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Effect of x-ray irradiation on anisotropic properties of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)

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We present the results of the effect of controlled disorder on the electrical resistivity of the one-dimensional conductor TTF-TCNQ. The resistivity was measured, both parallel ($\rho_{\parallel}$) and perpendicular ($\rho_{\perp}$) to the TTF-TCNQ chains, as a function of x-ray photon dose Φ. The longitudinal resistivity increases with photon dose, saturates at about twice its original value, and then increases again. The effect of irradiation on the transverse resistivity is much less pronounced. This behavior, as well as the observed dependence of the anisotropy on temperature and defect concentration, is explained within the framework of the theory which takes into account the libron-drag effect on the metallic transport properties of TTF-TCNQ.

I. INTRODUCTION

The metallic transport properties of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) above the Peierls transition have received much attention during the last few years. The metallic conductivity exhibits unique behavior and has posed many interesting questions. It has now been established[1] that the resistivity along the chains, at constant pressure and for pure samples ($\rho_0 < 70$ $\mu\Omega$ cm), may be expressed as $\rho = \rho_0 + AT^n$ with $n \simeq 2.3$ where ρ_0 is the residual resistivity. However, the metallic transport properties of TTF-TCNQ have been known to be sample dependent. Structural defects were usually invoked to explain the variation in experimental results. For better understanding of the role of defects Chiang *et al.*,[2] Zuppiroli *et al.*,[3] and Zuppiroli and Bouffard[4] studied experimentally the effect of controlled disorder on the electrical properties of TTF-TCNQ and related compounds, through radiation-induced defects. The radiation damage was produced using a deuteron beam[2] and fast neutrons and heavy ions.[3,4] The measured resistivity was recently interpreted[5] by including into the theory the effects of phonon drag and of libron drag. The analysis shows that the resistivity should be of the form

$$\rho(T,c) = \rho_0(c) + A(c)T^{2.3} + B(c)T \quad , \tag{1}$$

where c is the concentration of defects in the crystal. The coefficients A and B depend strongly on sample purity. It was found experimentally[2] that the linear term $B(c)T$ is absent for pure samples, but contributes a measurable value to $\rho(T,c)$ in highly irradiated samples for $T < 150$ K. It was also found that the coefficient $A(c)$ increases with radiation dose until it saturates at twice its initial value in the unradiated sample. Thus, for the room-temperature (RT) resistivity (where the linear term may be neglected) one can identify two regions: region (i) where the resistivity increases with radiation dose, and region (ii) where the resistivity saturates to about twice its unradiated value.

These results were recently explained[5] by taking into account the strong coupling between the electrons and the librons[6] which "drag" the librons from equilibrium. This "libron drag" causes an increase in the conductivity of pure samples. By irradiation, one produces many defects, which serve to return the librons to equilibrium via the libron-defect interaction, and the drag effect is quenched. According to this theory, the longitudinal inverse relaxation time $\tau_{\parallel}^{-1}$ can be written

$$\tau_{\parallel}^{-1} = \tau_{eq}^{-1}[1 - X(c)] \quad , \tag{2}$$

where τ_{eq}^{-1} is the inverse relaxation time for the case where the librons equilibrate rapidly between electron-libron collisions and $[1 - X(c)]$ is the correction factor that takes into account libron drag. For pure samples, the theory gives $X(c) \simeq \frac{1}{2}$ implying $\tau_{\parallel}^{-1} \simeq \frac{1}{2}\tau_{eq}^{-1}$ whereas for strongly irradiated samples, the librons equilibrate rapidly through the libron-impurity interaction implying that $\tau_{\parallel}^{-1} = \tau_{eq}^{-1}$. This dependence of electron-libron relaxation time on defect concentration explains the saturation in $A(c)$ to a value about a factor of 2 larger than its pure-limit value.

In this paper, we report the effect of x-ray irradiation on the RT dc resistivity both along ($\rho_{\parallel}$) and perpendicular ($\rho_{\perp}$) to the TTF-TCNQ chains.[7] At $T = 300$ K we can identify three regions. In region (i), $\rho_{\parallel}$ increases with radiation dose whereas in region (ii) $\rho_{\parallel}$ saturates to a value of about twice the pure-limit value. These results agree with those of Chiang *et al.*[2] However, for still heavier doses of irradiation

we found a third region, in which $\rho_{\parallel}$ again increases with the radiation dose.

We also report here the results of the first study of the effect of controlled disorder on the transverse resistivity $\rho_{\perp}$ above the Peierls transition.[8] We found marked differences in the sample dependences of $\rho_{\parallel}$ and $\rho_{\perp}$. While $\rho_{\parallel}$ changes by a factor of 2, $\rho_{\perp}$ is changed by only about 25% for the same dose. Moreover, the rapid increase of $\rho_{\parallel}$ which characterizes region (i) is *absent* for $\rho_{\perp}$. Also, there is no saturation effect for $\rho_{\perp}$. However, we identify two different regions for $\rho_{\perp}$ which we interpret as being closely correlated to regions (ii) and (iii) of $\rho_{\parallel}$.

In Sec. II we describe the experimental details. The results are presented in Sec. III. Section IV is devoted to a discussion of the results in the light of recent theories.

II. EXPERIMENTAL DETAILS

The radiation damage was produced by a Rigaku x-ray machine. This machine produces 4×10^{14} photons/kW sec, of which half are 8-keV Cu $K\alpha$ radiation. We operated the machine at a power of 15 kW. To avoid damage from machine vibration, the crystals were hung a few mm above the Be window, about 10 cm from the target, without touching the x-ray machine. Under these conditions the photon flux through the sample is about 1.5×10^{16} photons/cm^2 hour. For a typical sample about 3×10^{12} photons per hour impinge on the crystal, 10% of which are absorbed.

It is worthwhile to note here that in TTF-TCNQ crystals the sulfur atoms are most likely to interact with the photons and to emit photoelectrons. However, it is most probable that hydrogen atoms will be displaced by collisions with the energetic photoelectron. Detailed calculations of defect concentration in TTF-TCNQ under the above-mentioned x-rays irradiation conditions have been made by Zuppiroli[9] and will be published elsewhere.

The electrical resistivity was measured by the standard four-probe method. The resistivity of each sample was measured at RT before irradiation and then after each 10–15 h of irradiation. In order to deduce the temperature dependence part of the resistivity and hence the coefficient A ($\underline{C}$), the resistivity $\rho_{\parallel}$ of several samples was measured as function of temperature (in the high-temperature regime only) after each stage of irradiation. However, in order to avoid possible temperature-cycling damage (see, e.g., Cohen *et al.*[10]) the temperature dependence of $\rho_{\parallel}$ for the heavy irradiated samples and of $\rho_{\perp}$ for most of the samples was measured only twice, before any irradiation and after the last irradiation stage. During the intermediate stages, only RT values of $\rho_{\parallel}$ and $\rho_{\perp}$ were measured. This precaution is especially important for $\rho_{\perp}$, for which the slight changes due to irradiation might be masked by noncontrolled defects.

III. EXPERIMENTAL RESULTS

A. Longitudinal resistivity

Measurements were first carried out for longitudinal electric conductivity. For the pure samples, the ratio between maximum conductivity $\sigma_{\parallel}^{\max}$ and RT conductivity $\sigma_{\parallel}$(RT) was found to be 7–9. The irradiation effects with total dose up to 1.5×10^{18} photons/cm^2 exhibit the basic features described by Chiang *et al.*[2] In Fig. 1, the solid circles give the residual resistivity ρ_0, which is proportional to the concentration of defects, as a function of photon dose. As expected, ρ_0 is a linear function of the photon dose. To compare with the results of Chiang *et al.*[2] we also plot ρ_0 (crosses) as a function of deuteron dose. Note that a dose of about 10^{18} photons/cm^2 is equivalent to a dose of 5×10^{14} deuterons/cm^2.

In Fig. 2, we show the results for $\rho_{\parallel}$(RT) as a function of photon dose. A rapid change is observed in region (i) and saturation occurs in region (ii) as previously discussed. Finally, in Fig. 3(a) we show typical results for $\rho_{\parallel}$(RT) as a function of photon

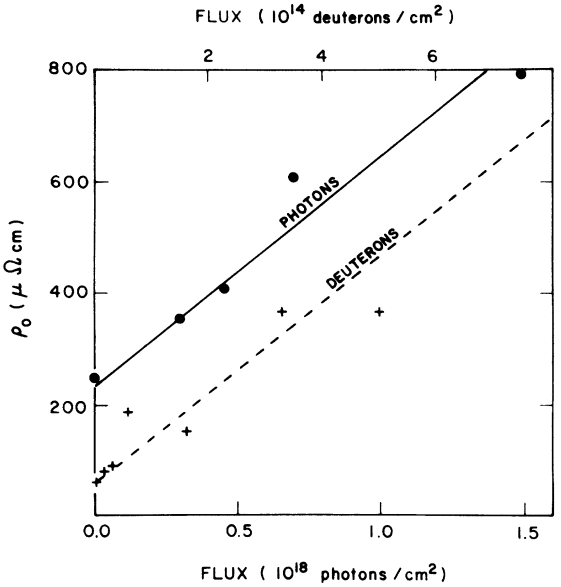

FIG. 1. Residual resistivity ρ_0 as a function of photon dose (●) and as a function of deuteron dose (×). The solid line is the best linear fit to the present data. The dashed line is based upon Fig. 8 of Ref. 2.

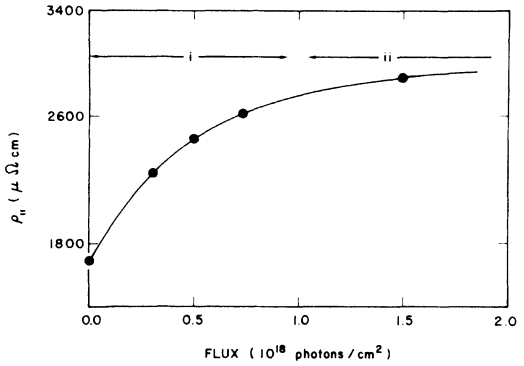

FIG. 2. Room-temperature longitudinal resistivity as a function of photon flux up to $1.5 \times 10^{18}/\text{cm}^2$. The saturation effect is observed in region (ii).

dose for a heavily irradiated sample. The rapid change in $\rho_{\parallel}$ and the saturation effect are denoted by (i) and (ii) as in Fig. 2. However, a dramatic increase in $\rho_{\parallel}$ occurs for the total dose greater than 3×10^{18} photons/cm^2. This is denoted as region (iii) in Fig. 3(a).

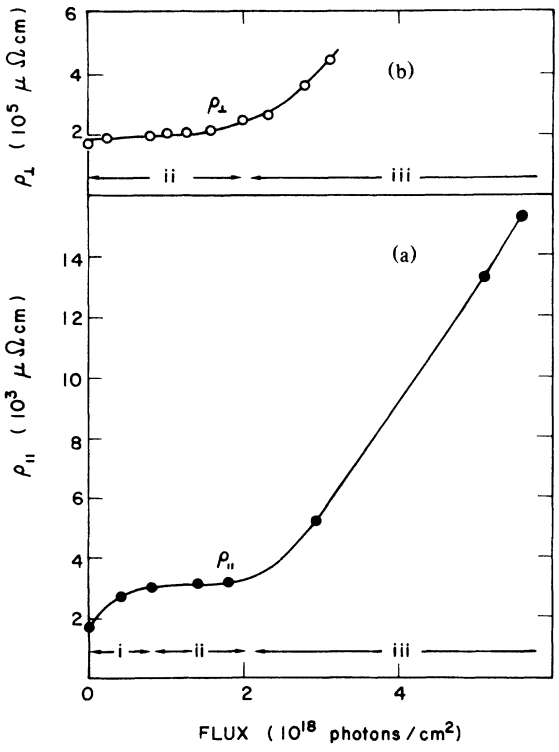

FIG. 3. (a),(b) Room-temperature resistivity as a function of photon flux up to $6 \times 10^{18}/\text{cm}^2$. The longitudinal resistivity increases in region (i), saturates at the onset of region (ii) and then increases again in region (iii). The transverse resistivity consists of only two regions.

B. Transverse resistivity

The temperature dependence of the transverse resistivity of several pure samples was measured. The ratio of $\sigma_{\perp}^{\max}$ to $\sigma_{\perp}(\text{RT})$ was found to be about 2. The dependence of $\rho_{\perp}(\text{RT})$ on defect concentration is shown in Fig. 3(b). As can be seen from this figure, $\rho_{\perp}(\text{RT})$ increases with irradiation much more slowly than $\rho_{\parallel}(\text{RT})$. For a dose of 10^{18} photons/cm^2, $\rho_{\perp}(\text{RT})$ increases by about 25% while $\rho_{\parallel}$ increases by about a factor of 2. A striking feature of Fig. 3(b) is that the monotonic increase in $\rho_{\perp}(\text{RT})$ with radiation dose consists of *two* regions in exactly the same way as regions (ii) and (iii) for $\rho_{\parallel}(\text{RT})$ of Fig. 3(a).

C. Anisotropy

The anisotropy ratio $\alpha = \sigma_{\perp}/\sigma_{\parallel}$ was previously found to be temperature dependent.[10,11] This temperature dependence is also clearly demonstrated by our results. Since $\sigma_{\parallel}^{\max}/\sigma_{\parallel}(\text{RT}) = 7-9$ and $\sigma_{\perp}^{\max}/\sigma_{\perp}(\text{RT}) \simeq 2$, it follows that the anisotropy ratio is changed by a factor of about 4 when the temperature increases from 60 to 300 K.

In addition to the above temperature dependence we found a marked dependence of $\alpha(RT)$ on defect concentration. At RT, an increase of the photon dose to $4 \times 10^{17}/\text{cm}^2$ causes $\alpha(\text{RT})$ to decrease from a value of 90 to a saturation value of 70.

IV. DISCUSSION

Several theoretical approaches for understanding the electrical resistivity of TTF-TCNQ are available: (1) We can assume that the Bloch "annahme"[12] applies here, and the phonons are in equilibrium with the lattice. This approach was adopted, among others, by Schafer *et al.*,[13] Conwell,[14] and Seiden and Bloch[15] in their attempt to account for the effect of radiation damage on the resistivity of TTF-TCNQ. (2) We can allow for "classical" phonon-drag, i.e., allow the possibility that the phonons are not in equilibrium with the lattice, but are dragged along by the electrons (when an electric current is flowing). "Classical" means, that the Boltzmann transport equation applies. This approach was proposed in Refs. 5, 16, and 17 and is adopted here. (3) We can have sliding rigid charge density waves, as proposed originally by Frohlich,[18] and suggested by Bardeen[19] as a possible mechanism for TTF-TCNQ.

As pointed out by Heeger *et al.*[20] it may be difficult to distinguish between possibilities (2) and (3) just from electrical resistivity measurements, since the ordinary Bloch mechanism is suppressed in both; the most striking example being $NbSI_3$ (Ref. 21) where the resistivity for strong electric field does not change

significantly at the Peierls transition, where there clearly is a transition between regimes 2 and 3.

We favor possibility (2) for TTF-TCNQ on the basis of thermal conductivity data (Salamon *et al.*[22]), NMR data (Soda *et al.*[23]), absence of nonlinearity in the I-V curves, (Jerome and Weger[24]), and a variety of other experimental properties. In the following we discuss our experimental result in the framework of this phonon-drag theory.

A. Longitudinal resistivity

For pure crystals, there is no contribution to the resistivity from normal-scattering processes because of drag effects and the only contribution comes from umklapp-scattering processes. For dirty samples, the librons equilibrate through the libron-impurity interaction and normal-scattering processes also contribute to the resistivity. Since there are an almost equal number of N and U processes,[5] it is expected that $\rho(T)$ will saturate to about twice its value. Thus the behavior of $\rho_{\parallel}(\mathrm{RT})$—the increase in region (i) and the saturation of region (ii) in Fig. 3—is well understood. The residual resistivity ρ_0 contributes only about 10–20% to the measured $\rho_{\parallel}(\mathrm{RT})$ and thus, the changes in ρ_0 due to the increase in defect concentration hardly affects $\rho_{\parallel}$ at RT. However, this is no longer the case for very heavy irradiation. In region (iii), where ρ_0 is of the same order of magnitude as the temperature dependent part of $\rho_{\parallel}$ even at RT, the change of ρ_0 clearly affects the measured resistivity. Indeed, by comparing Fig. 1 and region (iii) of Fig. 3(a), one finds $\partial\rho_{\parallel}/\partial\Phi \simeq \partial\rho_0/\partial\Phi$. The same equality should also apply to region (ii); it is not observed experimentally only because ρ_0 is such a small fraction of the measured $\rho_{\parallel}$ that changes in $\rho_0(c)$ are masked by the large constant term $AT^{2.3}$ where A is independent of irradiation in this region.

B. Transverse resistivity

The motion of the electrons perpendicular to the chains is diffusive, since the mean free path of the electrons in this direction is only a fraction of the distance between chains. Soda *et al.* have suggested[25] that there is a correlation between the diffusion time between the chains, $\tau_{\perp}$ and the relaxation time along the chains $\tau_{\parallel}$. The scattering of electrons along the chains destroys the phase relation between chains and thus increases the diffusion time and hence $\rho_{\perp}$. According to this picture, if every electron-scattering event contributed to $\rho_{\parallel}$ then one would obtain $\rho_{\perp} \propto \rho_{\parallel}$. This would imply that $\rho_{\perp}$ should have the same defect-concentration dependence as $\rho_{\parallel}$. However, our results show a clear anisotropy in the RT defect concentration dependence. This can be explained within the framework of the suggestion of Soda *et al.*[25] in the following manners.

(a) The simple proportionality between $\rho_{\perp}$ and $\rho_{\parallel}$ would occur only if each scattering event would increase both $\rho_{\parallel}$ and $\rho_{\perp}$. This is the case for the irradiated samples for which $X(c)$ of (1) is zero (i.e., when there is no drag effect). However, for pure samples the normal-scattering events destroy the phase relation between chains (and thus cause an increase in $\rho_{\perp}$) but *do not* contribute to $\rho_{\parallel}$ because of drag effect. Thus it follows that there does not exist for $\rho_{\perp}$ a region corresponding to region (i) of $\rho_{\parallel}$. A similiar approach is adopted by Andrieux *et al.*[26] and by Ishiguro *et al.*[27] and this is in precise agreement with our experimental results.

(b) Using the phonon-induced forward-scattering concept: Recently it was shown[28] that scattering of electrons by phonons is mainly forward, due to the large molecular size; thus this forward scattering contributes to $\rho_{\perp}$ (because it destroys the phase of the electronic wave function) but not to $\rho_{\parallel}$. If defect scattering is not so anisotropic, due to a small defect size (say, one hydrogen torn off a molecule, affecting mainly the carbon to which it was attached originally), the backward scattering due to the impurity will have a larger relative effect on $\rho_{\parallel}$, than the total-impurity scattering has on $\rho_{\perp}$.

One may conclude that libron drag is an anisotropic effect which exists *only* along chains and *only* for relatively pure crystals. In other words, for pure samples, there is a mechanism which reduces the longitudinal resistivity but does not affect the transverse resistivity. After sufficient irradiation, this mechanism of libron drag is quenched and both $\rho_{\parallel}$ and $\rho_{\perp}$ should be affected in the same manner by the irradiation. Indeed, for $\Phi > 10^{18}/\mathrm{cm}^2$, $\rho_{\perp}(\Phi)$ is found to be proportional to $\rho_{\parallel}(\Phi)$ as is shown in Fig. 3. Moreover, since $\rho_{\perp} \propto \rho_{\parallel}$ for such large values of Φ and $\rho_{\parallel} = \rho_0(c) + A(c)T^{2.3}$ and $A(c)$ has already saturated, one expects $\rho_{\perp}(c)$ to be a linear function of the flux because $\rho_0(c)$ depends linearly on the flux. This is indeed in accord with the experimental results.

C. Anisotropy

The observed temperature dependence of the anisotropy can be understood in terms of mechanisms (a) and (b), of Sec. IV B, as well as (c), the nondegeneracy of the electronic states on the donor and acceptor chains, proposed by Weger.[29]

As for (a), if phonon drag is stronger at low temperatures than at ambient, this will increase the anisotropy at low temperatures. If the $2K_F$-phonon drag[17] is complete at all temperatures, and the general-q (second-order) phonon drag[5] is temperature independent, this is no longer the case.

As for (b), forward scattering does not contribute to the longitudinal resistivity but destroys the phase relation between chains and thus contributes to the transverse resistivity and leads to an increase of

$\sigma_{\parallel}/\sigma_{\perp}$ at low temperatures. The relative number of forward-scattering events decrease with increasing temperature[28] and this explains the corresponding decrease of $\sigma_{\parallel}/\sigma_{\perp}$. From the theory[28] one can expect a decrease up to a factor of 10 in the anisotropy at RT relative to the value at 60 K.

As for (c), we are not yet in a position to make a quantitative estimate of the contribution of this mechanism to the increase in anisotropy at low temperatures. Probably the *difference* between the increase of σ_{cc} (where the electron jumps between degenerate states) and the increase of σ_{aa} (where it jumps between nondegenerate states) should be attributed to this effect.

Since all three mechanisms work in the same direction (increasing the anisotropy at low temperatures), it is not easy to determine quantitatively the fractional contribution of each mechanism.

In conclusion, we found experimentally three regions of different behavior of $\rho_{\parallel}$ as a function of controlled disorder induced by x-ray radiation. The effect of this disorder on the transverse resistivity $\rho_{\perp}$ is much less pronounced. However, a proportionality between $\rho_{\parallel}(c)$ and $\rho_{\perp}(c)$ is found for nonpure crystals. This behavior, as well as the dependence of the anisotropy on defect concentration, is explained within the framework of the recent theory[5] which takes into account the libron-drag effect on the metallic transport properties of TTF-TCNQ.

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