^{-2}. Several experimental results from Fontenay-aux-Roses and other groups make us confident about a model where the longitudinal as well as the transverse conductivity is dominated by a transverse short-range phonon-assisted hopping. To observe the direct effects of the defects on the scattering mechanisms within the chains requires defect concentrations less than a few 10^{-3} mole fraction. Only at this level can one explore the effects of the defects on the intrinsic temperature dependence of the conductivity and on the one-electron conductivity such as the collective Fröhlich mode.

Note added in proof: A recent experiment performed under pressure on irradiated TTF-TCNQ has demonstrated that irradiation defects in low molecular concentrations of the order of 10^{-3} are indeed effective in pinning the gliding charge density waves.[48]

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