Classification
 Physics Abstracts
 72.80L

THE EFFECTS OF IRRADIATION OF HMTSF-TCNQ AT 21 K

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(Reçu le 14 février 1978, révisé le 14 avril 1978, accepté le 24 avril 1978)

Résumé. — Nous avons irradié le conducteur organique HMTSF-TCNQ à basse température, avec des neutrons rapides (~ 1 MeV) et des ions lourds (~ 100 MeV). Nous avons mesuré la résistivité de plusieurs échantillons, en continu et *in situ* pendant l'irradiation. Lorsqu'on atteint une fraction molaire de défauts de l'ordre de 10^{-3} , la résistivité, mesurée à la température d'irradiation, a augmenté d'un facteur 4.

Ces résultats préliminaires sont l'occasion de présenter deux modèles simples :

- i) percolation du gaz d'électrons à travers un composite formé de volumes conducteurs et de volumes rendus isolants par l'irradiation ;
- ii) irradiation d'un semi-métal anisotrope mais homogène.

Abstract. — We present measurements of HMTSF-TCNQ (hexamethylenetetraselenaful-valenium-tetracyanoquinodimethanide) resistivity along the chain axis, during irradiation at 21 K with fast neutrons (~ 1 MeV) and heavy ions (~ 100 MeV).

A defect concentration estimated to be 10^{-3} mole fraction, increases the resistivity at 21 K by a factor of 4.

These preliminary results are used to discuss the validity of two very simple radiation damage models :

- i) three-dimensional percolation, and
- ii) semi-metal irradiation.

The effects of disorder on the properties of quasi-unidimensional conductors have been the subject of extensive studies (see, for example, the proceedings of the conference on organic conductors and semiconductors, Siofok 1976), [1]. Chiang, Cohen, Newman and Heeger [2, 3] recently reported the results of a study of the transport properties of TTF-TCNQ

after irradiation *at room temperature* with 8 MeV deuterons. Zuppiroli and Friend [4] have presented measurements of the electrical conductivity of polymeric sulphur nitride, $(\text{SN})_x$ for samples irradiated at *low temperature* with neutrons and heavy ions. These first radiation effect experiments have shown that one can obtain significant results on the atomic and

electronic properties of quasi-unidimensional conductors by introducing controlled disorder through radiation induced defects.

In the present letter we focus attention on the dependence of the quasi-unidimensional conductors low temperature resistivity on the irradiation dose Φ , that is to say on the defect concentration. We present measurements of the HMTSF-TCNQ resistivity along the chain axis for samples bombarded at 21 K with fast neutrons (~ 1 MeV) and heavy ions (~ 100 MeV). These preliminary results are used to discuss the validity of two very simple radiation damage models :

- i) three-dimensional percolation, and
- ii) semi-metal irradiation.

HMTSF-TCNQ is one of the most interesting charge transfer complexes. Magnetoresistance [5] and Hall-effect [6] measurements have demonstrated that this complex behaves at low temperatures as an anisotropic, yet three-dimensional semi-metal. In a *clean* specimen of HMTSF-TCNQ, the coherent transfer of the wave function between chains make the electronic band structure three dimensional and consequently suppresses the Peierls transition [7]. The huge anisotropic magnetoresistance and the Hall constant showing a carrier density of approximately 10^{-3} per molecule, are not present in HMTSF-TCNQ above 80 K nor are they present in TTF-TCNQ at any temperature. They are essential and sufficient criteria for the existence of the three-dimensional state.

The room temperature resistivity of HMTSF-TCNQ was found to be approximately $550 \mu\Omega\text{-cm}$. The resistivity drops to approximately $180 \mu\Omega\text{-cm}$ in the temperature range 50-80 K, and (at ambient pressure) rises somewhat below 30 K; at 21 K, it is about $250 \mu\Omega\text{-cm}$. Susceptibility measurements at helium temperatures, verify that only a few paramagnetic impurity centres are present.

Irradiation was performed using the Triton nuclear reactor at Fontenay-aux-Roses, and was always carried out at liquid hydrogen temperatures using the VINKA device described by Conte and Dural [8]. The neutron flux at the samples was 3.9×10^{11} neutrons/cm².s of which 6.5×10^{10} fast neutrons/cm².s had an energy greater than 1 MeV. The mean free path of any incident neutron, controlled by nuclear collisions with scattering cross sections of about 10^{-24} cm², is at least several centimeters. So the damage produced by neutron irradiation is perfectly homogeneous in the samples and produces no heating at all.

Heavy ions, with energies up to 100 MeV, were produced by neutron bombardement of two 2 000 Å thick films of uranium dioxide close to the sample causing fission of the uranium. The ranges of fission fragments in any material are essentially controlled by electronic stopping power; they depend on the total electron density and are only 10 to 15 μm in HMTSF-

TCNQ. So thin samples (20 μm thick) have been used for this irradiation. The flux of fission fragments was 2×10^9 F.F./cm³.s.

FIG. 1. — Dose curves of two HMTSF-TCNQ samples irradiated with neutrons at 21 K.

Figure 1 shows the fractional resistance increase as a function of the dose for two samples irradiated with neutrons. It can be seen that the resistance varies exponentially with the dose :

$$\rho = \rho(0) \exp \alpha_n \Phi$$

$$\alpha_n = 2.7 \times 10^{-16} (\text{fast neutrons/cm}^2)^{-1}.$$

The samples irradiated with fission fragments up to a dose of 1.2×10^{14} F.F./cm³ showed qualitatively the same behaviour with

$$\alpha_{\text{F.F.}} \sim 2 \times 10^{-14} (\text{F.F./cm}^3)^{-1}.$$

It is difficult to estimate precisely how many atomic displacements each incident particle is able to produce in a crystal containing 4 different kinds of atoms. A calculation is being performed to solve this problem accurately [9]. At the present time we are able to give an order of magnitude for the number of atomic displacements per collision cascade produced by an incident neutron i.e. $\gamma \simeq 10^4$. Thus, the maximum fast neutrons dose for $\Phi_n = 5 \times 10^{15}$ f.n./cm² corresponds to a fraction γ of displaced atoms which can be written as :

$$\gamma \sim \nu \sigma \Phi_n$$

ν : average number of displaced atoms per cascade $\sim 10^4$,

σ : average collision cross section of a neutron with a nucleus $\sim 10^{-24}$ cm².

It follows that $\gamma \sim 5 \times 10^{-5}$ at. fraction.

In contrast to the neutrons, most of the energy from the fission fragments is transferred to the crystal in the form of electronic excitations. Typically, a fission fragment will lose energy at a rate of the order of one keV per Å. The extent of the damage caused to the crystal depends crucially on the ability of the

conduction electrons to disperse this energy; in an insulator, fission fragments leave tracks; in a metal there are sufficient electrons to prevent any damage taking place from electronic excitations; $(\text{SN})_x$ consists of fine fibers with very weak contact between them, so that it is easy to heat one fiber and *burn* out a section of it [4]. HMTSF-TCNQ is 100 times less sensitive to fission fragments than $(\text{SN})_x$. The transfer of heat away from the electronic excitation thermal spikes is possible such as in bismuth. Only the fraction of the incident particle energy, available for atomic displacements production, is effective in producing permanent damage.

Because of the large increase in resistivity with the dose of neutrons — it may be the largest that has ever been observed — one can assume that each incident particle (either neutron or fission fragment) excludes a given volume from the conduction process. More precisely, in a clean system, the coherent transfer of the wave function between chains makes the electronic band structure three-dimensional, while in a dirty system, this coherent transfer is suppressed. The system is therefore one-dimensional, a Peierls transition takes place at about 20 K, and the resistivity increases.

Let us consider the three-dimensional approach where the electron gas is supposed to percolate in a random mixture of insulating damaged volumes in a conductive medium. From percolation theory [10] the conductivity decreases roughly linearly with the excluded volume fraction $1 - h$ up to about $2/3$ where it vanishes. This value varies only slightly with the details of the model :

$$\sigma/\sigma_0 \simeq (3h - 1)/2 \quad \text{when } h \geq 1/3$$

$$\sigma/\sigma_0 \simeq 0 \quad \text{when } h < 1/3$$

$h = \exp(-n\gamma)$, where n is the number of atoms excluded from the conducting process per radiation induced defect. Figure 2 is a logarithmic plot of ρ/ρ_0 versus $n\gamma$. The fit with the curve of figure 1 gives a value of $n \sim 16\,000$ excluded atoms per atomic

FIG. 2. — Conduction and three dimensional percolation. γ is the fraction of displaced atoms, n the number of atoms excluded from the conducting process per displacement.

displacement which corresponds to a radius r of about 30 Å around each point defect.

Let us compare this value of r with a theoretical estimation obtained in the following way : let us assume that a defect suppresses the coherent transfer between chains and let us estimate the phase shift of the wave function due to this charged defect at a distance r .

If the wavevector is changed by δk_y , the phase shift is given by

$$\delta\Phi = \int \delta k_y dy. \quad (1)$$

We are interested in the difference of the phase shifts of the neighbouring chains, $\Delta\Phi = \delta\Phi_1 - \delta\Phi_2$. Since $\hbar^2 k_y^2/2m^* = E - (V_0 - V)$, we have :

$$\delta k_y = -Vm^*/\hbar^2 k_y$$

and the difference between the two chains :

$$(\delta k_y)_1 - (\delta k_y)_2 = \frac{1}{\hbar v_F} [V(1) - V(2)] = \frac{[\partial V/\partial r] a}{\hbar v_F}$$

$$\Delta\Phi = \int (\delta k_{y1} - \delta k_{y2}) dy = \left[\int_{-\infty}^{\infty} (1+t^2)^{-3/2} dt \right] \times \\ \times V(x, 0) a/\hbar v_F = 2 V(r) a/\hbar v_F. \quad (2)$$

The interchain motion is impeded when $\Delta\Phi$ is of the order of unity. Let $V(r) = e^2/r$ and $v_F \approx 10^7$ cm/s. Then $\Delta\Phi = 1$ for $r \approx 2e^2 a/\hbar v_F \approx 300$ Å. The dielectric constant and screening probably reduce r somewhat.

This argument holds when the transverse tunnelling integral $t_\perp$ is not large compared to $(a \cdot \partial V/\partial r)$. In HMTSF-TCNQ, $t_\perp$ is sufficiently small [7] so that $(a \cdot \partial V/\partial r)$ can exceed it at a distance of the order of 100 Å. In contrast, in $(\text{SN})_x$, $t_\perp$ is much larger, so that the present mechanism may be effective only for much shorter distances.

While the percolation model assumes a non-uniform irradiated material, consisting of conducting and insulating regions, we can also consider a uniform irradiated material. Such a model, consistent with the low-temperature behaviour of HMTSF-TCNQ has been proposed for bismuth [11].

Point defects are considered to affect the conductivity of a semi-metal in two ways : first they will reduce the mobility of the carriers as in a good metal,

and second, because the carrier concentration is low, they may also be effective in reducing or increasing the number of carriers. When both effects are present, the dose curve exhibits a curvature. Let us define :

- c_0 : fraction of free carrier per atom before irradiation $\sim 10^{-5}$ [6],
- c : fraction of free carrier per atom after a low irradiation dose corresponding to a fraction γ of displaced atom,
- τ_0 : electronic relaxation time before irradiation,
- τ : electronic relaxation time after irradiation,
- ξ : variation of the number of free carriers per radiation induced defect,
- $\Delta\rho$: specific resistivity of the defect centre per atomic fraction.

Assume, for a short irradiation up to a dose γ measured in displacement per atom, that :

$$c = c_0 + \xi\gamma \quad \text{and} \quad 1/\tau = 1/\tau_0 + \frac{c_0 e^2 \Delta\rho}{m^*} \gamma.$$

It follows that :

$$\frac{\rho}{\rho_0} = \frac{c_0 \tau_0}{c\tau} = \frac{1 + \gamma \Delta\rho/\rho_0}{1 + \gamma\xi/c_0}. \quad (3)$$

Relation (3) also fits the experimental results of figure 1. One can obtain :

$$\xi \sim 0.1 \text{ carrier localized per displacement}$$

$$\Delta\rho \sim 30\,000 \mu\Omega.\text{cm/at. \% of defects}.$$

The value of $30\,000 \mu\Omega.\text{cm/at. \%}$ can be compared with the value obtained for the bismuth ($7\,500 \mu\Omega.\text{cm/at. \%}$) [9] and for $(\text{SN})_x$ ($8\,000 \mu\Omega.\text{cm/at. \%}$) [4].

At the present stage of our experimental work, we are not able to determine which is the best of these three models. Irradiation experiments are being actively pursued on HMTSF-TCNQ and other quasi one-dimensional conductors. A preliminary experiment has been carried on with TTT($\text{I}_{1.6}$) [12]. The dose curve is also quasi-exponential.

The question whether the irradiated material is to be treated as uniform or not, depends on the size of the damaged regions, compared with the mean free path. We saw that the diameter of the damaged region is of order $100 \text{ \AA}$; the mean free path is also of this order [6]. Therefore, the real situation may be intermediate between the two limiting cases of the second and third models.

Acknowledgments. — We would like to warmly thank Dr. D. Jerome and Dr. J. C. Jousset for many interesting discussions.

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