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Résumé. — Nous avons mesuré, en fonction de la température et de la concentration en défauts d’irradiation, les conductivités de TMTSF-DMTCNQ suivant les trois directions a, b et c* (b est l’axe de grande conductivité). A température ordinaire les anisotropies Ωc/Ωa et Ωc/Ωc* diminuent sous irradiation. En effet, les défauts découpent les chaînes conductrices en segments, mélangeant ainsi une fraction de la résistivité transversale à la résistivité longitudinale. Ces courbes d’anisotropie en fonction de la dose d’irradiation ou de la température peuvent être décrites par une loi qui tient compte de la segmentation des chaînes et des sauts entre segments. Cette loi, à deux paramètres, permet une détermination directe de la concentration en défauts.

A basse température (21 K), au contraire l’anisotropie augmente sous irradiation jusqu’à une dose où la transition de Peierls a complètement disparu des courbes de résistivité. Les valeurs atteintes sont celles de l’état métallique, et le comportement devient identique à celui des irradiations à haute température. Le modèle mentionné ci-dessus est étendu aux cas des grandes anisotropies (plusieurs milliers) et permet de discuter d’intéressants résultats sur Qn(TCNQ)₂.

Abstract. — The conductivity of TMTSF-DMTCNQ has been measured along the main axis of the crystal as a function of temperature and irradiation dose. At room temperature the anisotropies decrease with irradiation due to the defects cutting the conducting chains into decoupled segments. A quite satisfactory fit of all the dose and temperature curves in the longitudinal and transverse directions has been obtained with a law accounting for the chain segmentation and for the transverse hopping from segment to segment. The model contains only two parameters and allows a direct determination of the defect concentrations.

At low temperature (21 K) the anisotropies increase with irradiation dose up to a defect concentration where the Peierls transition has been smeared out of the resistivity vs. temperature curves. When the anisotropy values are those of the metallic state the anisotropies decrease with dose as in the case of room temperature irradiations. Our model describing the effects of irradiation on the resistivity of quasi one-dimensional systems is extended to the case of very large anisotropies (several thousands) and recent interesting results in Qn(TCNQ)₂ are discussed.

1. Introduction. — The most simple and effective way to investigate the influence of defects on quasi one-dimensional conductors is to study irradiated samples. Irradiation has the advantage that in situ measurements can be carried out and the defect concentration can be changed continuously in the same crystal. Although the nature of the irradiation induced defects in organic conductors built up from large molecules is in general not clear, they appear to act in the same way, independently of the irradiation source. Moreover there are calculations to estimate the number of damaged molecules caused by different irradiation regimes which take into account the composition of the irradiated material [1, 2].

The considerable experimental work in the field of well conducting quasi one-dimensional organic charge transfer salts has confirmed the expected large effect of defects in these compounds. It was shown that defect...
concentrations of a few tenths of a percent are able to smear out the phase transition characteristic of several organic conductors such as TTF-TCNQ and related compounds [1-4] or NPQm(TCNQ)$_2$ [5]. At higher defect concentrations an unusual break-down of Matthiessen's rule was found in all the quasi one-dimensional systems studied by irradiation [3, 4, 8]. Another general feature is that the temperature dependence of the conductivity becomes activated with the activation energy increasing with increasing defect concentration [8]. The dielectric constant [6], thermal power [9], spin diffusion rate [7,10] and magnetic susceptibility [11] are also strongly affected by irradiation.

Recently a simple and general model was proposed [8] to describe both the temperature and concentration dependence of the conductivity for high defect concentrations. The main assumptions of this model, which are similar to those suggested in the early work of Zeller [12] on the temperature dependence of the conductivity of KCP, are the following:

a) Irradiation induced defects cut the conducting chains into segments. The electrons in a given segment have different energy levels which depend on the segment length. The characteristic energy difference between available electronic states in different segments is proportional to the defect concentration.

b) At high defect concentrations, when the above energy difference becomes higher than the thermal energy ($kT$), the conductivity between the segments is by phonon activated hopping. If the anisotropy is not extremely high, hopping to a neighbouring chain is preferable to intrachain hopping or tunnelling through the high potential barrier of the defect [13].

c) Regarding the longitudinal conductivity: with increasing defect concentration or decreasing temperature the resistivity contribution of the hopping dominates the intrinsic resistivity along the chain segments which is believed not to be strongly influenced by the cutting mechanism.

This phenomenological model describes quite well the longitudinal conductivity of several compounds [8]. Our present purpose is a further study of the validity of the above assumptions applying them to a particular salt: TMTSF-DMTCNQ (tetramethyltetraselenafulvalene - dimethyltetracyanoquinodimethane). Defects were created in single crystals by room temperature X-ray and low temperature neutron irradiations. The simultaneous measurements of the resistivity along the main axis of the crystal as a function of the temperature and the defect concentration give new, complementary results which can be analysed in terms of the above model. The experiments were carried out over a wide range of both temperature and defect concentration (20-300 K, 0-4 %) and the measured curves are compared with the results of numerical calculations.

2. Unirradiated sample. — TMTSF-DMTCNQ was chosen for this study as a model material. It is one of the most X-ray sensitive organic conductor studied up to now, and X-ray irradiation is an easy method to use for high precision in situ measurements. TMTSF-DMTCNQ has also been the subject of a recent extended experimental investigation which gave several important results about its transport properties [14-16]. At high temperatures it can be considered as a one-dimensional metal with a bandwidth of $D \sim 0.8$ eV along the chain direction [15]. The transverse conductivities are diffusive and they are believed to be strongly connected to the intrachain conductivity through the carrier density along the chains [15, 17]. There is a phase transition at 42 K which is extremely sharp [15] as shown on the upper part of figure 1. Since, as shown below, a defect concentration of about 0.1 % of damaged molecules is sufficient to smear out this transition, we consider the existence of this sharp phase transition as proof of high sample purity.

![Fig. 1. Temperature dependences of the longitudinal conductivity measured on pure and irradiated crystals. The dotted lines show the variation calculated from equation (4).](image)
In the metallic state the anisotropies

\[ k_a = \frac{\sigma_b}{\sigma_a} \quad \text{and} \quad k_c = \frac{\sigma_b}{\sigma_c} \]
decrease with decreasing temperature. On figure 2 the points show the results of the Montgomery measurements, while the crosses are the ratio of the conductivities measured on two crystals in perpendicular directions with contact arrangements as shown on the figure. The direct measurement of the transverse conductivity depends strongly on the sample dimensions and the actual value of the anisotropy, so we only consider this method as a check for the Montgomery results.

We note that at and just below the phase transition, where the longitudinal resistivity increases by several orders of magnitude, there is no large variation in the anisotropy. This confirms the picture of Soda et al. [17]; in spite of the different conducting mechanisms, the transverse conductivities are connected to the longitudinal one.

3. Irradiation at room temperature with X-rays.

The room temperature irradiation was performed using a conventional X-ray generator with a copper tube. Eight samples were measured simultaneously during the experiment. The applied field was always below \(10^{-2}\) Vcm\(^{-1}\). The highest dose (\(\sim 10^9\) kRöntgen) corresponded to an irradiation time of two weeks.

Figure 3 shows the \(a\) direction and the longitudinal resistivities together with the anisotropy as functions of the irradiation dose. They were measured on the same crystal by the Montgomery method. The increase of the transverse resistivity is clearly exponential. The \(c\) direction resistivity exhibits qualitatively the same behaviour (Fig. 4).

These results are analysed in terms of the model outlined in the introduction. If the assumptions are justified then the transverse resistivity should become activated with an activation energy proportional to the defect concentration \((\Delta E = \epsilon c)\):

\[ \rho_\perp(c, T) = \rho_\perp(0, T) e^{\epsilon c/kT} \quad (1) \]
since in the damaged crystal it is a direct measure of the phonon activated hopping between the segments. Each defect also causes interchain hopping to occur along the longitudinal conduction path. The hopping contribution to the longitudinal resistivity is proportional to the defect concentration and has the same activation character as the transverse resistivity:
Fig. 4. — Dose dependence of the longitudinal and the \( c^* \) direction resistivities and the anisotropy as measured.

\[
\rho_l(c, T) = \rho_{l}(0, T) + c \frac{l}{b} \rho_{l}(c, T) = \\
\rho_{l}(0, T) + c \frac{l}{b} \rho_{l}(0, T) e^{\sigma c/kT} \tag{2}
\]

where \( l \) is the transverse hopping distance and \( b \) is the lattice constant along the chain. This assumes that the conductivity within the segments does not change, i.e. the mean free path (which is of the order of the lattice constant \([15]\)) is not influenced by the defects which are widely spaced compared to it.

The simultaneous measurements of the transverse and longitudinal conductivities make it possible to determine the two parameters of the equations; namely \( \sigma c \) and \( \alpha/b \), where \( \alpha \) relates the irradiation dose (\( \Phi \)) and the defect concentration (\( c \)):

\[
c = \alpha \Phi .
\]

The parameter \( \sigma c = 9.6 \times 10^{-4} \) Kelvin per kilo-Röentgen (K/kR) is given directly by the slope of \( \log \rho_{l} \) versus \( \Phi \). The second parameter can be determined from the longitudinal resistivity. We found that \( \alpha/b = 4 \times 10^{-6} \) % per kiloRöentgen. The same information is contained in the dose dependence of the anisotropy (\( k \)). From equations (1) and (2) one gets:

\[
k(c, T) = \frac{k(0, T)}{c \frac{l}{b} k(0, T) + \exp \left\{-\frac{\sigma c}{kT}\right\}} . \tag{3}
\]

This expression shows that the fit is also very sensitive to the second parameter. For example, at the highest dose on figure 3, the first term in the denominator exceeds the second one by an order of magnitude.

The defect concentration and the value of \( \sigma \) can be determined from these parameters if the geometrical factor \( l/b \) is known. We took \( l/b = 1 \) since in the real crystal it surely is of the order of unity. In addition, as we shall see in the next section, the number of defects determined from the transport properties with this choice coincides well with the number of damaged molecules calculated theoretically for neutron irradiations. The choice \( l/b = 1 \) gives that \( 2.5 \times 10^5 \) kR corresponds to \( c \sim 1 \% \) of molecular defects, and \( \sigma \sim 2.4 \times 10^4 \) K. Using this estimation enables us to have a concentration scale on the figures which is more meaningful than the dose scale. The value of \( \sigma \) will be compared with the parameters for the pure material. However, we emphasize that the real parameters of equations (1) and (2) are determined experimentally and the assumption of the value of \( l/b \) does not influence the fits at all.

The \( c^* \) direction resistivity shows the same qualitative behaviour (Fig. 4), but the anisotropy in this direction is considerably higher. Since the longitudinal resistivity is determined by the easier interchain hopping,

Fig. 5. — Temperature dependence of the \( a \) direction resistivity before irradiation and after a dose of \( 4.75 \times 10^5 \) kR (\( c = 1.9 \% \)).

The lower curve is their ratio. The dotted line shows the calculated variation using the parameters determined from the dose dependence curves.
a detailed analysis cannot be performed as before. The transverse resistivity, $\rho_c$, however, also increases exponentially with the dose, as the model predicts.

The temperature dependence provides further, independent controls for the model. Moreover, since $\varepsilon$ and $d\varepsilon/b$ have been determined from the dose dependences, equations (1) and (2) should describe the $\rho_l(c, T)$ and $\rho_1(0, T)$ curves at a fixed defect concentration as a function of the temperature, without any new parameters!

On figure 5 the transverse resistivity, $\rho_a$ is shown in the high temperature region before irradiation and after a dose of $4.75 \times 10^5$ kR corresponding to 1.9% molecular defects. It is clear that the diffusive, metallic like conduction is changed to an activated behaviour by the irradiation. According to equation (1), $\rho_l(c, T)/\rho_l(0, T)$ is expected to vary exponentially as a function of $1/T$. For this applied dose, the parameter $\varepsilon = 9.6 \times 10^{-4}$ K/kR gives an activation energy of 460 K, which agrees with the measured one.

The same agreement can also be observed on the temperature variation of the longitudinal conductivity in the metallic regime before and after irradiation as shown on figure 1.

The above comparisons of the measured and calculated curves show that in the high temperature region, i.e. above 150 K, the predicted variation agrees well with the experimental results. Note that this is not only a qualitative agreement with the shape of the measured curves, but also that equations (1) and (2) gave a quantitative description for four independent measurements using only two parameters.

4. Low temperature neutron irradiation. — In the previous section we showed that the effect of defects in the metallic phase of TMTSF-DMTCNQ can be well explained by our phenomenological model. We now try to answer the question of how irradiation influences the transport properties at low temperatures, that is in the semiconducting phase. It is certain that the original assumptions are not justified for the pure material; the intrachain conductivity is not metallic, three dimensional ordering takes place and even a simple one-electron picture is strongly questionable below the phase transition where correlation effects play an important role. We believe however that, in spite of the differences, at high defect concentrations the conductivity is governed by the same mechanism. This idea, which has been suggested earlier [1, 8], comes from the general observation that defect concentrations of a few tenths of a percent seem to restore the metallic phase in all the quasi one-dimensional materials irradiated at temperatures below their phase transitions [1]. Thus at higher doses the same assumptions may be applied as in the high temperature metallic phase.

The 21 K neutron irradiation was performed as described previously [1, 8]. The dependence of the longitudinal conductivity and the anisotropy on the defect concentration are shown on figures 6 and 7.

The neutron dose was converted to molecular defect concentration using the calculation of reference [1]. Compared with the room temperature irradiation, there is a significant difference below defect concent-
trations of 0.5 molecular percent; at 21 K \( \sigma_b \) and \( k \) increase with dose, which is just the opposite effect to that at room temperature. Moreover, the conductivity as well as the anisotropy reach their metallic values at defect concentration of about 0.1-0.2 molecular percent. This confirms the picture \([1, 8]\) that randomly created defects can prevent the three dimensional ordering of the 2 \( k_F \) charge density waves, this ordering having been proved to be the origin of the sharp phase transition in the pure material \([19]\). We therefore attribute the initial variation of \( \sigma_b \) and \( k \) to the decoupling effect of the defects which fix the phase of the charge density waves.

At higher doses the blocking mechanism plays the same role as at room temperature and so the conductivity and the anisotropy begin to decrease. The conductivity is given by equations (1) and (2) as:

\[
\sigma_b(\epsilon, T) = \frac{\sigma(0, T)}{1 + k(0, T) \epsilon \frac{1}{b} \exp \left\{ \frac{\epsilon c}{kT} \right\}}
\]

On figure 7 the dotted line is the calculated dose dependence of the longitudinal conductivity at 21 K, for a material in which no phase transition would take place. The parameters used in the calculation were \( \sigma_b(0, 21 K) = 5 \times 10^{-3} \, (\Omega cm)^{-1}, \) \( k(0, 21 K) = 70 \) (these being the values measured on the pure crystal just before the phase transition) and \( \epsilon = 1.15 \times 10^4 \, K \).

This \( \epsilon \) value is less than that estimated from the room temperature dose dependence measurements. In principle a difference could arise from the uncertainties in the calculations of the defect concentration scales. The real parameters of equations (1) and (2) are \( \epsilon \) and \( a/b \) and the estimation of \( f/b \) in the case of the X-ray irradiations, or the assumptions of the calculation for the neutron irradiations \([1]\) might result in a factor of two difference. However the 21 K conductivity values of the crystals irradiated with X-rays to doses of 4.75 \( \times 10^5 \) kR and 5.76 \( \times 10^5 \) kR, corresponding to 1.9 and 2.3 molecular percent of defects fall on the \( \sigma_b(\epsilon, 21 K) \) curve of the neutron irradiated sample. This indicates that the two scales coincide and that \( \epsilon \) (21 K) really differs from the room temperature value.

At high temperature (above 150 K) \( \epsilon \) was temperature independent. In order to find its temperature dependence at lower temperatures, sample 1 was cooled down, as far as its resistance allowed, after different irradiation times. The resulting variations of the longitudinal conductivity are shown on figure 1 for X-ray irradiated crystals containing 1.9, 2.3 and 3.8 molecular percent of defects and for a neutron irradiated sample containing 6\% of damaged molecules. Satisfactory fit of equation (4) can be obtained for the four curves assuming a temperature dependence of \( \epsilon \) as shown on figure 8. The dotted lines on figure 1 indicate the calculated temperature dependences using this common \( a(T) \) and the values of \( \sigma_b(0, T) \) and \( k(0, T) \) measured on the pure crystal. Between 20 and 42 K we took \( \sigma_b(0, T) = \sigma_b(0, 42 K) \) and \( k(0, T) = k(0, 42 K) \) on the assumption that the intrachain conductivity remains metallic along the segments in the irradiated material. This idea is justified by the fact that no sign of a phase transition can be observed on the conductivity vs. temperature curves of the irradiated crystals.

5. Discussion. — We have demonstrated that all the changes in the dc transport properties of irradiated crystals can be described by making only a few assumptions. In this part we discuss the physical background of the model employed and use it to carry out some comparisons with other measurements.

It is quite natural to assume that a molecule damaged by irradiation results in a high potential barrier along the conducting chain. A large molecule containing 10 to 20 atoms can surely be damaged in several different ways. We believe however, that in each possible new configuration the highest level electronic orbits are strongly disturbed and that the high overlaps with neighbouring molecules are destroyed. This is similar to the picture that one can imagine for the role of impurities. Indeed, a few percent of chemical impurities have the same effect on the conductivity as defects created by irradiation \([5, 6]\). On the other hand, alloying with \textit{isostructural} molecules results in only a smooth variation of the conductivity, especially for low concentrations \([20]\).

A rough estimation can be made for the characteristic energy \( \Delta E = \epsilon c \). In the case of metallic segments of finite length, both the kinetic and potential energies are quantized. If a segment consist of \( n \) molecules, the Fermi wave vector has discrete values with a separation of \( \pi/nb \); the corresponding energy step is \( \Delta E_{\text{kin}} \sim D/n \) where \( D \) is the bandwidth.

If the kinetic term dominates \( \Delta E \sim Dc \), thus \( \epsilon \) should be of the order of the original bandwidth, i.e. about 0.8 eV. The measured \( \epsilon \) value roughly agrees with this. Unfortunately it is hard to estimate the
potential energy difference, mainly because of unknown screening effects. The possibility that the electrostatic interactions may cause energy differences of the order of 0.05 eV for a few percent of defects can not be excluded.

The origin of the temperature dependence of $\varepsilon$ is not clear. It is probably connected to the presence of the charge density waves. Diffuse X-ray studies show that charge density waves appear at about 150 K and that their amplitude increases with decreasing temperature [19]. This is the same range where $\varepsilon$ becomes temperature dependent. The correlation effects in the irradiated crystal may be as important as in the pure material and though the three dimensional ordering is prevented they surely influence the electronic states on the chain segments.

Detailed NMR studies on pure and irradiated Qn(TCNQ)$_2$ showed that the onchain spin diffusion rate has the same dose and temperature dependence as the longitudinal conductivity [7, 10]. This seems to contradict our explanation for TMTSF-DMTCNQ, since we claim that defects introduce interchain hoppings into $\sigma_1$ while leaving the conductivity along the chain segments unaffected. The anisotropy of Qn(TCNQ)$_2$ however is much higher; $k \sim 3000$ as determined by NMR [10]. In this case one can not neglect the possibility of tunnelling occurring through the potential barrier of the defects. Even if tunnelling through the barriers dominates — explaining why the conductivity of Qn(TCNQ)$_2$ remained essentially one-dimensional after irradiation — the same dose and temperature dependences are expected, only the parameters are modified. A smaller but significant decrease of the anisotropy was also observed in Qn(TCNQ)$_2$ [10]. Thus we do not think that a real contradiction exists between the present model and the NMR results.

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References

[10] HOLCZER K. et al., To be published.